Metal-Support Interactions in Flame-made Metals on Metal Oxides for Environmental Applications

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

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2017
Acknowledgments

I would like to express my deepest gratitude to Prof. Dr. Sotiris E. Pratsinis for providing the opportunity to perform Ph.D. in his lab and his continuous encouragement, guidance, support and advice during this period. I am extremely grateful to Prof. Dr. Yiannis Deligiannakis and Prof. Dr. Georgios A. Sotiriou for his tireless scientific support and guidance, many inspiring and helpful discussions and for agreeing to co-advertise this thesis.

I am grateful to my past and present colleagues and all members of the Particle Technology Laboratory (PTL) at ETH Zurich, where this work was carried out, for the motivating and friendly working atmosphere. Special thanks for Dr. Robert Büchel help me technically throughout my stay at PTL and also, to translating the abstract from English to German. Many thanks go to Dr. Karsten Wegner for several discussions related to the flame synthesis of nanoparticles. I wish to acknowledge Rene Plüss from the IPE workshop for solving technical challenges in the lab, Agnes Günther for her indispensable bureaucratic work and organizing various social events and Dr. Frank Krumeich from the Electron Microscopy Center, EMEZ, of ETH Zurich for providing microscopy images and Dr. Ulrich Müller from Laboratory for Nanoscale Materials Science of Empa for X-ray photoemission spectroscopy.

Many thanks go to the students who performed their projects and worked as an assistant with me: Severin Hahn, Joanna Rupacher, Georgios Kelesidis, Michel Seitz, Samuel Regli, Diamantopoulou Marianna, Andrei Chirkunov, Marc Suter, Ping Shu Ho and Vaios Moschos. Many thanks go to all my friends who continuously surrounded and supported me during this journey and helped me to develop both personally and scientifically.

Financial support by Swiss National Science Foundation (grant no. 200021_149144) and the European Research Council under the European Union’s Seventh Framework Program (FP7/2007-2013, ERC grant agreement no. 247283) is gratefully acknowledged.

Finally, I would like to express my deepest gratitude to my parents (Akihiro and Chihiro) and sister (Megumi) for their love, support and faith in me.
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Summary

This thesis presents the interactions between noble metals and metal-oxides made by flame spray pyrolysis (FSP) technique. Such interactions enhance the photocatalytic activity for environmental remediation of these materials and contribute to understanding intrinsic nanosilver dissolution in ambient conditions.

In chapter 1, the catalytic and solar-photocatalytic oxidation of organic pollutants under air at room temperature has great potential for application in environmental remediation. Careful control of the synergistic effects between metal catalysts and metal oxide supports provides opportunities to improve the oxidation activity of organic pollutants at/near room temperature and the photocatalytic degradation of pollutants under solar irradiation. We herein present two types of interactions between metals and supports, namely strong metal-support interactions (SMSIs) and strong metal oxide-support interactions (SOSIs). Such interactions alter the characteristics (catalyst size, morphology, metal and support oxidation states, bonding structure at the metal-support interface, etc.) of the materials, thus reducing the light-off temperature of the catalytic oxidation of pollutants and improving their visible light photocatalytic activity. Unique preparation techniques for the active sites and phases under these strong interactions are also highlighted.

In chapter 2, Pd subnano-clusters (< 1 nm) on TiO$_2$ nanoparticles are prepared in one step by FSP. Under solar light irradiation, their photocatalytic NO$_x$ removal in a standard ISO reactor are 3 or 7 times more active than commercial TiO$_2$ (P25, Evonik) with or without photodeposited Pd on it, respectively. X-ray photoelectron spectroscopy (XPS) reveals that such photodeposited Pd consists of metallic Pd along with several Pd oxidation states. In contrast, flame-made Pd subnano-clusters on TiO$_2$ dominantly consist of an intermediate Pd oxidation state between metallic Pd and PdO. In that intermediate state, the Pd subnano-clusters are stable up to, at least, 600 °C for 2 hours in air. However, a fraction of them is reduced into relatively large (> 1 nm) metallic Pd nanoparticles by annealing in N$_2$ at 400 °C for 2 hours, as elucidated by XPS and scanning transmission electron microscopy. The Pd subnano-clusters interact with oxygen defects on the TiO$_2$ surface as shown by Raman spectroscopy. This interaction suppresses CO adsorption on Pd as observed by diffuse
reflectance infrared Fourier transform spectroscopy (DRIFTS), analogous to SMSIs of nano-sized noble metals on TiO$_2$.

In chapter 3, to understand the above discoveries, the characteristics and solar NO$_x$ removal of Pd/TiO$_2$ are explored at different Pd concentrations (0-3 wt%) and preparation conditions that alter TiO$_2$ crystallinity and the Pd cluster size from a few nanometers to that of single atoms. Annealing such materials at appropriate temperatures leads to solar photocatalytic NO$_x$ removal in a standard ISO reactor up to 10 times faster than that of commercial TiO$_2$ (P25). Such superior performance can be attained by only 0.1 wt% Pd loading on TiO$_2$. Annealing these flame-made powders in air up to 600 °C decreases the amorphous TiO$_2$ fraction and increases its crystal and particle sizes as observed by X-ray diffraction (XRD) and N$_2$ adsorption. The growth of single Pd atoms to Pd clusters on TiO$_2$ prepared at different Pd loading and annealing conditions was investigated by scanning transmission electron microscopy (STEM) and XRD. The clusters and even single Pd atoms on TiO$_2$ are stable up to, at least, 600 °C for 2 hours in air but at 800 °C they grow into PdO nanoparticles whose fraction is comparable with the nominal Pd loading. Hence, most of Pd atoms are on the TiO$_2$ surface where at 800 °C they diffuse and sinter. DRIFTS reveals NO adsorption on single, double, 3- and 4-fold coordinated Pd atoms depending on their synthesis and annealing conditions. The peak intensity of NO adsorption sites involving multiple Pd atoms is substantially lower in TiO$_2$ containing 0.1 wt% than 1 wt% Pd but that intensity from single Pd atoms is comparable. This indicates the dominance of isolated Pd atoms compared to clusters in Pd/TiO$_2$ containing 0.1 wt% Pd that match or exceed the photocatalytic NO$_x$ removal of Pd/TiO$_2$ of higher Pd contents.

In chapter 4, formation of highly visible-active “black” TiO$_2$ consisting of crystalline TiO$_x$ (e.g., Ti$_4$O$_7$, Ti$_3$O$_5$) layers onto nanosilver and nanostructured TiO$_2$ by FSP is presented. Abundant combustion intermediates present during flame synthesis of these materials partially reduce TiO$_2$ and induce strong metal-support interactions (SMSIs) in Ag-TiO$_2$ resulting in crystalline TiO$_x$ as determined by XRD. The growth of such TiO$_x$ can be controlled through the FSP synthesis conditions allowing for tuning the light absorption intensity in the visible spectrum. The as-prepared crystalline TiO$_x$ are stable upon annealing in air, at least, up to 350 °C for two hours. Their presence on the Ag/TiO$_2$ particle surface and efficiency in generating photoinduced charge separation under visible light is demonstrated by electron paramagnetic resonance spectroscopy. Under visible light (λ > 400 nm), these nanoparticles exhibit strong photo-reduction of cationic species (Cr$^{6+}$) and photo-oxidation of methylene blue.
In chapter 5, Ag\(^+\) ion release from nanosilver with closely controlled average particle diameter (7 - 30 nm) in water exposed to ambient air is presented. Fully exposed nanosilver immobilized on silica that does not form SMSIs allows to investigate the intrinsic nature of nanosilver dissolution. The size of nanosilver is determined by XRD and transmission electron microscopy. The presence of Ag\(_2\)O on the as-prepared nanosilver surface is confirmed by UV-vis spectroscopy and quantified by thermogravimetric analysis and mass spectrometry. The release of Ag\(^+\) ions in de-ionized water is monitored electrochemically and traced quantitatively to the dissolution of a preexisting Ag\(_2\)O monolayer on the nanosilver surface. During this dissolution, the pH of the host solution rapidly increases, suppressing dissolution of the remaining metallic Ag. When however a nanosilver suspension is exposed to a CO\(_2\)-containing atmosphere, like ambient air during its storage or usage, then CO\(_2\) is absorbed by the host solution decreasing its pH and contributing to metallic Ag dissolution and further leaching of Ag\(^+\) ions. So the release of Ag\(^+\) ions from the above closely-sized nanosilver solutions in the absence and presence of CO\(_2\) as well under synthetic air containing 200 - 1800 ppm CO\(_2\) is investigated along with the solution pH and related to the antibacterial activity of nanosilver.

Finally, in chapter 6, recommendations for further research are presented. FSP technology enables to control the size of noble metal clusters on ceramics supports in subnano-scale that is often challenging in conventional wet-technologies. This controllability of FSP allows to investigate the size effect of the subnano-clusters on ceramic supports systematically, which provide deep understandings on metal-support interactions facilitating to develop noble catalyst and photocatalysts.

In appendices A-C, the supplemental information of Chapter 2-4 are presented. Also, in appendix D, the controllability of crystalline TiO\(_x\) formation in Ag/TiO\(_2\) by FSP and post-annealing conditions is presented. Optimizing these conditions dramatically improve the photocatalytic activity of these materials resulting in a 4-minute half-life for methylene blue under solar light that is six times faster than that (24 min) of commercial TiO\(_2\) (P25).
Zusammenfassung

Diese Arbeit stellt die Wechselwirkung zwischen Edelmetallen und Metalloxiden vor, welche mit Flammen Spray Pyrolyse (FSP) hergestellt wurden. Eine solche Wechselwirkung verstärkt die photokatalytische Aktivität dieser Materialien für die Umweltsanierung und tragen zum Verständnis der intrinsischen Auflösung von Nanosilber unter Umgebungsbedingungen bei.


Kapitel 2 zeigt Pd-subnanomerter-Klumpen (< 1 nm) auf TiO₂-Nanopartikel welche in einem Schritt mit FSP hergestellt werden. Unter Sonnenlichtbestrahlung war die photokatalytische NO₃ Reduktion im Standard ISO Reaktor im Vergleich zu kommerziellen TiO₂ (P25, Evonik) 3 Mal so aktiv ohne beziehungsweise 7 Mal so aktiv mit photochemisch

In Kapitel 3, um die oben genannten Entdeckungen besser zu verstehen, wurde die solare NO$_x$ Abscheidung für Pd/TiO$_2$ für verschiedene Pd Beladungen (0- 3 Gewichts%) und Herstellungsbedingungen untersucht, dadurch änderte sich die TiO$_2$ Kristallinität und die Pd Klumpengrösse von ein paar Nanometer bis zu einem einzelnem Atom. Das Brennen solcher Materialien bei der richtigen Temperature führt zu einer 10 fachen Beschleunigung der photokatalytischen NO$_x$ Abscheidung im standard ISO Reaktor im Vergleich zu kommerziell erhältlichem TiO$_2$ (P25). Eine solche Leistung kann mit 0.1 Gewichts% Pd beladen auf TiO$_2$ erreicht werden. Wenn diese in der Flamme hergestellten Pulver bei 600 °C gebrannt werden, sinkt der Anteil an amorphem TiO$_2$ und die Kristalle und Partikel werden grösser, so gesehen in Röntgendiffraktometrie (XRD) und N$_2$ adsorption (BET). Das Wachstum von einzelnen Pd Atomen zu Pd Klumpen auf TiO$_2$ wurde untersucht bei unterschiedlichen Pd Beladungen und Brennbedingungen und mit Rastertransmissionselektronenmikroskop (STEM) und XRD charakterisiert. Die Klumpen und sogar die einzelnen Pd Atome auf TiO$_2$ sind stabil bis mindestens 600 °C für 2 Stunden in Luft doch ab 800 °C wachsen sie zu PdO Nanopartikel.
mit einem Gewichstanteil welchem dem Nominalen Anteil entspricht. Folglich sind die meisten Pd Atome auf der TiO$_2$ Oberfläche wenn sie bei 800 °C diffundieren und sintern. DRIFTS zeigt NO adsorption auf einzel, doppelt, 3- und 4-fach koordiniertem Pd Atomen, abhängig von der Synthesemethode und Brennkondition. Die Intensität der NO Adsorption auf mehreren Pd Atomstellen ist wesentlich tiefer bei TiO$_2$ mit 0.1 Gewichts% Pd im Vergleich zu 1 Gewichts% Pd, die Intensität der einzelnen Pd Atome jedoch ist vergleichbar. Dies ist ein Hinweis, dass die isolierten Pd Atome auf den 0.1 Gewichts% Pd dominieren und gleich oder sogar höhere photokatalytische Abreinigung von NO$_x$ bewirkt wie Pd/TiO$_2$ mit höherer Pd Konzentration.


In Kapitel 5 wir die Freigabe von Ag$^+$ Ionen von Nanosilber mit genau kontrollierten Durchschnittsgrössen (7-30 nm) in Wasser bei Umgebungstemperatur gezeigt. Mit Nanosiber welches auf Silika befestist ist und keinen SMSI aufweist, konnte die Basiseigenschaften der Nanosilber Auflösung untersucht werden. Die Grösse der Nanosilberpartikel wurde mit XRD
und Elektronenmikroskopie bestimmt. Die Präsens von Ag₂O auf der unbehandelten Nanosilberoberfläche wurde durch UV-Vis-Spektroskopie bestätigt und quantifiziert mit thermogravimetrischen Analyse gekoppelt mit Massenspektrometrie. Die Freisetzung von Ag⁺ Ionen in destilliertem Wasser wurde elektrochemisch gemessen und wurde mit der Auflösung von Bestehendem Ag₂O Monolayer auf der Silberoberfläche in Verbindung gebracht. Während diesem Auflösungsprozess erhöht sich der pH der Trägerlösung sehr schnell und unterdrückt dabei die Auflösung von weiterem metallischen Ag. Wenn nun eine Suspension mit Nanosilber einer CO₂ haltigen Atmosphäre ausgesetzt wird, wie zum Beispiel Umgebungsluft, dann wird das CO₂ in der Trägerflüssigkeit aufgenommen und senkt den pH, dadurch kann weiteres Ag aufgelöst werden da die Ag⁺ Ionen nicht weiter ausgewaschen werden. Die Freisetzung von Ag⁺ Ionen von den oben genannten Suspensionen wurde künstlicher Luft in Abwesenheit und mit 20 -1800 ppm CO₂ untersucht zusammen mit dem pH und wurde mit der antibakteriellen Aktivität von Nanosilber korreliert.

Schlussendlich in Kapitel 6 werden Empfehlungen für zukünftige Forschungsprojekte vorgestellt. Die FSP Technologie ermöglicht die Kontrolle der Edelmetallklumpengrösse auf Keramischenträgern, was oft eine Herausforderung in konventionellen Nasschemischentechnologien ist. Die Kontrolle des FSP ermöglicht den Grösseneffekt von Subnanometer Klumpen auf Keramischenträgermaterialien gründliche zu untersuchen was ein tiefes Verständnis von Metall-Träger Wechselwirkung erlaubt und es ermöglicht neue Edelmetallkatalysatoren und Photokatalysatoren zu entwickeln.

Chapter 1

Metal-support interactions in catalysts for environmental remediation

Abstract
The catalytic decomposition of organic air pollutants has high potential for environmental remediation but is challenging because such reactions take place at room temperature. To achieve the sufficient catalytic activity at these conditions, the size, morphology and electric state of metal catalysts are critical. To attain the desired performance, the interaction between noble metal catalysts and their ceramic supports is crucial. We herein elucidate the unique catalytic impact of strong metal-support interactions (SMSIs) and strong metal oxide-support interactions (SOSIs). The SMSIs lead to embedded metal nanoparticles into ceramic supports hindering metal particle growth, especially, SMSIs in Pt-TiO$_2$ formed by NaBH$_4$ at room temperature allows to stabilize 1-2 nm of Pt clusters. On the other hand, SMSIs in Ag-TiO$_2$ composites form crystalline TiO$_x$ (x < 2) that is a highly active photocatalyst under the full range of visible light (400–800 nm). Furthermore, such embedded structure could enhance visible light absorption by plasmonic materials. The SOSIs take place between metals and supports through oxygen ligands forming their hetero-bimetallic structure (e.g. Cu-O-Ti). This enables visible-light absorption and facilitates the transfer of photo-excited electrons to the co-catalysts (e.g. TiO$_2$ to Cu) resulting in superior visible-light activity with > 50% of quantum yield. Furthermore, such interactions allow to stabilize small metal clusters and even single atoms on the supports, significantly facilitates the catalytic oxidation of pollutants at room temperature. The nature of these interactions depends on material preparation method altering its catalytic activity and durability.

Part of it is be submitted to Environmental Science: Nano, In preparation
1.1 Introduction

Human activity generates a range of pollutants that can threaten health and environment. Their removal pollutants can be achieved by filtration through adsorbents,\(^1,2\) catalysts\(^3-5\) and photocatalysts\(^5,6\) which have been developed to address specific operation requirements and conditions. For example, in the removal of metal cations\(^1\) and arsenic compounds\(^2\), filtration is favorable, as the catalytic decomposition of such species into harmless ones is challenging. In contrast, nitrogen oxides\(^3\) and volatile organic compounds\(^4\) are catalytically decomposed into \(\text{N}_2\), \(\text{CO}_2\) and \(\text{H}_2\text{O}\) with high efficiency and selectivity under either reducing or oxidizing environments at high temperatures (>200 °C). However, these processes are unable to completely remove pollutants. Thus, to remove the released species, photocatalysis is an attractive approach, as it can be carried out under air using solar energy.\(^6\) In addition, a number of organic compounds (e.g. CO, formaldehyde) can be decomposed catalytically under atmospheric temperature, although careful design of catalyst composites and structures is required.

To date, one of the most widely studied systems is nano-gold supported on metal oxides for oxidation of CO at/near room temperature.\(^7\) In this system, the catalytic activity depends greatly on type of oxide support\(^8,9\) and preparation routes\(^8\) employed, indicating synergistic effects between Au (metal) and the oxides (support). Indeed, such effects have received much attention, with different types of interactions being revealed depending on the combination of metals and supports and their preparation routes. Strong metal-support interactions (SMSIs)\(^10\) and strong metal oxide-support interactions (SOSIs)\(^11\) can alter significantly the catalytic activity by changing the properties of the catalysts (size, morphology and electronic states). The purpose of Chap. 1 is to highlight the significance and potential of metal-support interactions in development of superior catalysts for environmental remediation.

1.2 Strong metal-support interactions (SMSI)

1.2.1 Formation

Strong metal-support interactions (SMSIs) were originally observed by Tauster et al.\(^10\) for group VIII metals on reducible metal oxides (e.g. \(\text{TiO}_2\) and \(\text{Nb}_2\text{O}_5\)). A schematic representation of strong metal-support interactions is shown in Fig. 1.1.
Figure 1.1 Schematic representation of strong metal-support interactions.

They are initiated by H₂ reduction of the metal oxide support by several routes: A1: Spillover of the activated hydrogen species from the metal surface,¹² A2: direct injection of electrons to the metal oxide support from hydrogen adsorbed on the metal surface,¹³ and A3: direct reduction by molecular H₂.¹⁴ Indeed, route A1 is well accepted, since Ag¹² and Au¹⁵ that generally do not activate H₂, do not form SMSIs by H₂ reduction. In addition, the transfer of electrons from metals to metal oxides via route A2 depends on their Fermi levels.¹⁶ Recent
DFT calculations on a Pt cluster-CeO$_2$ nanoparticle predict electron transfer from Pt to CeO$_2$, thus forming oxygen vacancies and oxidizing Pt upon contact.$^{17}$ The oxidized Pt then can be converted easily back into metallic Pt in the presence of H$_2$. Furthermore, metal oxides (e.g. ceria$^{14}$ and titania$^{18}$) can be reduced by molecular H$_2$ at ~500 °C, with the metal-metal oxide interface being reduced at significantly lower temperatures (route A3)$^{14}$.

As indicated by routes B1 and B2, the formation of reduced metal cations (M$_s^{(5-1)+}$) modifies the Fermi levels of metal oxides, promoting electron transfer between metals and metal oxides to form mixed oxides (e.g. Co-O-Ti$^{19}$ and Au-O-Zn$^{20}$) and alloys (e.g. Pt-Zn$^{21}$ and Au-Zn$^{20}$). As outlined in route C, at relatively high temperatures, the reduced species migrates onto the metal surface, forming “decoration” layers of reduced support oxides,$^{22}$ in addition to alloys (Au-Zn$^{20}$, Pt-Zn$^{21}$ and Pt-Ce) and mixed Co-Ti oxides$^{19}$ of the metal and metal oxide support. Although the detailed mechanism of layer formation is still under debate, such layers prevent H$_2$ and CO from reaching the covered metal surface, thus resulting in suppression of their chemisorption.$^{10}$ These layers can be removed by thermal treatment generally under an oxidative environment, as both formation and removal of “decoration” layers are reversible.$^{10}$

### 1.2.2 Effect of temperature

![Figure 1.2 High resolution TEM images of (a) Pd, (b) Co, and (c) Rh particles on titanium oxide reduced in H$_2$ at 500 °C for 2 h (Co and Rh) and at 390 °C for 1 hour (Pd). Adopted from Ref. 19, 24 and 26. High resolution TEM images of 4 wt.% Pt on CeO$_2$ reduced in H$_2$ for 1 hour at (d) 700 °C and (e) 900 °C. (f) Digital diffraction pattern from the circled section in (e). Adopted from Ref. 28.](image-url)
Although the mechanism of layer formation is comparable to that discussed in Fig. 1.1, this process depends greatly on the employed metal and ceramic supports, in addition to reduction conditions (i.e. temperature, H\textsubscript{2} concentration and CO concentration) and precursor residues.\textsuperscript{23} In the case of TiO\textsubscript{2} support, for example, depending on the metal-support combination, the “decoration” layers (Fig. 1.1C) on the metals can be either amorphous\textsuperscript{24} or crystalline\textsuperscript{25} reduced oxides of the support or mixed oxides\textsuperscript{19} of the metal and support.

Figure 1.2a shows high resolution TEM (HRTEM) images of Pd particles on titanium oxide reduced in H\textsubscript{2} at 390 °C for 1 h. The lattice fringes, i.e. 0.28 and 0.52 nm, correspond to Ti\textsubscript{4}O\textsubscript{7}\textsuperscript{26} that has migrated onto the Pd surface. In contrast, the lattice fringe at 0.35 nm corresponds to anatase TiO\textsubscript{2} which is separated from the Pd particles. Crystalline Ti\textsubscript{4}O\textsubscript{7} is also formed by SMSIs in Pt-TiO\textsubscript{2} at 200 - 825 °C under H\textsubscript{2}.\textsuperscript{25} In contrast, SMSIs of (b) cobalt\textsuperscript{19} and (c) rhodium\textsuperscript{24} particles on titanium oxide reduced at 500 °C for 2 hours resulted in amorphous titania layers on these metals. In the case of Co, X-ray photoemission spectroscopy (XPS) elucidated the formation of Co-O-Ti bonding with reduction of Ti\textsuperscript{4+} to Ti\textsuperscript{3+} through SMSIs.\textsuperscript{19} This implies that the layers consist of Co-Ti mixed oxides and/or that Co-O-Ti bonding exists at the interface between Co particles and Ti layers. Such SMSIs are not observed in Co/silica\textsuperscript{19} because of the low reducibility\textsuperscript{27} (or strong Si-O bonding) of silica.

Notably, SMSIs between TiO\textsubscript{2} and Co (or Rh) particles do not form crystalline TiO\textsubscript{x} by H\textsubscript{2} reduction at 500 °C, despite this temperature being higher than that where crystalline TiO\textsubscript{2} is formed during SMSIs in Pd-TiO\textsubscript{2} (390 °C)\textsuperscript{26}. In addition, Pt,\textsuperscript{28} Pd\textsuperscript{29} and Rh\textsuperscript{30} form crystalline CeO\textsubscript{x} layers by H\textsubscript{2} reduction on CeO\textsubscript{2} support while the number of “decorated” Pt particles is significantly larger than that of Rh particles.

As indicated in Fig. 1.2d,e, SMSIs are influenced also by the H\textsubscript{2} reduction temperature. In Pt-CeO\textsubscript{2}, H\textsubscript{2} reduction at 700 °C forms “decoration” CeO\textsubscript{x} layers on and below the Pt particles (Fig. 1.2d), while H\textsubscript{2} reduction at 900 °C forms a CePt\textsubscript{5} alloy (Fig. 1.2e), as confirmed by the diffraction pattern (Fig. 1.2f).\textsuperscript{28} Interestingly, oxidation of reduced Pt/CeO\textsubscript{2} at 700 °C using O\textsubscript{2} removes the “decoration” layers but leaves the CePt\textsubscript{5} alloy intact, while oxidation at 900 °C converts it into segregated Pt particles on CeO\textsubscript{2}. Thus, the formation of both “decoration” layers and CePt\textsubscript{5} alloys is reversible, although the Pt particles increase in size during high temperature treatment.\textsuperscript{28}
1.2.3 Oxidative SMSIs in gold nanoparticles

Figure 1.3 STEM images of 2.8 wt.% Au nanoparticles supported on hydroxyapatite (HAP) annealed at (a) 200, (b) 300, (c) 400, (d) 500, and (e) 600 °C in air, followed by annealing at (f) 500 °C under H₂. (g) In-situ DRIFT spectra of the CO adsorption of these particles and for those reduced in H₂ at 500 °C. (h) CO oxidation at 33.3 mL/min of 1% CO + 1% O₂ in He at 100 °C, using 50 mg of (d) and 40 mg of (f) with alternative pretreatment in 10% of O₂ in He and H₂ at 500 °C (top panels) and 200 °C (bottom panels). Adopted from Ref. 33
In general, SMSIs are induced by the H₂ reduction of group VIII metals on reducible metal oxides above ~400 °C. Recently, SMSIs of Au nanoparticles on lanthanum phosphate, hydroxyapatite and ZnO have been reported also following treatment in oxidative conditions at 300 - 500 °C. Such modifications alter the catalytic activity of these materials towards CO oxidation. For Au on hexagonal lanthanum phosphate, the temperature required to achieve 50% CO oxidation decreases by ~50 °C (to be - 71 °C) following calcination in air at 500 °C, which is 40 °C lower than that of the conventional Au/TiO₂ (supplied by the World Gold Council). It is speculated that calcination in air at 500 °C induces SMSIs, thus enhancing Au dispersion and restructuring of the Au-lanthanum phosphate interface. Recently, clear evidence of SMSIs between Au and a phosphate support under an oxidative environment was reported.

Figure 1.3a-e shows STEM images of Au nanoparticles on hydroxyapatite (HAP) annealed in air at (a) 200, (b) 300, (c) 400, (d) 500 and (e) 600 °C. At 200 °C, the Au particles were simply deposited on the HAP, without formation of decoration layers (Fig. 1.3a). However, upon increasing the annealing temperature, the Au nanoparticles gradually became embedded into HAP, and at 600 °C (Fig. 1.3e), were covered by thin layers composed of Ca, P and O. However, these layers were removed by H₂ reduction at 500 °C (Fig. 1.3f).

This cycle of Au decoration was further confirmed by CO adsorption using in situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, as shown in Fig. 1.3g. Following annealing in air at 200 °C (in the absence of SMSIs), an intense signal at 2102 cm⁻¹ was observed for CO adsorption on metallic Au, which was gradually blue-shifted and depressed with increasing annealing temperature in air. Note that the peak at 2175 cm⁻¹ corresponds to gaseous CO rather than CO on cationic Au⁺ or Au³⁺ whose peak appears at 2170-2190 cm⁻¹ and disappears by He purging. Therefore this blue-shift could be attributed to the positive charge on the Au particle surface. A similar positive charge was observed on the Au surface of Au-ZnO, caused by electron transfer from Au to ZnO through the higher Fermi level of Au compared to ZnO initiating SMSI formation (i.e. Au-O-Zn bonding), as confirmed by EXAFS. In addition, for phosphates such as lanthanum phosphate and HAP, interactions between Au and PO₄⁻ ions may result in Au-(O-P)ₓ bonding.

Following annealing in air at 600 °C, the intensity of the CO adsorption peak (~2110 cm⁻¹) decreased significantly, which is consistent with the presence of “decoration” layers on Au, as shown in Fig. 1.3e. As expected, this significant drop in CO adsorption over the entire Au surface is unfavorable for CO oxidation. However, following H₂ reduction at 500 °C, CO adsorption on the Au surface was restored (Fig. 1.3g) by removal of these layers (Fig.
1.3f). Furthermore, the CO peak position shifts back to that after air annealing at 200 °C (2102 cm\(^{-1}\)) indicating the end of SMSIs. As a result, the CO oxidation activity following H\(_2\) treatment at 500 °C was higher than that obtained following oxidative treatment at 500 °C (Fig. 1.3h, top panel). Thus, the changes in activity due to reversible SMSIs occur through cycling oxidative and reducing treatments at 500 °C but not at 200 °C (Fig. 1.3h, bottom panels) where SMSIs do not take place. These phenomena are analogous to conventional SMSI\(^{31}\) as discussed in Sec. 2.1 but the SMSIs with Au on lanthanum phosphate,\(^{32}\) hydroxyapatite\(^{33}\) and ZnO\(^{20}\) are generated under oxidizing conditions and end under reducing conditions, in stark contrast to conventional SMSIs.\(^{37}\)

Despite the above reversibility of SMSI, the peak position is not completely recovered to 2102 cm\(^{-1}\) that corresponds to CO adsorption on metallic Au (Fig. 1.3g). This is likely due to some Au particles remaining partially embedded in HAP (Fig. 1.3f), similar to Au-ZnO.\(^{20}\) Perhaps, SMSIs occur at the metal-support interface stabilizing small metal catalysts under harsh reaction conditions. In fact, the size of Au particles on the HAP surface remained relatively constant (i.e. 3 nm) during the oxidation-reduction cycles at 500-600 °C (Fig. 1.3d-f).

**1.2.4 SMSIs in Pt/TiO\(_2\) by NaBH\(_4\) treatment at room temperature**

The formation of well-controlled SMSIs at room temperature is desirable for stabilization of small metal clusters limiting their growth. For example, Rui et al.\(^{38}\) reported that SMSIs took place with Pt clusters on TiO\(_2\) during reduction with an aqueous NaBH\(_4\) solution at room temperature. Their light-off temperature for toluene combustion is about 50 °C lower than that by H\(_2\) reduction at 500 °C.
Figure 1.4 (a) Catalytic oxidation of toluene with a flow rate of 100 mL/min of 300 ppm toluene and 20% O₂ in N₂ as a function of temperature by 200 mg of 0.4 wt.% Pt on anatase TiO₂ as-prepared (green diamonds), reduced in H₂ at 500 °C (black squares) and in aqueous NaBH₄ at room temperature (blue triangles) as well as on commercial TiO₂ (red circles, P25, Evonik) reduced in aqueous NaBH₄ at room temperature. (b) Ti 2p XPS spectra of these powders. For comparison, the peak position of Ti⁴⁺ in TiO₂ (459.3 and 464.9 eV)⁹⁹ is shown (broken line). Adopted from Ref. 38

Figure 1.4a shows the effect of temperature on the catalytic oxidation of toluene by 0.4 wt.% Pt nanoparticles on anatase TiO₂ as-prepared (green diamonds), reduced in H₂ at 500 °C (black squares) and in solutions of aqueous NaBH₄ at room temperature (blue
triangles). The H₂ reduction slightly improves the activity for toluene combustion but those treated in NaBH₄ show light-off temperature of ~100 °C, which is about 50 °C lower than those of as-prepared and H₂-reduced Pd/TiO₂. Also, the NaBH₄ treatment enhances the activity of Pt on commercial TiO₂ (red circles, P25, Evonik).

Figure 1.4b shows the Ti 2p XPS spectra of the Pt nanoparticles on anatase TiO₂ reduced in H₂ at 500 °C (black spectrum) and on anatase TiO₂ (blue spectrum) and commercial TiO₂ (red spectrum, P25, Evonik) reduced in aqueous NaBH₄ solution at room temperature. The binding energy of the 2p₃/2 and 2p₁/2 Ti peak position of Pt/TiO₂ reduced in H₂ at 500 °C is significantly lower than that of stoichiometric TiO₂ (459.3 and 464.9 eV) indicating SMSIs in Pt-TiO₂ as confirmed by the suppression of CO chemisorption on Pt surface. Notably, the peak position of the NaBH₄-treated particles was lower than that of H₂ reduced one. This indicates significant reduction of both Pt and TiO₂ as well as stronger SMSI in Pt-TiO₂ by the NaBH₄ treatment. In addition, such treatment can induce SMSIs in Pt/TiO₂ at room temperature, thus minimizing the growth of Pt particles and decreasing the light-off temperature for toluene combustion. Similarly, the NaBH₄ treatment enhances the catalytic activity of Pt nanoparticles for oxidation of benzene and formaldehyde.

A detailed mechanism for this process, however, has not yet been established. For instance, the effect of Na, which improves the activity of Pt for formaldehyde oxidation at room temperature, should be examined for a better understanding of SMSIs during toluene combustion. Finally, these results suggest that the use of small metal clusters along with appropriate stabilization through SMSIs will be applicable for low temperature catalytic oxidation of pollutants.

1.2.5 Visible light-active crystalline TiOₓ formation by SMSIs in a flame

Both CO and formaldehyde can be decomposed catalytically into CO₂ at room temperature but the majority of pollutants consisting of aromatic ring(s) cannot. Thus, the photocatalytic degradation of such pollutants (e.g. toluene) has received significant attention, with the overall aim being total pollutant removal. For such applications, photocatalysts with strong visible light activity are required to effectively utilize solar light.

Recently, “black” titania, which contains titanium suboxides (TiOₓ, x < 2) and/or point Ti³⁺ defects in TiO₂ exhibited remarkable activity under visible light (> 400 nm) attracting attention due to its potential for efficient solar energy utilization. However, the majority of synthetic routes to “black” titania nanoparticles require extreme processing conditions (reduction under high pressure or temperature with H₂, organic solvents, NaBH₄ or
CaH$_2$ for several hours/days making their applicability to mass production quite challenging.

Figure 1.5 (a) STEM and (b) high resolution TEM images of 30Ag/TiO$_2$ prepared by flame spray pyrolysis (FSP). The blue arrow and red broken lines indicate titanium oxide onto nanosilver and TiO$_2$. (c) XRD patterns and (d) UV-Vis absorption spectra of 30Ag/TiO$_2$ as-prepared (red) and annealed in air for 2 hours at 350 (green), 500 (blue) and 600 °C (purple). The crystalline TiO$_x$ absorbs entire range of visible light and is stabilized by SMSIs with TiO$_2$.  

\[ TiO_2 (P25, Evonik) \]
Recently, crystalline TiO$_x$ has been formed by SMSIs between TiO$_2$ and nanosilver made by scalable flame spray pyrolysis (FSP). The STEM image of FSP-made TiO$_2$ loaded with 30 wt.% of Ag (30Ag/TiO$_2$) in Fig. 1.5a shows spherical bright spots indicating Ag nanoparticles on TiO$_2$ (gray) confirmed by energy-dispersive x-ray analysis. Its high resolution TEM image in Fig. 1.5b shows that the light and dark portions correspond to titanium oxide and Ag, respectively, with the latter being embedded and partially coated or decorated (Fig. 1.5b) by layered titanium oxide (indicated by broken red lines), which is analogous to structures generated by SMSIs (Fig. 1.2).

As shown in Fig. 1.5c, anatase TiO$_2$ (diamonds) and Ag (stars) as well as crystalline TiO$_x$ phases were detected by XRD in 30Ag/TiO$_2$ particles, including Ti$_3$O$_5$ at 33° (inverse triangles) and Ti$_4$O$_7$ at 28.5° and 29.5° (triangles). These TiO$_x$ phases are consistent with formation through SMSIs and are stable, at least, for 2 hours in air up to 500 °C that is higher than the phase transition temperature of TiO$_x$ to TiO$_2$ because of TiO$_x$ stabilization by SMSI. Furthermore, during this annealing (< 500 °C), the width at half maximum of the Ag peak (at 44°) remains almost the same due to hindered Ag particle growth by the TiO$_x$ layers (see. Fig. 1.5b), which is similar to Au on hydroxyapatite as discussed in Sec. 2.3. At 600 °C (purple pattern), TiO$_x$ and anatase TiO$_2$ are completely converted to rutile TiO$_2$ accompanied by drastic Ag growth.

As shown in Fig. 1.5d, the presence of crystalline TiO$_x$ improved visible-light absorption (360 - 800 nm) compared to commercial TiO$_2$ (P25, Evonik). The visible-light absorption gradually decreases with increasing annealing temperature (350 - 500 °C) in air, although the fraction of TiO$_x$ remains at the same level. This indicates surface oxidation of TiO$_x$ and/or progressive exposure of TiO$_2$ surface.

Interestingly, the absorption band at 550 nm attributed to the Ag plasmon was not observed in all particles other than the particles annealed in air for 2 hours at 600 °C. This is most likely due to SMSI-induced electron interactions between Ag and Ti. Indeed, at 600 °C where SMSIs cease, the Ag plasmon band around 550 nm appears. Thus, the improved light absorbance at visible wavelengths (400-800 nm) of FSP-made Ag/TiO$_2$ is attributed predominantly to the presence of TiO$_x$. The visible-photocatalytic activity of such FSP-made Ag/TiO$_2$ is higher than that of wet-made Ag/TiO$_2$ and Ag-loaded P25 as high Ag (z > ~ 2%) loadings typically diminish photocatalytic activity.
1.2.6 Spatial metal-support interactions and Au plasmon

Ag and Au nanoparticles exhibit strong visible light absorption by their surface plasmons. Furthermore, as the loading of such metal particles on photocatalysts enhances charge separation and electric field, the effect of plasmon particle characteristics (i.e., size, shape, crystalline phase, etc.) on photocatalysis has been extensively studied, as these factors greatly alter the intensity and wavelength of absorption as reviewed recently. However, to date, the effect of metal-photocatalyst (support) interactions on plasmon absorption has not been investigated.

**Figure 1.6** HRTEM image of Au nanoparticles deposited using the NaBH₄ reduction method on (b) N-doped TiO₂ and (c) pure TiO₂. (c) Schematic of Au-TiO₂ model used in the finite element method (FEM) simulations to investigate the electric field enhancement by Au plasmon for 6 nm of Au particle size, the interparticle distance, d_{Au-Au} = 4-10 nm, and the embedding depth into TiO₂, d_{Au-Ti} = 0-2 nm. (d) The Au plasmon-generated electric field intensity simulations at different Au NP configurations of d_{Au-Au} (4, 6 and 10 nm) and d_{Au-Ti} (0, 1 and 2 nm) in H₂O. The dark red color in the contour plots indicates a strong electric field. Adopted from Ref. 57.

Naldoni et al. deposited Au nanoparticles on N-doped and pure TiO₂ using the NaBH₄ reduction method, inducing SMSIs as discussed in Sec. 2.4. As shown in the HRTEM image (Fig. 1.6a,b), the Au nanoparticles are embedded or partially coveted by both N-doped and pure TiO₂, a typical SMSI-driven particle morphology. To simulate the effect of
Au-TiO$_2$ interactions on the Au plasmon-generated electric field intensity, the interparticle distance and the embedding depth into TiO$_2$ were varied as indicated in Fig. 1.6c.

Figure 1.6d shows the contour plots of the Au plasmon-generated electric field intensity at different Au NP configurations of $d_{\text{Au-Au}}$ (4-10 nm) and $d_{\text{Au-Ti}}$ (0-2 nm) in H$_2$O. With decreasing $d_{\text{Au-Au}}$ (from left to right panels), the electric field intensity increased, reaching a maximum at $d_{\text{Au-Au}} = 4$ nm, which is about half of the Au particle diameter ($d_{\text{Au}} = 6$ nm), consistent with experimental observations.$^{59}$

Interestingly, the progressive inclusion of Au nanoparticles into the TiO$_2$ structure enhanced the intensity of the TiO$_2$ electric field, indicating that SMSIs strengthen the plasmon-induced electric field. However, SMSIs also cause electric interactions between metal and support$^{31}$ resulting in suppression of plasmon absorption$^{50}$ as discussed in Fig. 1.5d. Therefore, the presence of electric interactions through the bonding at the metal-photocatalyst interface should be considered to gain a better understanding of plasmon enhancement of the electric field by SMSIs and the effect of oxidative or reductive SMSIs.

### 1.3 Strong oxide-support interactions (SOSIs)

Strong interactions between group VIII platinum group metal oxides (PGM, e.g. Pt,$^{11}$ Pd,$^{11}$ Ir,$^{11}$ and Rh$^{60}$) and CeO$_2$ supports that induce high sinter resistivity into the VIII metal oxide particles are known as strong oxide-support interactions (SOSIs).$^{11}$ Raman spectroscopy has revealed the presence of PGM-O bonding, with a constant number of PGM-O bonds per unit surface area of CeO$_2$ of $\sim 1$ #/nm$^2$ which is stable under high temperature.$^{11}$ Later, researchers in Toyota systematically investigated the effect of support materials on the SOSIs.$^{27}$
Figure 1.7 (a) Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra at the Pt L3-edge of Pt supported on Al2O3 and CZY after aging at 800 °C in air for 5 hours. The spectra of Pt foil and PtO2 powder are shown for reference. (b) Pt particle size on different metal oxide supports after 800 °C aging, and the oxidation state of Pt based on the height of the “white-line” in the X-ray absorption near-edge structure (XANES) spectra as a function of the binding energy of O1s in the support. Pt particle size is estimated by CO adsorption. Adopted from Ref. 27.
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The Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectra at the Pt L3-edge of Pt supported on Al₂O₃ and Ce-Zr-Y mixed oxide (CZY) after aging at 800 °C in air for 5 h are shown in Fig. 1.7a, in addition to those for the reference Pt foil and PtO₂ powder. The FT-EXAFS spectrum of Pt on CZY exhibits signals corresponding to Pt-O and Pt-O-Ce, but not Pt-O-Pt and Pt-Pt, indicating that Pt stabilization took place through Pt-O-Ce bonding, as expected. In addition, the shorter Pt-O-Ce bond distance compared to that of Pt-O-Pt indicates its greater bond strength, thus resulting in high sinter resistance. Such bonding structures have been observed at the interface of metal-support under both reductive and oxidative SMSIs (i.e. Co-O-Ti and Au-O-Zn), as discussed in Sec. 2.2 and 2.3, and have also been reported in atomically dispersed noble metals (e.g. Pt-O-Ce, Au-O-Ce, and Pd-O-Ti) on metal oxides. In contrast, the spectrum of Pt on Al₂O₃ indicated dominant Pt-Pt bonding, corresponding to metallic Pt particles pointing out the significance of support effect.

These differences can be accounted for by the O1s binding energy in the supports, as a weaker binding energy due to the higher electron density of oxygen creates fewer antibonding states, thus leading to stronger bonding (Fig. 1.7b). Thus, with increasing the O1s binding energy in the support, an increase in Pt size was observed after aging at 800 °C in air for 5 h. In addition, at lower binding energies (and smaller Pt particles), the oxidation state of Pt becomes more positive due to Pt-O-Ce bonding. These facts confirm that the stronger bonding in Pt-O-Ce compared to Pt-O-Al limits Pt sintering. The extent of such anchoring seems to be proportional to the number of surface oxygen defects in the support. Indeed, density functional theory predicts stronger binding of subnano-clusters of noble metals (Au, Pt, and Pd) to TiO₂ with a surface oxygen defect compared to that of defect-free TiO₂. Based on this understanding, Toyota’s researchers designed CZY oxides containing 0.25 wt.% Pt and applied them in practical three-way catalysts.

1.3.1 Stable single metal atoms on supports

The preparation of atomically dispersed noble metal catalysts on supports faces challenges of increasing the loading fraction of small clusters and their scalable production while hindering their growth. Flytzani-Stephanopoulos et al. washed Au and Pt nanoparticles on CeO₂ surface with a solution of NaCN that leached most of the metallic Au and Pt leaving behind residues of cationic Au and Pt atoms that were strongly bonded to CeO₂. Through this technique, the metal loading fraction following leaching corresponded to the intrinsic fraction of the atoms bonded strongly with the support. This fraction is increased by subjecting Au/TiO₂ in ethanol to UV irradiation, resulting in an Au loading of ~1 wt.% Au on
TiO$_2$ following leaching of about 4 wt.% of Au (i.e. 25% of yield for the residues of single Au atoms). However, the use of cyanide might not be favorable in industrial processes because of its toxicity.

More recently, single Pd atoms on TiO$_2$ are stabilized using ethylene glycol (EG) radicals (Fig. 1.8a). These radicals were formed by UV irradiation and adsorbed onto the TiO$_2$ surface (Fig. 1.8a, I to III). Subsequently, PdCl$_4^{2-}$ ions are adsorbed there through the EG radicals, accompanied by a partial dechlorination of PdCl$_4^{2-}$ ions (III to IV). Two chlorine
atoms of the adsorbed PdCl\textsubscript{2} on TiO\textsubscript{2} are then removed by interaction with EG radicals (IV to V) and reaction with H\textsubscript{2} (V to VI). As a result, single Pd atoms are bonded to the TiO\textsubscript{2} surface (Pd\textsubscript{1}/TiO\textsubscript{2}) via Pd-O-Ti bonds. The transformation of Pd atomic structure was confirmed by the Pd/Cl ratio using inductively coupled plasma mass spectrometry as well as Pd K-edge FT-EXAFS spectroscopy (Fig. 1.8b). The FT-EXAFS spectra show the presence of Pd-O and Pd-Cl. The Pd-Cl peak decreases during dechlorination (IV to VI). Also, the absence of Pd particles in Pd\textsubscript{1}/TiO\textsubscript{2} is confirmed by the absence of Pd-Pd bonding in the Pd K-edge FT-EXAFS spectrum of Pd\textsubscript{1}/TiO\textsubscript{2}. In addition, single Pd atoms can be observed in the yellow circles in the STEM image (Fig. 1.8c).

The removal of Cl ligands from Pd (PdCl\textsubscript{2}/TiO\textsubscript{2}) is crucial for catalysis; the styrene hydrogenation rate with PdCl\textsubscript{2}/TiO\textsubscript{2} declines to about 10\% after the first cycle while that with Pd\textsubscript{1}/TiO\textsubscript{2} is stable for, at least, 20 cycles. The above techniques (i.e., NaCN leaching\textsuperscript{61,69} and stabilization by EG radicals\textsuperscript{62}) allow for deposition of \textasciitilde1 wt.\% of single metal atoms on the support by controlling the atomic level structure. However, they require multiple steps to stabilize single atoms on the support surface making their scale-up quite challenging.

The preparation of atomically dispersed Pd on TiO\textsubscript{2} nanoparticles can be carried out in flames in a single step while controlling the Pd cluster size from a few nanometers to the size of a single atom through the concentration of Pd-precursor in the sprayed solution for the flame.\textsuperscript{70} As shown in a schematic of this process (Fig. 1.9a), an organic solvent containing the Pd and Ti precursors is fed though a thin capillary nozzle and dispersed as a fine spray using O\textsubscript{2}. This spray is ignited and sustained by a premixed CH\textsubscript{4}/O\textsubscript{2} flame, vaporizing the Pd and Ti species that subsequently nucleate into Pd and TiO\textsubscript{2} particles, and grow by coagulation and coalescence. Thus, careful tuning of Pd concentration and flame residence time can limit Pd particle growth allowing for control of the Pd cluster size onto TiO\textsubscript{2}. 
Figure 1.9 (a) Schematic representation of Pd cluster formation and its deposition on TiO$_2$ nanoparticles using flame spray pyrolysis. STEM images of Pd/TiO$_2$ prepared by FSP in relatively cold flame (precursor feed rate, 3 mL/min) with Pd contents of (b) 1 and (c) 0.1 wt.% and (d) in relatively hot flame (precursor feed rate, 8 mL/min) with Pd contents of 0.1 wt.%, followed by annealing in air at 600 °C for 2 hours. Pd clusters size on TiO$_2$ is controlled from a few nanometers to that of single atoms by the concentration of Pd species in the flame and flame conditions (e.g. temperature, length) and single Pd atoms on TiO$_2$ boost its photocatalytic NO removal.\textsuperscript{70}

Figure 1.9b,c shows the STEM images of the Pd clusters (squares) on the TiO$_2$ surface, as prepared by FSP in relatively cold flame (precursor feed rate, 3 mL/min), with Pd contents of (b) 1 and (c) 0.1 wt.% (annealed in air at 600 °C for 2 hours). At 1 wt.% of Pd content (b), the majority of Pd clusters were on the subnano-meter scale, even after annealing at 600 °C.
for 2 hours indicating the strong Pd-TiO₂ interactions. Notably, upon decreasing the Pd content down to 0.1 wt.% (c), no Pd subnano-clusters were observed, even at high magnification, with only weak bright points (circles) being observed, which quite likely corresponded to single Pd atoms.⁶² Their presence is elucidated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with a probing molecule⁷⁰ and it reveals the oxidation state of isolated Pd atoms as Pd⁵⁺ indicating SOSIs-like Pd-Oₓ-Ti interaction. At the same Pd content (0.1 wt.%), however, Pd clusters (squares) appear on Pd/TiO₂ made in relatively hotter and less oxidizing flame (precursor feed rate, 8 mL/min) as shown in Fig. 1.9d. In this flame condition, Pd clusters are formed as the flame temperature and residence time of Pd in the flame is higher than in the cold flame (precursor feed rate, 3 mL/min)⁷¹ as expected.

Although it is currently only possible to deposit 0.1 wt.% of single Pd atoms on TiO₂ by FSP (Fig. 1.9c), its solar-photocatalytic activity in NOₓ removal is four and nine times greater than that of commercial TiO₂ (P25, Evonik) with and without 1 wt.% of photodeposited Pd, respectively.⁷⁰,⁷² This remarkable activity is also better than that of Pd nanoparticles (0.5 wt%) deposited on TiO₂ by photodeposition and precipitation methods.⁷³

### 1.3.2 Design at atomic-level interactions between metal and support

As discussed above, single atom sites consist of M-O-M<sub>support</sub> bonding similar to that by SOSIs. Such single hetero-bimetallic sites supported on mesoporous silica are currently receiving attention for next generation visible-light photocatalysts.⁷⁴ In these sites, light irradiation excites an electron trapped in a metal site. This electron is transferred to another metal site via the oxygen ligand.⁷⁵ This is known as metal-to-metal charge-transfer (MMCT)⁷⁶ and occurs by visible-light irradiation in various hetero-bimetallic sites (e.g. Ti-O-Ce,⁷⁴ Ti-O-Sn,⁷⁷ Ti-O-Cu,⁷⁷ and Zr-O-Cu).⁷⁸ This high flexibility of MMCT makes it attractive for developing new visible-light photocatalysts.
Figure 1.10 (a) Schematic of anchored Ti(IV)/Ce(III) sites on mesoporous silica (MCM-41) and the electron excitation/transfer processes during photocatalysis. (b) Diffuse reflectance UV-vis spectra of single Ti/Ce (black spectrum), Ti (red spectrum) and Ce (blue spectrum) sites on mesoporous silica. (c) Schematic of electric band structures for (i) Cu(II) or Fe(III) nanocluster-grafted TiO$_2$, (ii) metal/nitrogen-doped TiO$_2$ and (iii) sensitizer-modified TiO$_2$. (d) Diffuse reflectance UV-vis spectra of TiO$_2$ with Cu subnano-clusters (0, 0.1 and 0.27 wt%). The inset shows a STEM image of Cu subnano-clusters (0.27 wt.%) on TiO$_2$. (e) FT-EXAFS spectra at the Cu K-edge of CuO, Cu(OH)$_2$ and 0.27 wt.% of Cu subnano-clusters on TiO$_2$. Adopted from ref. 74, 82 and 100.
Figure 1.10a shows a schematic for photocatalysis on a Ti$^{4+}$-O-Ce$^{3+}$ hetero-bimetallic site supported on mesoporous silica.\textsuperscript{74} Upon light irradiation to Ti-O-Ce, an electron in the Ce$^{3+}$ site is excited and transferred to the Ti$^{4+}$ site by MMCT resulting in Ti$^{3+}$-O-Ce$^{4+}$. These Ti$^{3+}$ and Ce$^{4+}$ lead to a reduction and oxidation, respectively. The quantum yield for 2-propanol oxidation to CO$_2$ under 460 nm of light irradiation by Ti/Ce on mesoporous silica is five times higher than that of N-doped\textsuperscript{79} TiO$_2$.

Figure 1.10b elucidates MMCT in Ti-O-Ce by visible-light irradiation showing the diffuse reflectance spectra of single Ti/Ce (black line), Ti (red line) and Ce (blue line) sites on mesoporous silica. Visible light is absorbed only by the co-presence of Ti and Ce. Furthermore, the redox potential of Ce$^{3+}$/Ce$^{4+}$ and TiO$_2$/Ti$^{3+}$ are +1.72 and -0.67 eV, respectively, and, thus, the energy gap is 2.39 eV ($h\lambda = 523$ nm) corresponing to the edge of visible-light absorption (520 nm).

Also, similar charge transfer between Cu\textsuperscript{80} or Fe\textsuperscript{81} subnano-clusters and conventional photocatalysts (e.g. TiO$_2$ and WO$_3$) is reported (Fig. 1.10(i)).\textsuperscript{82} By XPS and XANES, the oxidation state of Cu\textsuperscript{82} and Fe\textsuperscript{81} clusters on TiO$_2$ is revealed as Cu$^{2+}$ and Fe$^{3+}$. The energy state of such clusters located between the conduction (CB) and valence (VB) bands receive not only excited e$^-$ in the CB but also e$^-$ directly from the VB via the so-called interfacial charge transfer (IFCT) process\textsuperscript{37} resulting in visible light absorption.

Figure 1.10d shows diffuse reflectance spectra of TiO$_2$ with Cu subnano-clusters (0, 0.1 and 0.27 wt%) and the STEM image. Regardless of Cu loading, a characteristic absorption of TiO$_2$ in UV range (~ 400 nm) is observed. The Cu loading extends the absorption edge to 450-500 nm which is comparable to the energy gap (2.66-2.85 eV) between the redox potential of Cu$^{2+}$ (Cu$^{2+}$/Cu$^{+}$: +0.15 eV or Cu$^{2+}$/Cu$^0$: +0.34 eV)\textsuperscript{83} and the potential of the VB in TiO$_2$ (+3.0 eV)\textsuperscript{84}. Also this absorption edge does not correspond to the band gap of CuO (1.35 eV)\textsuperscript{85}. These facts elucidate the IFCT from the VB of TiO$_2$ to Cu clusters (Fig. 1.10d). Note that a broad absorption band at 600-800 nm corresponds to d-d transition in Cu$^{2+}$\textsuperscript{80}.

Figure 1.10e shows the FT-EXAFS spectra at the Cu K-edge of CuO, Cu(OH)$_2$ and 0.27 wt.% of Cu subnano-clusters on TiO$_2$. All spectra have a characteristic peak at 1.5 Å corresponding to Cu-O bonding. The spectrum of Cu/TiO$_2$ is similar to that for CuO, in particular, exhibiting two peaks at ca. 2.5 and 3.1 Å. Their peak positions and intensities, however, are slightly different implying distorted CuO structure. Presumably, the distortion is induced by the interaction with TiO$_2$ though SOSI-like oxygen bonding that plays a role in the IFCT.
The biggest advantage of visible-light absorption by IFCT on TiO$_2$ is the higher oxidation potential of the hole in the VB (+3.0 eV) than that of OH$^*$ radical formation (H$_2$O → OH$^*$ + e$^-$ + H$^+$; +2.55 eV) that is often the main pathway in photocatalytic decomposition of organics.$^{86}$ Doping TiO$_2$ with cations$^{87}$ or anions (e.g. N$^{88}$ and S$^{89}$) creates intermediate energy states (IES) between the CB and VB narrowing the band gap as shown in Fig. 1.10c(ii). Also, combining a visible-light sensitizer (e.g. CdS$^{90}$ and organic-dyes$^{91}$) to TiO$_2$ enables visible-light photocatalysis (Fig. 1.10c(iii)). However, the energy level of the IES by dopants and the VB in the sensitzers is comparable to or less positive than that of the OH$^*$ radical formation resulting in inferior performance due to the limited OH$^*$ radical formation.

Additionally, the e$^-$ in the subnano-clusters catalytically reduce O$_2$ via multi-electron reduction (O$_2$ + 2H$^+$ + e$^-$ → H$_2$O$_2$, +0.68 eV) that seems to hardly take place in the absence of co-catalysts.$^{92}$ Thus, the effective OH$^*$ radical formation and O$_2$ reduction in the presence Cu or Fe subnano-clusters are attributed to the superior visible-light photocatalytic performance with > 50% of the quantum yield.$^{82}$

As discussed in Sec. 2.3 and 2.4, small metal clusters effectively catalyze the oxidation of hydrocarbons, with recent studies reporting that atomically dispersed noble metals (i.e., Pt$^{42}$ and Ag$^{93}$) supported on metal oxides are highly active in the oxidation of formaldehyde at/near room temperature. The catalytic activity appears to depend on the strength of the metal-support interaction that occurs through metal-O-support bonding.$^{94}$
Figure 1.11 (a) Arrhenius plots for the reaction rate constants \( (k) \) with corresponding activation energy \( (E_a) \) values for HCHO oxidation at 100 mL/min of 400 ppm HCHO and 10% \( O_2 \) in \( N_2 \) using 200 mg microporous hollandite manganese oxide (HMO) and single Ag atom catalysts on HMO, prepared by precipitation of silver particles on HMO (Ag\textsubscript{NPs}), followed by anti-Ostwald ripening (AOR) at 500 °C in air for 6 h (Ag\textsubscript{AOR}), and conventional wet impregnation with AgNO\textsubscript{3} as a precursor (Ag\textsubscript{IMP}). (b) FT-EXAFS spectra at the Ag K-edge of single Ag atom catalysts on HMO (Ag\textsubscript{AOR} and Ag\textsubscript{IMP}) and Ag nanoparticles on HMO (Ag\textsubscript{NPs}). The spectra of Ag\textsubscript{2}O and metallic Ag are shown for reference. Adopted from Ref. 94.

Figure 1.11a shows the Arrhenius plots for the reaction rate constants \( k \), along with the corresponding activation energy \( E_a \) for formaldehyde oxidation at 100 mL/min of 400 ppm HCHO and 10% \( O_2 \) in \( N_2 \), by 200 mg of microporous hollandite manganese oxide (HMO) and single Ag atoms on it. Such catalysts were prepared by precipitation of Ag
particles on HMO, followed by anti-Ostwald ripening (AOR) at 500 °C in air for 6 hours (Ag\textsubscript{AOR}, red circles), and conventional wet impregnation with AgNO\textsubscript{3} as a precursor (Ag\textsubscript{IMP}, blue diamonds). The presence of single atom catalysts reduces the activation energy of the process compared to pure HMO (black squares) reducing by 30 °C the temperature of formaldehyde oxidation. In addition, the activity of the catalyst prepared by AOR was also higher than that prepared by wet impregnation methods.

Moreover, as shown in the STEM images (Fig. 1.11b,c), both preparation routes led to formation of similar line-shaped arrays of silver atoms (bright dots) in one-dimensional 0.47 × 0.47 nm\textsuperscript{2} square tunnels of the HMO (light gray parts). Indeed, FT-EXAFS spectra at the Ag K-edge of the single Ag atoms on HMO prepared by different methods (red line, Ag\textsubscript{AOR} and blue line, Ag\textsubscript{IMP}) in Fig. 1.11d indicate similar Ag local structures, with intermediate valence states between Ag\textsuperscript{0} and Ag\textsuperscript{+}. Such cationic Ag\textsuperscript{+δ} species have been proposed as the active sites for oxidation\textsuperscript{95} and found in several atomically dispersed noble metals (Pt\textsuperscript{61}, Au\textsuperscript{61}, Rh\textsuperscript{96} and Pd\textsuperscript{70}) on ceramic supports. However, the distances between the nearest neighbor atoms (i.e., Ag-O and Ag-Ag) of Ag\textsubscript{AOR} were slightly shorter than those of Ag\textsubscript{IMP}, indicating its stronger interactions between Ag and HMO than those of Ag\textsubscript{IMP}. Furthermore, the catalyst exhibiting stronger interactions in terms of electronic states is often more favorable for the O\textsubscript{2} activation step.\textsuperscript{97} Indeed, for silver-based catalysts in particular, the oxidation of formaldehyde predominantly followed a Mars-van Krevelen mechanism, with O\textsubscript{2} activation being one of the rate-limiting steps.\textsuperscript{98}

1.4 Conclusions

Two types of metal-support interactions (i.e., strong metal-support interactions (SMSIs) and strong metal oxide-support interactions (SOSIs) create new opportunities for improving both the catalytic oxidation of organic pollutants at room temperature and the photocatalytic degradation of pollutants under solar light by stabilizing small metal clusters and even their single atoms on ceramic supports. The effect of such interactions on catalysts becomes prominent with decreasing metal cluster or particle size due to the increase of the metal fraction interacting with the support. The interactions modify the electronic state of single atom catalysts which depends on the preparation method altering the catalytic activity at room temperature (e.g. formaldehyde oxidation by single Ag atom catalysts) and durability. Therefore, careful design of catalyst preparation is necessary for a desired interaction. Also, the interactions play a key role in photo-excited electron transfer from a photocatalyst to the
co-catalyst and the visible-light activity and, by tuning the interactions, the solar-
photocatalytic activity can be boosted to extremely high quantum yield (> 50 %).

1.5 References


89. Ohno T, Mitsui T, Matsumura M. Photocatalytic activity of S-doped TiO₂


Chapter 2

Pd subnano-clusters on TiO$_2$ for solar-light removal of NO

Abstract

Palladium subnano-clusters (< 1 nm) on TiO$_2$ nanoparticles are prepared in one step by flame aerosol technology. Under solar light irradiation, these materials remove NO$_x$ 3 or 7 times faster than commercial TiO$_2$ (P25, Evonik) with or without photodeposited Pd on it. X-ray photoelectron spectroscopy (XPS) reveals that such photodeposited Pd consists of metallic Pd along with several Pd oxidation states. In contrast, flame-made Pd subnano-clusters on TiO$_2$ dominantly consist of an intermediate Pd oxidation state between metallic Pd and PdO. In that intermediate state, the Pd subnano-clusters are stable up to, at least, 600 ºC for 2 hours in air. However, a fraction of them is reduced into relatively large (> 1 nm) metallic Pd nanoparticles by annealing in N$_2$ at 400 ºC for 2 hours, as elucidated by XPS and scanning transmission electron microscopy. The Pd subnano-clusters interact with oxygen defects on the TiO$_2$ surface as shown by Raman spectroscopy. This interaction suppresses CO adsorption on Pd as observed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), analogous to strong metal support interactions (SMSI) of nano-sized noble metals on TiO$_2$.

Published in part in ACS Catalysis 2016;6(3):1887-1893.
2.1 Introduction

Typical nitrogen oxides, NO\textsubscript{x} (NO and NO\textsubscript{2}) removal processes from combustion off-gases such as the three-way catalyst\textsuperscript{1} or selective catalytic reduction\textsuperscript{2} require high temperature (~ 300 °C) and reducing agents (e.g. NH\textsubscript{3}) making difficult the emission of NO\textsubscript{x} at sub-ppm level at ambient temperature. So solar photocatalytic NO\textsubscript{x} removal that requires only sunlight is quite attractive.\textsuperscript{3} Titanium oxide is the most widely used photocatalyst for air cleaning\textsuperscript{4} including environmental NO\textsubscript{x} removal.\textsuperscript{5} Under light excitation, TiO\textsubscript{2} converts NO\textsubscript{x} into nitrate\textsuperscript{3} but some NO is converted also into unfavorable NO\textsubscript{2}. So high conversion and selectivity for nitrate formation are essential. The activity under sunlight can be enhanced by narrowing the TiO\textsubscript{2} band gap by S/N-doping\textsuperscript{6} and plasma-treatment.\textsuperscript{7} For the selectivity, TiO\textsubscript{2} composition and preparation are crucial: Pure anatase TiO\textsubscript{2} and flame-made anatase-rutile TiO\textsubscript{2} composites exhibit high selectivity.\textsuperscript{8} Furthermore, selectivity can be improved by combining NO\textsubscript{2} or nitrate storage compounds such as active carbon\textsuperscript{3} or CaO,\textsuperscript{9} respectively and metal co-catalysts (Ag\textsuperscript{10}, Pd,\textsuperscript{11} Cu\textsuperscript{12}).

Sub-nanometer sized metal clusters induce high conversion and high selectivity minimizing the use of expensive noble metals on such catalysts.\textsuperscript{13} At small sizes on metal oxide supports, the surface free energy increases by the quantum size effect\textsuperscript{14} and low coordination number,\textsuperscript{15} enhancing performance\textsuperscript{16} as well as metal-support interactions\textsuperscript{17} that prevent subnano-cluster sintering\textsuperscript{18}. Strong metal-support interactions (SMSI\textsuperscript{19}) decrease chemisorption of H\textsubscript{2} and CO on noble metals because either the surface of noble metal is covered by reduced support (e.g. TiO\textsubscript{x}\textsuperscript{20}) or the noble metal oxidation state is modified. In SMSI, formation of oxygen vacancies in the support is the key process\textsuperscript{18} and, analogously, subnano-sized noble metals are often anchored at such surface defects.\textsuperscript{21}

Here Pd subnano-clusters on TiO\textsubscript{2} were prepared by flame spray pyrolysis (FSP)\textsuperscript{22} which can be scaled up\textsuperscript{23} to yield production rates of several kg/h. Particle composition and size of FSP- and wet-made Pd/TiO\textsubscript{2} photocatalysts were investigated by X-ray diffraction (XRD) and N\textsubscript{2} adsorption. The characteristics of these Pd clusters were investigated by scanning transmission electron microscopy (STEM) as well as X-ray photoelectron (XPS), Raman and diffuse reflectance infrared Fourier transform (DRIFTS) spectroscopies. Furthermore, the thermal stability of Pd subnano-clusters in air and N\textsubscript{2} was examined. The photocatalytic NO\textsubscript{x} conversion by such Pd/TiO\textsubscript{2} under solar light was compared to that of commercial TiO\textsubscript{2} (P25, Evonik) with or without photodeposited Pd on it.\textsuperscript{24}
2.2 Experimental

2.2.1 Catalyst preparation

Titanium dioxide was prepared in one step by FSP with or without 1 wt.% of Pd (f-TiO$_2$ or f-Pd/TiO$_2$). In a 1:1 volumetric mixture of 2-ethylhexanoic acid (Aldrich, purity > 99 %):acetonitrile (Aldrich, purity > 99.5 %), 159 mM of titanium isopropoxide (Aldrich, purity > 97 %) and 0.6 mM of Palladium acetylacetonate (Aldrich, purity 99 %) were dissolved, as needed. This precursor solution was fed through the FSP capillary nozzle at 8 mL/min, dispersed to a fine spray by 5 L/min O$_2$ (Pan Gas, purity >99%) through the adjacent burner ring and ignited/sustained by a support premixed methane/O$_2$ flame (CH$_4$ = 1.5 L/min, O$_2$ = 3.2 L/min). So high purity Pd/TiO$_2$ particles are produced and collected on a glass-fiber filter (Whatman GF, 24.7 cm effective diameter) 77 cm above the FSP nozzle by a gas pump (Busch Mink MM 1202 AV). For photocatalysis tests, such particles were collected for 4 min resulting in 170 ± 19 mg of homogeneous particle layer on the filter.

Also, 1 wt.% of Pd was photodeposited on commercially available (P25, Evonik) titania (c-TiO$_2$) and FSP-made (f-TiO$_2$) that will be referred to as w-Pd/c-TiO$_2$ and w-Pd/f-TiO$_2$, respectively. Such particles were prepared by dispersing 1 g of c-TiO$_2$ (or f-TiO$_2$) in 0.3 L of distilled water and sonication (Sandelin DT106, 480 W, 35 kHz) for 10 min. Then, 118 mg of Pd(NO$_3$)$_2$ solution (Alfa Aesar, Pd cont. 8.5 wt.%) were added and the pH was adjusted to 7.5 - 8.0 by a 0.8M NaOH solution. Furthermore, 0.1 L of ethanol (Aldrich, purity > 99.8 %) was added to this suspension, stirred magnetically at 600 rpm for 30 min under dark and, subsequently, irradiated by UV light (Konrad Benda, UV-Lamp UV-8 S) for 12 hours. Afterwards, the particles were separated by centrifugation at 10$^4$ rpm for 10 min and dried at 50 °C in a vacuum chamber (10 mbar) for 12 hours.

For photocatalysis tests, 10 g/L of every powder were dispersed by ultrasonication (Sonics Vibra-Cell 500 W, 100 kJ, 30/1 s on/off pulse) in a 1:1 ethanol:water solution. Five ml/min of that suspension were fed through the same FSP capillary nozzle and dispersed to a fine spray by 5 L/min oxygen but without the support flame resulting in homogeneous collection of 170 ± 10 mg) particles on the glass-fiber filter 62 cm above the nozzle. The photocatalytic performance of this particle layer is within 2-4% to that made by direct particle deposition by FSP as described above (Table A.1).

2.2.2 Catalyst characterization

The XRD patterns of all powders, with and without 20 wt.% of NiO (Aldrich, size: -325 mesh) as an internal standard were obtained by a AXS D8 Advance diffractometer.
The crystalline and amorphous mass fractions of TiO$_2$, $f(x)$, were calculated from the integrated peak area of the XRD patterns at 25.5°, 27.5° and 42.5° for anatase, rutile and NiO, respectively:

$$f(\text{anatase/rutile}) = \frac{\text{Area}_{\text{anatase/rutile}}}{5 \cdot \text{Area}_{\text{NiO}}}$$

and

$$f(\text{amorphous}) = 1 - f(\text{anatase}) - f(\text{rutile}).$$

The average anatase (ISDC: 663711) and rutile (ISDC: 663710) sizes were obtained by software Topas 4.2 while an average crystalline TiO$_2$ size, $s$, was calculated accounting for the mass fractions of anatase and rutile. The specific surface area (SSA) of all powders was obtained by N$_2$ adsorption at 77 K, using the Brunauer-Emmett-Teller (BET) method (Micromeritics, Tristar II PULS). The BET equivalent particle diameter, $d$, was calculated assuming the weighted density of the particles ($\rho(\text{anatase})$, $\rho(\text{rutile})$ and $\rho(\text{amorphous}) = 3.8$, 4.2 and 3.8 g/cm$^3$) as follow:

$$d = \frac{6000}{\sum (f(x) \cdot \rho(x))} \text{[nm]}.$$ 

Images by STEM were recorded with a high-angle annular dark-field detector (Hitachi, HD 2700-Cs, 200 kV).

Raman spectroscopy was performed on a Renishaw InVia Reflex spectrometer with an Ar-ion laser as excitation source focused with a microscope (Leica, magnification 50×). These samples were pressed into tablets and placed on a glass plate. The spectra were recorded for 10 s with 20 accumulations to obtain sufficient signal-to-noise ratio with a CCD camera after being diffracted by a prism (1800 lines per millimeter) using 2.5 mW laser energy. The Raman spectra were fitted using spline-B interpolation and Origin 8.6 to find the peak position.

XPS was performed using an X-ray photoemission spectrometer (Physical Electronics, Quantum 2000) with monochromatic Al Kα radiation ($h\nu = 1486.7$ eV). The Au 4f$_{7/2}$ peak at 83.96 eV is used for the energy calibration of the instrument. The electron take-off angle was 45° and the diameter of the measured spot was ~150 µm. The samples were mounted on a stainless steel sample holder with an adhesive carbon tape. To compensate for eventual surface charging, built-in electron and argon ion neutralizers were used. The base pressure of the system was below 5 × 10$^{-7}$ Pa. For the analysis the C 1s peak at 284.6 eV was used for charge correction and for the background subtraction the Shirley method was used. The Pd 3d$_{5/2}$ peak (334-339 eV) was deconvoluted by four different oxidation states of Pd: metallic$^{28,29}$ Pd, intermediate Pd, PdO$^{28,30}$, ionic$^{30}$ Pd$^{2+}$ using Origin 8.6 and the Pd 3d$_{3/2}$ peak (339-344 eV) was fitted keeping the full-width at half-maximum (FWHM) and setting the heights of the deconvoluted spectra of the 3d$_{3/2}$ peak to 60%.

Diffuse reflectance infrared Fourier transform (DRIFTS) of the FSP-, wet-made and commercial powders were performed using a Vertex 70v spectrometer (Bruker Optics). Spectra were obtained by averaging 100 scans (100 scan/min) at 4 cm$^{-1}$ resolution.
powders were placed in an in situ DRIFTS cell\textsuperscript{31} that was heated to 40 °C in He (Pangas, purity > 99.999 %) for 10 min. Afterwards 10% of CO in He was passed over the sample and the spectra were recorded continuously (at least for 20 min) until the spectrum reached steady state.

2.2.3 Photocatalytic evaluation for NO removal under solar-light

The glass-fiber filters coated with the catalysts (as described above) were cut in 5 cm × 10 cm rectangular sheets that were held in a standard continuous-flow reactor (ISO 22197-1:2007) and uniformly irradiated through a 5 mm thick Pyrex glass by 100 mW/cm\textsuperscript{2} of solar light (Solarsim 150, Solaronix). An air stream of 3 L/min at 50 % relative humidity containing 1 ppm of NO flowed over the catalyst sheet while NO and NO\textsubscript{2} concentrations were monitored every 3 s by a NO\textsubscript{x} detector (CLD 882 S, Eco Physics) at the reactor outlet. After the test for 5 hours, the filter coated with the catalysts was immersed in DI-water (10 mL), at least, for 12 hours to leach any nitrate remaining on the catalyst surface and the amount of leached nitrate, \(m_{NO_3^-}\), was measured by a nitrate ion meter (LAQUAtwin B-742, Horiba). The average NO and NO\textsubscript{x} (NO + NO\textsubscript{2}) removals (\(\eta_{NO}\) and \(\eta_{NOx}\)) and NO\textsubscript{2} and nitrate formations (\(\eta_{NO2}\) and \(\eta_{NO3^-}\)) under solar-light for \(t_i = 5\) hours were defined as follows:

\[
\eta_{NO} = \int_{0}^{t_i=5h} \frac{C_{NO_{in}[ppm]} - C_{NO_{out}[ppm]}}{C_{NO_{in}[ppm]}} dt
\]

\[
\eta_{NO2} = \int_{0}^{t_i=5h} \frac{C_{NO2_{out}[ppm]}}{C_{NO_{in}[ppm]}} dt
\]

\[
\eta_{NOx} = \int_{0}^{t_i=5h} \frac{C_{NO_{in}[ppm]} - C_{NO_{out}[ppm]} - C_{NO2_{out}[ppm]}}{C_{NO_{in}[ppm]}} dt
\]

\[
\eta_{NO3^-} = \frac{m_{NO3^-}[mol]}{\frac{3 \text{ [L/min]}}{22.4 \text{ [L/mol]}}} \int_{0}^{t_i=300 min} \frac{C_{NO_{in}[ppm]} dt}{C_{NO_{in}[ppm]}}
\]
2.3 Results and Discussion

2.3.1 Solar light photocatalysis and properties of catalysts

Figure 2.1 Evolution of NO and NO\textsubscript{2} concentrations during NO\textsubscript{x} removal test (ISO 22197-1:2007) with commercial TiO\textsubscript{2} (c-TiO\textsubscript{2}, squares) and FSP-made TiO\textsubscript{2} with 1 wt.% of Pd (f-Pd/TiO\textsubscript{2}, circles) under artificial solar-light (100 W/cm\textsuperscript{2}). The initial NO and NO\textsubscript{2} concentrations is 1 and 0 ppm, respectively.

Figure 2.1 shows the evolution of NO (filled symbols) and NO\textsubscript{2} (open symbols) concentrations from solar light photocatalysis of NO (ISO 22197-1:2007) using commercial TiO\textsubscript{2} (c-TiO\textsubscript{2}, squares) and FSP-made TiO\textsubscript{2} with 1 wt.% of Pd (f-Pd/TiO\textsubscript{2}, circles). For the first 40 min under dark, both NO and NO\textsubscript{2} are at 1 and 0 ppm, respectively, indicating no conversion of NO and removal of catalytic NO\textsubscript{x}, as expected. When solar light is on, NO and NO\textsubscript{2} concentrations rapidly reach steady state by both photocatalysts during 5 h of irradiation (40-340 min). The net difference, \( C_{NO\text{in}} - C_{NO\text{out}} - C_{NO_2\text{out}} \), corresponds to the formation\textsuperscript{3} of nitrate as NO\textsubscript{x} removal. Under light irradiation, more NO is removed by f-Pd/TiO\textsubscript{2} than c-
TiO$_2$ due to Pd presence$^{32}$. On the other hand, c-TiO$_2$ forms slightly more NO$_2$ than f-Pd/TiO$_2$, while formation of N$_2$O by these powders was not detected by FTIR.

Table 2.1 Mass fraction, average crystal size, $s$, and BET-equivalent particle diameter, $d$, of commercial TiO$_2$ (c-TiO$_2$), FSP-made (f-TiO$_2$ and f-Pd/TiO$_2$) and wet-photodeposited Pd on TiO$_2$ (w-Pd/c-TiO$_2$ and w-Pd/f-TiO$_2$) and their average efficiencies of NO and NO$_x$ removals ($\eta_{NO}$ and $\eta_{NOx}$) as well as NO$_2$ formation ($\eta_{NO2}$) for 5 hours under artificial solar-light.

<table>
<thead>
<tr>
<th>Powders</th>
<th>Mass fraction wt.%</th>
<th>Size/diameter, nm</th>
<th>Performance, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Rutile</td>
<td>Amorphous</td>
</tr>
<tr>
<td>c-TiO$_2$</td>
<td>82.6</td>
<td>8.4</td>
<td>9.1</td>
</tr>
<tr>
<td>f-TiO$_2$</td>
<td>73.4</td>
<td>3.6</td>
<td>23.0</td>
</tr>
<tr>
<td>w-Pd/c-TiO$_2$</td>
<td>82.1</td>
<td>8.5</td>
<td>8.4</td>
</tr>
<tr>
<td>w-Pd/f-TiO$_2$</td>
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<td>3.3</td>
<td>23.9</td>
</tr>
<tr>
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<td>73.8</td>
<td>1.9</td>
<td>22.5</td>
</tr>
<tr>
<td>f-Pd/TiO$_2$/air</td>
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<td>8.0</td>
<td>5.9</td>
</tr>
<tr>
<td>f-Pd/TiO$_2$/N$_2$</td>
<td>74.1</td>
<td>2.5</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Table 2.1 shows TiO$_2$ mass fractions (anatase, rutile and amorphous), average crystal size, $s$, and BET-equivalent particle diameter, $d$, of c-TiO$_2$ and f-TiO$_2$ as well as with photodeposited 1wt.% Pd on them (w-Pd/c-TiO$_2$ and w-Pd/f-TiO$_2$) and FSP-made Pd/TiO$_2$ as prepared (f-Pd/TiO$_2$) as well as annealed for 2 hours in air at 600 °C (f-Pd/TiO$_2$/air) and in N$_2$ at 400 °C (f-Pd/TiO$_2$/N$_2$) along with their average efficiency of NO and NO$_x$ removals ($\eta_{NO}$ and $\eta_{NOx}$) as well as NO$_2$ formation ($\eta_{NO2}$) for 5 hours under artificial solar-light as in Figure 2.1. Regardless of preparation method, no detectable Pd and PdO peaks appear by XRD in all powders containing Pd (Fig. A.1). Furthermore, the low Pd presence (1 wt.%) does not affect their crystal size, particle diameter and phase composition as seen with trace Au$^{22}$ and Pt$^{26}$ on TiO$_2$. Anatase is the dominant crystalline phase for all powders here and the mass ratio of anatase and rutile (= the fraction in total crystalline content in Table A.2) in FSP-made powders is consistent with that in similarly made$^{26}$ Pt/TiO$_2$. Most interestingly, the amorphous fraction in commercial TiO$_2$ (c-TiO$_2$) is 9.1 wt%, in agreement with Ohtani et al.$^{25}$ but it is significantly smaller than that in FSP-made powders, $\sim$33 wt.%, as indicated by their non-straight XRD base lines compared to those of c-TiO$_2$. In c-TiO$_2$ and w-Pd/c-TiO$_2$, both crystal, $s$, and primary particle, $d$, sizes are similar, as expected. In FSP-made powders, the BET size, $d$, is slightly smaller than the crystalline size, $s$, indicating the presence of small amorphous TiO$_2$ particles. This is in agreement with similarly flame-made TiO$_2$ using propionic acid as solvent with low enthalpy.$^{33}$
As shown in Fig. 2.1 and Table 2.1, the $\eta_{NO}$ of f-Pd/TiO$_2$ is much higher than that of c-TiO$_2$ but their $\eta_{NO2}$ are similar resulting in 7 times higher $\eta_{NOx}$ (NO removal as NO$_x$) for f-Pd/TiO$_2$ than c-TiO$_2$. For all the catalysts, $\eta_{NOx}$ is comparable with $\eta_{NO3}$ indicating that most of converted NO becomes NO$_2$ and nitrate, which is consistent with photocatalytic NO removal by pure TiO$_2$. Only the $\eta_{NOx}$ of f-Pd/TiO$_2$ (as-prepared and annealed in air and N$_2$) is slightly higher than $\eta_{NO3}$ implying some N$_2$ formation which is hardly detected because of the low concentration. This activity of f-Pd/TiO$_2$ is higher than that of N-doped TiO$_2$ that was about 1.4 and 2 times higher than c-TiO$_2$ in UV and visible light, respectively. Furthermore, the activity of plasma-treated TiO$_2$ and Ti$^{4+}$ complex were only about 2 times higher than that of commercial pure TiO$_2$ (ST-01, Ishihara).

Most importantly, the $\eta_{NO}$ and $\eta_{NO2}$ of f-Pd/TiO$_2$ is higher and lower, respectively, than those of wet-made (w-Pd/c-TiO$_2$ and w-Pd/f-TiO$_2$) indicating that the high selectivity of f-Pd/TiO$_2$ for nitrate formation. As a result, the $\eta_{NOx}$ of f-Pd/TiO$_2$ is about 3 times higher than w-Pd/c-TiO$_2$ as Pd photodeposition doubles the $\eta_{NOx}$ of c-TiO$_2$, in agreement with Wu et al. but hardly affects that of f-TiO$_2$. Also, the $\eta_{NOx}$ of f-TiO$_2$ is higher than that of c-TiO$_2$, probably due to the higher SSA and low rutile TiO$_2$ content of the former. As shown in Table 2.1, both Pd deposition methods do not influence the size and composition of TiO$_2$. Interestingly, annealing f-Pd/TiO$_2$ in air at 600 °C (f-Pd/TiO$_2$/air) slightly improves the $\eta_{NO}$ and $\eta_{NOx}$ because of crystallization of amorphous TiO$_2$ that is not photocatalytically active. On the other hand, annealing in N$_2$ at 400 °C degrades the $\eta_{NO}$ and $\eta_{NOx}$, although its size and crystalline composition of TiO$_2$ remain almost the same. As a result, the characteristics of Pd (size, oxidation state, etc.) play a crucial role on NO$_x$ removal efficiency.
2.3.2 Properties of Pd subnano-clusters

![Figure 2.2](image)

Figure 2.2 STEM images of (a) w-Pd/c-TiO$_2$, (b) w-Pd/f-TiO$_2$, f-Pd/TiO$_2$, (c,d) as-prepared at two magnifications, annealed for 2 hours in (e) air at 600 °C and (f) N$_2$ at 400 °C.

Figure 2.2 shows representative images of photodeposited Pd particles (bright spots) on (a) commercial and (b) FSP-made TiO$_2$ (gray) along with two magnifications (c, d) of as-prepared f-Pd/TiO$_2$ as well as annealed for 2 hours in (e) air at 600 °C and (f) N$_2$ at 400 °C. The size of photodeposited Pd (1-10 nm) on c-TiO$_2$ (a) is slightly larger than that (1-5 nm) on
f-TiO$_2$ (b) probably due to smaller SSA of c-TiO$_2$, a difference that does not affect their photocatalyst activity (Table 2.1). In f-Pd/TiO$_2$ (c), however, there are no distinguishable Pd particles (> 1 nm) because of the extremely small size of Pd clusters that can be seen only (circles) at the higher magnification (Fig. 2.2d).

Most interestingly, after annealing in air at 600 °C, the Pd size in f-Pd/TiO$_2$ is still in the subnano range (e) even though such Pd clusters (< 1 nm) should have melted at this temperature$^{36}$. On the other hand, annealing that powder under N$_2$ converted most of the Pd clusters into nanoparticles (1-5 nm) as shown in Fig. 2.2f. Even though some Pd clusters could still remain, these are hardly detected because of the comparable z-contrast of Pd and TiO$_2$. Therefore, the presence of Pd subnano-clusters that are stable in air up to 600 °C for 2 hours seems crucial for the superior photocatalytic NO$_x$ removal. Conversion of some subnano-clusters into Pd nanoparticles by N$_2$ annealing at 400 °C decreases this activity (Table 2.1). In Pd clusters on TiO$_2$, theoretical calculations suggest that Pd subnano-cluster bonds to several terminated O and Ti on TiO$_2$ surface forming Pd-O$_x$-TiO$_2$ structure.$^{21}$ Similar bonding structure is observed also with atomically dispersed Pt and Au on CeO$_2$ and the bonding oxidizes such noble metals.$^{16}$

Figure 2.3 shows XPS spectra of photodeposited Pd on FSP-made (a), and commercial TiO$_2$(b) along with as-prepared f-Pd/TiO$_2$ (c) and annealed for 2 hours in air at 600 °C (d, f-Pd/TiO$_2$/air) and in N$_2$ at 400 °C (e, f-Pd/TiO$_2$/N$_2$). These spectra are deconvoluted by four different states of Pd: metallic Pd (red)$^{28,29}$, intermediate Pd oxidation (green), PdO (blue)$^{28,30}$, ionic Pd$^{2+}$ (orange)$^{30}$ along with their cumulative fitting (black). The obtained spectra and deconvolutions are reproducible as shown with two samples prepared in different batches (Fig. A.2). The reasonably good match in the 3d$_{3/2}$ peak (339-344 eV) using the fraction of peak area of the 3d$_{5/2}$ peak (334-339 eV) indicates appropriate baseline correction and peak fitting. Both photodeposited Pd on f-TiO$_2$ (a) and c-TiO$_2$ (b) consist of mainly metallic Pd and different Pd oxidation states, in agreement with literature$^{29}$. The peak position of metallic Pd (~334.6 eV) is slightly lower than known values (335.0 eV)$^{28}$, as observed also with photodeposited Pd on TiO$_2$ in aqueous-alcohol solutions$^{29}$. This shift could be attributed to charge injection$^{37}$ by intermediate products of ethanol oxidation whose redox potential is higher than the Fermi level of metallic Pd and the conduction band of TiO$_2$.

In contrast, for Pd on FSP-made f-Pd/TiO$_2$ (Fig. 2.3c) an intermediate Pd oxidation state dominates. Its peak (green, ~335.6 eV) lies between metallic Pd (red, ~334.6 eV) and PdO (blue, ~336.6 eV). The absence of a separate metallic Pd peak is attributed to the weak signal intensity at 334.6 eV in contrast to Fig. 2.3a,b. With Pd clusters, Pd-O$_x$-TiO$_2$
interaction\textsuperscript{21} and/or sub-stoichiometric PdO\textsubscript{x} (x < 1) could induce different intermediate oxidation states broadening that peak, consistent with the broader FWHM of the intermediate Pd oxidation states than that (= 1.1 eV) of the other Pd forms (Fig. A.2d). The peak intensity of PdO (blue, \~336.6 eV) is weaker than that of the intermediate Pd oxidation state indicating some presence of PdO subnano-clusters and/or particles. When the size of FSP-made Pd on TiO\textsubscript{2}, however, is above 10 nm, PdO is the primary state as detected by XRD.\textsuperscript{38} Therefore, the intermediate oxidation state is a characteristic feature of the Pd subnano-clusters on oxides. Regardless of Pd preparation method, the fractions of ionic Pd\textsuperscript{2+} and PdO are rather minor and nearly equivalent indicating that these Pd states are probably irrelevant. As a consequence, the intermediate Pd oxidation state (\~335.6 eV) seems crucial for the remarkable NO removal activity of FSP-made Pd/TiO\textsubscript{2} (Fig. 2.1).

After annealing f-Pd/TiO\textsubscript{2} in air for 2 hours at 600 °C, its Pd oxidation spectra (Fig. 2.3d) are still identical to those of as-prepared f-Pd/TiO\textsubscript{2} (Fig. 2.3c). This implies that the Pd subnano-clusters remain largely intact by annealing as seen also by microscopy (Fig. 2.2e). On the other hand, annealing f-Pd/TiO\textsubscript{2} in N\textsubscript{2} decreases drastically the intermediate Pd oxidation state spectrum while the metallic Pd spectrum becomes stronger (Fig. 2.3e). Metallic Pd is created mainly from intermediate Pd and to a lesser extent by PdO\textsuperscript{39} (Fig. A.2) resulting in metallic Pd particles from their clusters (Fig. 2.2f). Nevertheless, a certain fraction of intermediate Pd oxidation state is still preserved after annealing in N\textsubscript{2} indicating the presence of some subnano-Pd clusters.
Figure 2.3 XPS spectra (circles) of a) w-Pd/c-TiO₂, b) w-Pd/f-TiO₂ and f-Pd/TiO₂ c) as prepared and annealed for 2 hours in d) air at 600 °C (f-Pd/TiO₂/air) and e) N₂ at 400 °C (f-Pd/TiO₂/N₂) for 2 hours along with their deconvolution by four oxidation states of Pd: metallic Pd (red), intermediate Pd (green), PdO (blue), ionic Pd²⁺ (orange) and cumulative fitting (black).

2.3.3 Interaction of Pd subnano-clusters and TiO₂

Figure 2.4 shows FTIR spectra of CO adsorption on the above powders. The peaks around 2130 and 2180 cm⁻¹ that are assigned to CO adsorption on TiO₂ appear in all spectra. The CO-Pd peaks around 1800-2000 and 2090 cm⁻¹ that correspond to multiple-coordinated CO on Pd and linear CO-Pd, respectively, are notably lower for f-Pd/TiO₂ (blue spectrum) than photodeposited and annealed in N₂ powders. Furthermore, the weaker CO
adsorption on that powder is maintained even after annealing it in air (purple spectrum) indicating the presence of PdOₙ (x < 1) and/or Pd-O-TiO₂ interaction.

![Figure 2.4](image)

**Figure 2.4** DRIFTS of CO adsorption on c-TiO₂, photodeposited Pd on TiO₂ (w-Pd/c-TiO₂ and w-Pd/f-TiO₂) and FSP-made powders as-prepared (f-TiO₂ and f-Pd/TiO₂) as well as annealed for 2 hours under air at 600 °C (f-Pd/TiO₂/air) and N₂ at 400 °C (f-Pd/TiO₂/r-N₂).

To form and stabilize such subnano-clusters, the number of oxygen defects in the oxide support could be the critical parameter as more reducible oxides provide more anchoring sites. The importance of defects to stabilize Pd clusters on TiO₂ is also predicted by density functional theory. The presence of oxygen defects in TiO₂ and their stability were investigated by Raman spectroscopy to correlate the stability of the anchoring sites with catalyst performance.
Figure 2.5 Raman spectra of c-TiO$_2$, photodeposited Pd on TiO$_2$ (w-Pd/c-TiO$_2$ and w-Pd/f-TiO$_2$) and FSP-made powders as-prepared (f-TiO$_2$ and f-Pd/TiO$_2$) as well as annealed for 2 hours under air at 600 °C (f-Pd/TiO$_2$/air) and N$_2$ at 400 °C (f-Pd/TiO$_2$/r-N$_2$). The vertical dashed line indicates the peak position of stoichiometric (defect-free) anatase$^{44}$ TiO$_2$ at 143 cm$^{-1}$.

Figure 2.5 shows the Raman E$_g$ peak of anatase TiO$_2$ of the above powders. Its position correlates with the number of defects in the anatase lattice.$^{44,45}$ The peak position of c-TiO$_2$ (purple spectrum) is almost identical to the stoichiometric anatase TiO$_2$ (dashed line) while that from f-TiO$_2$ (blue spectrum) slightly shifts to larger wavenumbers, indicating the presence of more defects than in c-TiO$_2$.$^{44}$ Photodeposition of Pd to either commercial (w-Pd/c-TiO$_2$, orange spectrum) or FSP-made TiO$_2$ (w-Pd/f-TiO$_2$, black spectrum) shifts further that peak, indicating the formation of oxygen defects$^{44}$ that could be attributed to charge injection by intermediate products of ethanol oxidation.$^{37}$

The peak position of FSP-made Pd on TiO$_2$ (f-Pd/TiO$_2$, red spectrum) also shifts to larger wavenumbers but it does not change by annealing for 2 hours under air at 600 °C (f-Pd/TiO$_2$/air, purple spectrum) and N$_2$ at 400 °C (f-Pd/TiO$_2$/N$_2$, green spectrum). The peak position of f-Pd/TiO$_2$/N$_2$, however, shifts to small wavenumbers when it is annealed in air indicating removal of oxygen defects (Fig. A.3).$^{44}$ This is attributed to the growth of Pd.
subnano-clusters into particles (Fig. 2.2f) that spatially segregates Pd clusters from TiO_2 oxygen defects ceasing such Pd-O_x-TiO_2 interaction.

2.4 Conclusions

Solar-light photocatalysts consisting of palladium subnano-clusters (< 1 nm) on nanostructured TiO_2 (f-Pd/TiO_2) were prepared by flame aerosol technology. Under solar light they exhibited 3 or 7 times higher NO removal efficiency as NO_x than commercial TiO_2 (c-TiO_2) with or without photodeposited Pd on it. The Pd subnano-clusters are interacting strongly with oxygen defects on the TiO_2 surface creating an intermediate oxidation state of Pd as proven by XPS that hinders CO chemisorption on Pd. Such strong Pd-O_x-TiO_2 interactions hold to annealing up to 600 °C in air for 2 hours but partially cease upon annealing at 400 °C in N_2 converting most Pd subnano-clusters into Pd nanoparticles as detected by CO chemisorption and seen by STEM. This particle growth deteriorates the NO_x removal activity of flame-made Pd/TiO_2 indicating that Pd subnano-clusters are critical for the remarkable photocatalytic NO_x removal under solar light.

2.5 Acknowledgements

The research leading to these results has received funding from the Swiss National Science Foundation (grant no. 200021_149144). The help of Severin Hahn in particle characterization is appreciated. TEM work was performed at the Electron Microscopy Center of ETH Zurich (EMEZ).

2.6 References


Chapter 3

Atomically dispersed Pd on TiO$_2$ for NO removal by solar light

Abstract

Reducing the particle size of noble metals on ceramic supports can maximize noble metal performance and minimize its use. Here Pd clusters onto nanostructured TiO$_2$ particles are prepared in one step by scalable flame aerosol technology while controlling the Pd cluster size from a few nanometers to that of single atoms. Annealing such materials at appropriate temperatures leads to solar photocatalytic NO$_x$ removal in a standard ISO reactor up to 10 times faster than that of commercial TiO$_2$ (P25, Evonik). Such superior performance can be attained by only 0.1 wt% Pd loading on TiO$_2$. Annealing these flame-made powders in air up to 600 °C decreases the amorphous TiO$_2$ fraction and increases its crystal and particle sizes as observed by X-ray diffraction (XRD) and N$_2$ adsorption. The growth of single Pd atoms to Pd clusters on TiO$_2$ prepared at different Pd loading and annealing conditions was investigated by scanning transmission electron microscopy (STEM) and XRD.

The single Pd atoms and clusters on TiO$_2$ are stable up to, at least, 600 °C for 2 hours in air but at 800 °C they grow into PdO nanoparticles whose fraction is comparable with the nominal Pd loading. So most of Pd atoms are on the TiO$_2$ surface where at 800 °C they diffuse and coalesce. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reveals NO adsorption on single, double, 3- and 4-fold coordinated Pd atoms depending on their synthesis and annealing conditions. The peak intensity of NO adsorption sites involving multiple Pd atoms is substantially lower in TiO$_2$ containing 0.1 wt% than 1 wt% Pd but that intensity from single Pd atoms is comparable. This indicates the dominance of isolated Pd atoms compared to clusters in Pd/TiO$_2$ containing 0.1 wt% Pd that match or exceed the photocatalytic NO$_x$ removal of Pd/TiO$_2$ of higher Pd contents.

Published in part in *AIChE J.* 2017;63(1):139-146.
3.1 Introduction

Reducing the size of noble metals onto ceramic supports can enhance catalyst activity while minimizing the use of expensive noble metals. Especially, size reduction to subnanoscale\(^1\) and, ultimately, to single-atom\(^2\) is currently receiving renewed interest because in that scale, the fraction of noble metal atoms on the catalyst surface drastically increases compared to that of noble metal nanoparticles.\(^3\) Such size reduction induces unique and superior catalytic activity though the optimal cluster size seems to vary for different reactions: for instance, single-atom catalysts (e.g. Au\(^4\), Pt\(^4\) and Ir\(^5\)) appear suitable for the water gas shift reaction while clusters of Au\(^6,7\) (2 - 3 nm) and Pd\(^8\) (~ 1 nm) are optimal for CO oxidation.

For photocatalytic NO removal by TiO\(_2\), NO is converted to nitrate ions (NO\(_3^-\)) by photo-excited holes and O\(_2\) created via O\(_2\) reduction by photo-excited electrons.\(^9\) Thus, the second mechanism is facilitated by noble-metal co-catalysts (Au\(^10\), Pd\(^11\) and Pt\(^12,13\)) through their well known O\(_2\) reduction activity. The size of co-catalysts plays a critical role through the transfer of photoexcited-electrons to reactants. Size reduction of co-catalysts up-shifts their Fermi level resulting in effective electron transfer from photocatalysts (e.g. TiO\(_2\)) to co-catalysts.\(^10\) In addition, such size reduction increases the co-catalyst specific surface area, further facilitating such electron transfer from the co-catalysts to oxygen\(^11,14\) reducing it to reactive oxygen species (e.g. O\(_2\)) that react with organics\(^15\) and NO\(^9\).

While nanosized co-catalysts have been studied extensively, little is known about the subnano-scale (< 1 nm). Zhao et al.\(^16\) demonstrated that Pt subnano-clusters (~ 0.85 nm) improve the photocatalytic activity of TiO\(_2\) by a factor of five compared to that of Pt nanoparticles (~3 nm). Beer et al.\(^17,18\) prepared two differently sized Pt subnano-clusters and nanoparticles (4.8 nm) by laser ablation under ultrahigh vacuum and found an optimal Pt subnano-cluster size (~ 1 nm) for H\(_2\) generation. Highly active single atom catalysts have been prepared by cyanide leaching\(^4\) of Au and Pt nanoparticles or anchoring of single Pd atoms by ethylene glycolate\(^19\) on TiO\(_2\). Despite such promising results, a systematic study of the size effect in subnano-cluster and single atom co-catalyst on photocatalysts is challenging due to the difficulty in controlling the co-catalyst size from subnano-scale down to a single atom progressively.

Recently, Pd subnano-clusters (1 wt%) on TiO\(_2\) that were prepared by scalable flame spray pyrolysis (FSP) were three times more active for solar-photocatalytic NO\(_x\) removal than the same mass fraction (1 wt%) of Pd nanoparticles (~ 5 nm) on TiO\(_2\).\(^20\) Furthermore, such subnano-clusters consisted of an intermediate oxidation state of Pd were thermally stable up to 600 °C under air because of their strong interaction with TiO\(_2\). This allowed their post-
annealing for removal of any impurities (e.g. incomplete combustion products) from the particle surface\textsuperscript{21} and conversion\textsuperscript{22} of amorphous TiO\textsubscript{2} to photocatalytically active\textsuperscript{23} anatase and/or rutile.

Here, we try to understand the above discoveries by exploring the characteristics and photocatalytic performance of Pd/TiO\textsubscript{2} at different Pd contents (0 - 3 wt\%) and cluster sizes (from a single atom to a few nanometers). All photocatalysts are prepared by FSP at relatively cold and hot flame conditions and annealed in air for 2 hours at 400 - 800 °C to investigate the optimal Pd cluster size and TiO\textsubscript{2} crystallinity for solar NO\textsubscript{x} reduction; following ISO standards. In fact, here we reveal that isolated Pd atoms constitute the most active site rather than any Pd clusters or particles of equal mass.

3.2 Experimental

3.2.1 Catalyst preparation

Titanium dioxide particles containing 0 - 3 wt.% Pd were prepared in one step by FSP.\textsuperscript{20} The Pd fraction was controlled by varying the palladium acetylacetonate (Aldrich, purity 99 \%) concentration (0 - 3.6 mM) in a 1:1 volumetric mixture of 2-ethylhexanoic acid (Aldrich, purity > 99 \%) : acetonitrile (Aldrich, purity > 99.5 \%) containing 159 mM of titanium isopropoxide (Aldrich, purity > 97 \%). This precursor solution was fed through the FSP capillary nozzle at P = 3 or 8 mL/min, dispersed to a fine spray by 5 L/min O\textsubscript{2} (Pan Gas, purity >99\%) through the adjacent burner ring and ignited/sustained by premixed methane/O\textsubscript{2} support flame (CH\textsubscript{4} = 1.5 L/min, O\textsubscript{2} = 3.2 L/min)\textsuperscript{24}. The high feed rate of precursor solution (P = 8 mL/min) led to hotter flame and more concentrated product aerosol than the low feed rate (P = 3 mL/min).\textsuperscript{25} Product particles are collected on a glass-fiber filter (Whatman GF, 24.7 cm diameter) 62 and 77 cm above the FSP nozzle for “cold” (P = 3 mL/min) and “hot” (P = 8 mL/min) flames, respectively, by a gas pump (Busch Mink MM 1202 AV). For photocatalytic tests, such particles made in cold and hot flames were collected for 7 and 4 min, respectively, resulting in 165 ± 15 mg of a homogeneous particle layer on the filter that was cut in 5 cm × 10 cm rectangular sheets that were annealed in air at 400 - 600 °C for 2 hours, as needed. Since the glass fiber filter is not stable at 800 °C, the powders annealed at that temperature were deposited on the glass fiber filter by spray drying\textsuperscript{20} resulting in homogeneous particle layers of 170 ± 10 mg.

3.2.2 Catalyst characterization
The X-ray diffraction (XRD) patterns of product powders, with and without 20 wt.% of NiO (Aldrich, size: -325 mesh) as an internal standard, were obtained by a diffractometer (AXS D8 Advance, Bruker, Cu Kα, 40 kV, 40 mA). The crystalline and amorphous mass fractions of TiO₂ were calculated as described elsewhere. The specific surface area (SSA) of all powders was obtained by N₂ adsorption at 77 K using the Brunauer-Emmett-Teller (BET) method (Micromeritics, Tristar II PULS). Scanning transmission electron microscopy (STEM) images of particles were recorded with a high-angle annular dark-filed detector (Hitachi, HD 2700-Cs, 200 kV).

Adsorption of NO on Pd clusters was investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Vertex 70v spectrometer (Bruker Optics). To minimize the interference of any reactions with NO and incomplete combustion products, only the powders annealed in air at 600 °C for 2 hours were investigated. The powders were placed in an in situ DRIFTS cell that was heated to 110 °C in synthetic air (Pangas, purity) for 15 min to remove physically absorbed water and subsequently, cooling down to 50 °C. Afterwards 0.1% of NO in N₂ was passed over the sample for 20 min and then, the spectra were recorded by averaging 100 scans (100 scan/min) at 4 cm⁻¹ resolution.

3.2.3 Photocatalytic evaluation for NO removal under solar-light

Photocatalytic NO removal by the product catalysts under solar light (100 mW/cm², Solarsim 150, Solaronix) for 5 hours was carried out in a standard continuous-flow reactor (ISO 22197-1:2007) as described elsewhere. Briefly, the 5 cm × 10 cm rectangular glass-fiber filter coated with the catalysts (as described above) was placed in the middle part of the reactor as defined by the ISO standard. An air stream of 3 L/min at 50 % relative humidity containing 1 ppm of NO flowed over the catalyst sheet while NO and NO₂ concentrations were monitored every 3 s by a NOx detector (CLD 882 S, Eco Physics) at the reactor outlet. After the test, the filter coated with the catalysts was immersed in DI-water (10 mL), at least, for 12 hours to leach any nitrate remaining on the catalyst surface. The amount of leached nitrate ions, \( m_{NO_3^-} \), was measured by a nitrate ion meter (LAQUAtwin B-742, Horiba). The average NO removal efficiency as NOx, \( \eta_{NOx} \), and nitrate formation, \( \eta_{NO_3^-} \), under solar-light for \( t = 5 \) hours were:

\[
\eta_{NO_x} = \frac{\int_{t=5h}^{t=5h} \frac{C_{NO_{in}}[ppm] - C_{NO_{out}}[ppm] - C_{NO_2_{out}}[ppm]}{C_{NO_{in}}[ppm]} \, dt}{C_{NO_{in}}[ppm]} 
\]

\[
\eta_{NO_3^-} = \frac{3 \cdot [L/min] \cdot \int_{t=300min}^{t=300min} \frac{C_{NO_{in}}[ppm]}{C_{NO_{in}}[ppm]} \, dt}{22.4 \cdot [L/mol] \cdot \int_{0}^{t=5h} \frac{C_{NO_{in}}[ppm]}{C_{NO_{in}}[ppm]} \, dt}
\]
3.3 Results and Discussion

3.3.1 Photocatalytic evaluation for NO removal under solar-light

![Graph showing NO removal efficiency as NOx, % for different Pd/TiO2 samples under solar-light](image)

**Figure 3.1** Solar light photocatalytic NO removal activity as NOx, \( \eta_{\text{NOx}} \), of as-prepared Pd/TiO2 with 0 (stars), 0.1 (circles) and 1 (triangles) wt% Pd made in hot (filled symbols: \( P = 8 \text{ mL/min} \)) and cold (open symbols: \( P = 3 \text{ mL/min} \)) flames and annealed at 400 - 800 °C in air for 2 hours. For comparison, the \( \eta_{\text{NOx}} \) of commercial TiO2 (cross, P25, Evonik) is shown.

Figure 3.1 shows the solar-light removal efficiency of NO, \( \eta_{\text{NOx}} \), by nanostructured Pd/TiO2 as-prepared in hot (filled symbols: \( P = 8 \text{ mL/min} \)) and cold (open symbols: \( P = 3 \text{ mL/min} \)) flames and annealed at 400 - 800 °C in air for 2 hours containing 0 (stars), 0.1 (circles) and 1 (triangles) wt% Pd. Most of the removed NOx is converted into nitrate ions that remain on the particle surface (Fig. B.1). All \( \eta_{\text{NOx}} \) are slightly higher than the corresponding \( \eta_{\text{NO3}} \) implying some \( \text{N}_2 \) and/or \( \text{N}_2\text{O} \) formation which are hardly detected because of their low concentration. The presence of Pd on TiO2 greatly enhances the NO removal activity compared to pure TiO2 FSP-made (stars) and the “gold standard” P25 TiO2 by Evonik (cross). The \( \eta_{\text{NOx}} \) of Pd/TiO2 with 1 wt% Pd content made in cold flame (open triangles) and annealed at 400 °C is the highest and slightly decreases with increasing annealing temperature till 600 °C confirming the superior performance of these materials. Similarly the \( \eta_{\text{NOx}} \) of Pd/TiO2 made in hot flames (filled circles and triangles) reaches the maximum by annealing at 400 °C.
and slightly decreases above 500 °C. These minor decrease of the $\eta_{\text{NO}_x}$ might be due to slight growth of Pd subnano-clusters at high temperature (~ 600 °C).\textsuperscript{20} Interestingly, the $\eta_{\text{NO}_x}$ of Pd/TiO$_2$ with 0.1 Pd content made in the cold flame continuously increases up to 600 °C but drastically decreases at 800 °C where Pd clusters grow to PdO nanoparticles as detected by XRD (Fig. B.2).

![Figure 3.2](image)

**Figure 3.2** Solar light photocatalytic NO removal activity as NO$_x$, $\eta_{\text{NO}_x}$, of Pd/TiO$_2$ with 0 - 3 wt% Pd made in a cold flame ($P = 3 \text{ mL/min}$) as-prepared and annealed at 400 - 800 °C in air for 2 hours.

Figure 3.2 shows, in more detail, the effect of Pd content (0 - 3 wt%) on $\eta_{\text{NO}_x}$ by Pd/TiO$_2$ prepared in the cold flame and annealed at 400 - 800 °C. Up to 0.5 wt% Pd, the $\eta_{\text{NO}_x}$ continuously increases as well as with annealing temperature up to 600 °C but drastically drops at 800 °C. Further increase of Pd content up to 1 wt% has minor effect on the $\eta_{\text{NO}_x}$ while excess Pd loading (3 wt%) deteriorates the $\eta_{\text{NO}_x}$. As a result, the $\eta_{\text{NO}_x}$ of Pd/TiO$_2$ containing only 0.1 wt% Pd and annealed at 600 °C is comparable to the best $\eta_{\text{NO}_x}$ by the catalyst containing 1 wt% Pd and annealed at 400 °C, even though the Pd content of the former is 10 times less than that of the latter, which is still nearly 10 times superior than
commercial TiO$_2$ (P25) as shown in Fig. 3.1. Clearly low Pd contents (< 0.5 wt%) perform quite well even after annealing at 600 °C indicating the photocatalytic potential and thermal stability of these subnano-clusters.

### 3.3.2 Properties of photocatalysts

![XRD patterns](image)

**Figure 3.3** XRD patterns of Pd/TiO$_2$ made in the cold flame ($P = 3$ mL/min) with 0 - 3 wt% Pd contents (a) as-prepared and (b) annealed at 600 °C in air for 2 hours.
Figure 3.3 shows XRD patterns of Pd/TiO$_2$ from the cold flame (P = 3 mL/min) with different Pd (0 - 3 wt%) contents (a) as-prepared and (b) annealed at 600 °C in air for 2 hours. The XRD patterns of as-prepared powders are almost identical for all Pd contents because of their relatively low values (0 - 3 wt%).$^{13}$ There is no distinguishable Pd (squares) and PdO (star) peaks in these patterns except for annealed Pd/TiO$_2$ containing 3 wt% Pd at 2θ ≃ 33° corresponding PdO (b, orange pattern). Such a peak does not appear in Pd/TiO$_2$ containing 0.1 - 1 wt% Pd even after annealing. This indicates the stability of such Pd subnano-clusters.$^{20}$

In the as-prepared powders, anatase TiO$_2$ (diamonds) is the dominant phase, which is consistent with flame-made TiO$_2$ in excess O$_2$.$^{30}$ A broad hump around 22 - 35° appears for all as-prepared powders and is assigned to amorphous TiO$_2$.$^{31}$ Annealing at 600 °C reduces that hump and sharpens the peaks of anatase and rutile TiO$_2$ (especially for 0 wt% Pd) indicating conversion of amorphous to anatase and rutile TiO$_2$. The intensity of these rutile peaks decreases with increasing content of Pd, indicating its role on TiO$_2$ crystallinity. The growth of particle size and TiO$_2$ crystallinity in different Pd contents and annealing temperatures are quantitatively analyzed.

![Figure 3.4](image_url)

Figure 3.4 (a) Specific surface area (SSA) and mass fraction of (b) amorphous, (c) anatase and (d) rutile TiO$_2$ of nanostructured Pd/TiO$_2$ containing 0 (stars), 0.1 (circles) and 1 (triangles) wt% Pd and as-prepared in hot (filled symbols: P = 8 mL/min) and cold (open symbols: P = 3 mL/min) flames and annealed at 400 - 800 °C in air for 2 hours.
Figure 3.4 shows the SSA (a), and mass fractions of amorphous TiO<sub>2</sub> (b), anatase (c) and rutile (d) of Pd/TiO<sub>2</sub> containing 0 (stars), 0.1 (circles) and 1 (triangles) wt% Pd made in hot (filled symbols) and cold (open symbols) flames as-prepared and annealed at 400 - 600 °C in air for 2 hours. The SSA of TiO<sub>2</sub> made in hot flames is smaller than that in cold flames because of longer high temperature particle residence time in the former. Annealing reduces the SSA that becomes 80 - 110 m<sup>2</sup>/g for all particles at 600 °C regardless of Pd content and synthesis conditions (Fig. 3.4a). This reduction of SSA is induced largely by particle growth accompanying crystallization of amorphous TiO<sub>2</sub> that is not photocatalytically active.

More amorphous TiO<sub>2</sub> (in as-prepared particles at 25 °C) is formed in cold flames (~40 wt%) because its shorter high temperature particle residence time limits TiO<sub>2</sub> crystallization. The fraction of amorphous TiO<sub>2</sub> decreases by increasing annealing temperature, independent from Pd fraction and it is almost completely converted to anatase and rutile.

The presence of Pd, however, alters the growth of anatase and rutile TiO<sub>2</sub> as shown in Fig. 3.4c,d. Figure 3.4c shows that the anatase fraction increases with increasing temperature but, only for pure TiO<sub>2</sub> (stars), drops at 600 °C as the rutile fraction increases drastically (Fig. 3.4d). The formation of rutile is more pronounced in as-prepared pure TiO<sub>2</sub> that contains larger amorphous fraction (Fig. 3.4a). This indicates the selective phase transition of the amorphous to anatase below 500 °C but rutile above 600 °C. The rutile formation at 600 °C, however, is suppressed by increasing Pd content. This could be beneficial, since rutile TiO<sub>2</sub> is unfavorable for photocatalytic NO<sub>x</sub> removal. For these particles, however, the η<sub>NO<sub>x</sub></sub>, with 0.1 wt% Pd is better than that with 1 wt% Pd, even though the former contains more rutile that the later. Thus, the nature of Pd may play a critical role in the NO<sub>x</sub> removal activity.

### 3.3.3 Properties of Pd subnano-clusters with different sizes

Figure 3.5 shows two magnifications of STEM images of Pd/TiO<sub>2</sub> prepared by the cold flame with (a, b) 3, (c, d) 1 and (e, f) 0.1 wt% of Pd content annealed in air at 600 °C for 2 hours. The darker (or gray) and lighter parts correspond to TiO<sub>2</sub> and Pd clusters/nanoparticles, respectively. At 3 wt% Pd (a, b), Pd nanoparticles of 1 - 5 nm in diameter (blue triangles) are observed at low-magnification (a) but also some Pd subnano-clusters (in yellow squares) are present (b). At 1 wt% Pd, there are no visible Pd nanoparticles (> 1 nm) at low-magnification (c) and only Pd subnano-clusters in the yellow squares can be seen at high-magnification. At 0.1 wt% Pd (e, f), there are no Pd clusters even at higher
magnifications (more images are provided in Fig. B.3). Higher Pd contents induce the growth of Pd clusters and nanoparticles by coagulation and/or surface growth of Pd onto TiO$_2$; thus, lower Pd contents result in smaller cluster sizes as with all flame-made noble metals on ceramic supports.$^{24,36}$ This indicates that the size of Pd clusters in 0.1Pd/TiO$_2$ is smaller than Pd subnano-clusters in 1Pd/TiO$_2$ and could be single Pd atoms. Such single-atoms might correspond to the bright points in red circles (Figure 3.5f) that are hardly visible because of the comparable z-contrast of Pd and TiO$_2$ but similar weak bright points in STEM images were observed with single Pd atoms on TiO$_2$.\textsuperscript{19}

\textbf{Figure 3.5} STEM images of Pd/TiO$_2$ prepared by cold flames ($P = 3$ mL/min) with (a, b) 3, (c, d) 1 and (e, f) 0.1 wt\% of Pd contents and annealed in air at 600 °C for 2 hours.
Inferred Pd fraction from the measured XRD PdO fraction of Pd/TiO$_2$ as-prepared (circles) and annealed at 600 (triangles) and 800 °C (squares) as a function of nominal Pd loading. Inferred Pd fraction, f(Pd), was obtained by $f(Pd) = 0.87 \times f(PdO)$. The broken line corresponds to the nominal PdO and Pd fractions.

To infer the Pd fraction on the TiO$_2$ surface, the Pd cluster growth to PdO nanoparticles is followed by annealing at 800 °C in the XRD patterns (Fig. B.2) as the PdO nanoparticles should be formed by diffusing and coalescing Pd atoms and/or clusters during annealing. Thus, the mass fraction of Pd clusters on TiO$_2$ surface can be obtained from such XRD patterns. Figure 3.6 shows that the inferred Pd fraction from the XRD-measured PdO (e.g. Fig. 3.3b and B.2) from Pd/TiO$_2$ as-prepared (circles) and annealed at 600 (triangles) and 800 °C (squares) as a function of nominal Pd loading on TiO$_2$. In all as-prepared and annealed powders at 600 °C, the measured PdO fraction is zero except for TiO$_2$ containing 3 wt% and annealed at 600 °C (Fig. 3.3b). By annealing at 800 °C, there is no detectable PdO peak below 0.2 wt% of Pd content probably because of the extremely small Pd contents that cannot be detected by XRD. In contrast, above 0.5 wt%, the measured Pd fraction is slightly smaller than the nominal content (broken line). This might be attributed to Pd substitution to TiO$_2$ lattice or Pd clusters that have not coalesced yet. This indicates that most of Pd is on the TiO$_2$ surface. The presence of Pd and its structure on TiO$_2$ surface are further examined by NO adsorption on fresh Pd/TiO$_2$ catalysts below.
Figure 3.7 DRIFTS of NO adsorption on Pd/TiO$_2$ containing 0, 0.1 and 1 wt% Pd and made in hot (a) and cold (b) flames and annealed at 600 °C in air for 2 hours.

Figure 3.7 shows DRIFTS of NO adsorption on (a) hot and (b) cold flame-made Pd/TiO$_2$ containing 0, 0.1 and 1 wt% Pd annealed at 600 °C in air for 2 hours where all catalysts have similar SSA (Fig. 3.4a) and minimal, if any, incomplete combustion products on their surface (Fig. B.4). For pure TiO$_2$ made in both flames (black spectra), there are several broad peaks corresponding to NO$_2$ (1470 - 1550 cm$^{-1}$) and bidentate and bridging
nitrates (1575 and 1620 cm\(^{-1}\))\(^{40}\) on the TiO\(_2\) surface. Such species (NO\(_2\) and nitrates) are the products of NO and surface adsorbed oxygen or OH\(^{-}\)\(^{39,40}\) as anatase TiO\(_2\) is more active than rutile because of its high surface OH\(^{-}\) density as observed in flame and wet-made TiO\(_2\)\(^{41}\). A broad negative peak around 1660 cm\(^{-1}\) assigned to OH\(^{-}\) on the surface\(^{39}\) and the steeper peak in pure TiO\(_2\) made in hot than in the cold flame indicates more OH\(^{-}\) loss. This explains the lower peak intensity of NO\(_2\) and nitrate species (especially bidentate nitrate at 1575 cm\(^{-1}\)) on pure TiO\(_2\) made in the cold than in the hot flame because of its smaller anatase fraction (Fig. 3.4c).

Most importantly, several NO adsorption peaks arise in the presence of Pd on the surface.\(^{24,36}\) This differs from Pd\(^{2+}\) ions substituted in TiO\(_2\) sub-surface that do not show any NO adsorption peaks.\(^{38}\) At 1 wt% Pd content (blue spectra), NO adsorption\(^{42}\) on double (1620 cm\(^{-1}\)), 3- (1510 cm\(^{-1}\)) and 4-fold (1420 cm\(^{-1}\)) coordinated Pd atoms are observed. The peak intensity of these adsorption sites involving multiple Pd atoms in Pd/TiO\(_2\) containing 0.1 wt% Pd (red spectra) is lower (1620 cm\(^{-1}\)) and even non-existent (1420 and 1510 cm\(^{-1}\)) as they are comparable to those in Pd-free TiO\(_2\) made in both flames (black spectra). Nevertheless a weak peak for NO adsorption appears on 3-fold coordinated Pd atoms (1510 cm\(^{-1}\)) in Pd/TiO\(_2\) containing 0.1 wt% Pd prepared by the hot flame. The peak intensity of the linear NO adsorption on single Pd atom\(^{43-45}\) (1845 cm\(^{-1}\)) is comparable for all Pd contents and flames, although the intensity from particles containing 0.1 wt% Pd and made in the hot flame (red spectrum in Figure 3.7a) is slightly lower than the others. Perhaps the high temperature of these flames may have facilitated formation of Pd subnano-clusters with NO adsorption sites involving multiple Pd atoms (1420, 1510 and 1620 cm\(^{-1}\)). Therefore, Pd subnano-clusters provide different NO adsorption sites involving double Pd atoms, the hollows of 3- and 4-fold coordinated Pd atoms as well as single Pd atoms. If only isolated Pd atoms are present without any Pd clusters, the adsorption sites involving multiple Pd atoms should not appear but only the one on single Pd atoms. Indeed, CO adsorption on single Pd atoms on TiO\(_2\) without any bridge or hollow Pd sites has been reported.\(^{19}\) Figure 3.7 indicates the co-existence of Pd clusters and isolated atoms in Pd/TiO\(_2\) containing 1 wt% Pd from both flames as well as the dominance of isolated Pd atoms (compared to any clusters) in Pd/TiO\(_2\) containing 0.1 wt% Pd made, especially, in cold flames, which is consistent with their STEM images (Figure 3.5).

Notably, the peak width of the linear NO adsorption (1845 cm\(^{-1}\)) on FSP-made Pd/TiO\(_2\) (~ 50 cm\(^{-1}\)) is much narrower than that on Pd nanoparticles (6.4 nm) prepared by Almusaieter et al. (~100 cm\(^{-1}\))\(^{43}\). Such narrow peak width originates from the uniformity of the bonding structure, NO-Pd-support, which is analogous to NO adsorption on single Pd
atoms supported on zeolites (ZSM-5\textsuperscript{44} and MOR\textsuperscript{45}) by ion-exchange methods. The single Pd atoms on metal oxide supports are bonded to several terminal O atoms on the support surface forming a homogeneous Pd-O\textsubscript{x}-support structure inducing Pd\textsuperscript{+2} oxidation states\textsuperscript{44}. Similar bonding structure is observed also in atomically dispersed Pt\textsuperscript{4} and Au\textsuperscript{4,46} on metal oxides leading to Pt\textsuperscript{2+,4+} and Au\textsuperscript{+3+} oxidation states. Indeed, the peak position (1845 cm\textsuperscript{-1}) is located between metallic Pd (1750 cm\textsuperscript{-1})\textsuperscript{43} and Pd\textsuperscript{2+} (1860-1880 cm\textsuperscript{-1})\textsuperscript{44,45} indicating the presence of Pd\textsuperscript{+} and/or Pd\textsuperscript{2+} that is consistent with the observation of an intermediate Pd oxidation state in FSP-made Pd/TiO\textsubscript{2}\textsuperscript{20}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{drifts.png}
\caption{DRIFTS of NO adsorption on Pd/TiO\textsubscript{2} containing 0 - 3 wt\% Pd made in the cold flame ($P = 3$ mL/min) and annealed under air at 600 °C for 2 hours.}
\end{figure}

Figure 3.8 shows DRIFTS of NO adsorption on Pd/TiO\textsubscript{2} annealed under air at 600 °C for 2 hours and containing 0 - 3 wt\% Pd that were made in the cold flame as in Fig. 3.2. The peak intensity of NO adsorption on single Pd atom (1845 cm\textsuperscript{-1}) increases with increasing Pd content from 0 (black spectrum) to 0.1 (red spectrum) wt\% but it levels off above that. This trend seems to be correlated to the $\eta_{\text{NO}}$ of Pd/TiO\textsubscript{2} containing 0 - 1wt\% made in cold flame (Fig. 3.2); the $\eta_{\text{NO}}$ increases with increasing Pd content from 0 to 0.1 wt\% but comparable...
above that till 1 wt% Pd. At 3 wt% Pd, the presence of PdO nanoparticles as detected by XRD (Fig. 3.3b) seems to reduce the $\eta_{NO_x}$ consistent with literature.\textsuperscript{34}

A weak shoulder peak at 1420 cm\textsuperscript{-1} related to the adsorption on 4-fold coordinated Pd atoms appears at 0.2 wt% Pd (yellow spectrum). Above 0.5 wt% Pd, NO adsorption\textsuperscript{42} on double Pd atoms (1620 cm\textsuperscript{-1}) and at the 3- and 4-fold coordinated Pd atoms (1510 cm\textsuperscript{-1} and 1420 cm\textsuperscript{-1}) are observed. Their peak intensities increase with increasing of Pd content, indicating growth of Pd clusters. Furthermore, at excess Pd content (3 wt%, orange spectrum), a new peak emerges at 1560 cm\textsuperscript{-1} that could correspond to NO adsorption on step sites. Notably the peak intensity of Pd/TiO\textsubscript{2} containing 1 and 3 wt% Pd are comparable, although the Pd content of the former is three times less than the later. This could be attributed to the presence of PdO in 3Pd/TiO\textsubscript{2} as detected by XRD (Fig. 3.3b). Therefore, formation of Pd clusters is initiated, at least, above 0.1 wt% Pd content. The clusters grow with increasing Pd content and/or high temperature residence time. This results in comparable linear NO adsorption on single Pd atoms\textsuperscript{43-45} at different Pd contents (0.1 - 3 wt%). The adsorption on single Pd atoms indicates the presence of isolated Pd atoms on TiO\textsubscript{2} surface that seems the dominant active site whose number reaches a maximum at 0.1 wt% Pd.

3.4 Conclusions

Titania containing 0 - 3 wt% Pd was prepared by FSP at cold and hot flames resulting in Pd sizes ranging from a single atom to a few nanometer-clusters on the TiO\textsubscript{2} surface. The solar photocatalytic NO\textsubscript{x} removal performance of Pd/TiO\textsubscript{2} made in the cold flame ($P = 3$ mL/min) is higher than that in the hot flame ($P = 8$ mL/min) because of higher SSA and smaller Pd size. The best NO\textsubscript{x} removal efficiency was achieved by TiO\textsubscript{2} containing 1 wt% Pd made in the cold flame and annealed at 400 °C in air and it is about 10 times superior to that of commercial TiO\textsubscript{2} (P25, Evonik). Notably, comparable performance was attained by TiO\textsubscript{2} containing just 0.1 wt% Pd and annealed at 600 °C. Annealing removes incomplete combustion products and amorphous TiO\textsubscript{2} that hinder NO\textsubscript{x} removal. Adsorption of NO on Pd clusters reveals the presence of single Pd atoms on TiO\textsubscript{2}. Their NO adsorption peak intensity is comparable for all TiO\textsubscript{2} containing more than 0.1 wt% Pd where NO adsorption sites on multiple Pd atoms appear whose peak intensities increase with increasing Pd content indicating growth of Pd clusters. This indicates co-existence of Pd clusters and isolated atoms in Pd/TiO\textsubscript{2} for contents above 0.1 wt% Pd and the dominance of isolated Pd atoms compared to clusters in Pd/TiO\textsubscript{2} containing only 0.1 wt% Pd. Such single Pd atoms on TiO\textsubscript{2} seem to be
the dominant active site for solar photocatalytic NO\textsubscript{x} removal, which allows maximizing the noble metal performance while minimizing its use.

### 3.5 Acknowledgements

This research was funded by the Swiss National Science Foundation (grant no. 200021_149144). STEM work was performed by Dr. Frank Krumeich at the Electron Microscopy Center of ETH Zurich (EMEZ).

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Chapter 4

Visible-light active black TiO$_2$-Ag/TiO$_x$ particles

Abstract

Visible-light active materials are sought in photocatalysis and solar energy utilization. Here a material architecture active under visible-light and comprising of TiO$_x$ (e.g. Ti$_4$O$_7$, Ti$_3$O$_5$) layers onto nanosilver on nanostructured TiO$_2$ is formed by flame aerosol technology. Abundant combustion intermediates present during flame synthesis of these materials partially reduce TiO$_2$ and induce strong metal-support interactions (SMSI) resulting in crystalline TiO$_x$ as determined by X-ray diffraction. The growth of such suboxides can be controlled through their flame spray synthesis conditions allowing for tuning the light absorption intensity in the visible spectrum. The as-prepared TiO$_x$ are stable upon annealing in air, at least, up to 350 °C for two hours. Their presence on the Ag/TiO$_2$ particle surface and efficiency in generating photoinduced charge separation under visible light is demonstrated by electron paramagnetic resonance spectroscopy. Under visible light (λ > 400 nm), these nanoparticles exhibit strong photo-reduction of cationic species (Cr$^{6+}$) and photo-oxidation of organics (methylene blue).

Published in part in *Applied Catalysis B: Environmental*. 2014;154-155:9-15.
4.1 Introduction

Recently, a so-called “black” titania with remarkable activity under visible light (λ>400nm) has been proposed for efficient solar energy utilization\(^1\); the photoactivity occurs preferentially on the surface of these particles. This “black” titania consists of either a crystalline stoichiometric TiO\(_2\) core and a disordered reduced self-doped shell\(^1\) or by a crystalline reduced TiO\(_2\) core (with oxygen vacancies) surrounded by a nearly stoichiometric amorphous shell\(^2\). Such a titanium suboxide (TiO\(_x\), x < 2) with TiO\(_2\) particles can be produced by laser irradiation\(^3\) or by reduction under high pressure\(^1\) or temperature\(^2\) with H\(_2\), organic solvents\(^4\), NaBH\(_4\)\(^5\) or CaH\(_2\)\(^6\) for several hours/days. In addition, binary TiO\(_2\)-Ti\(_2\)O\(_3\) is formed under prolonged UV irradiation (several hours) of sol-gel-made TiO\(_2\).\(^7\) The improved visible-light photoresponse of TiO\(_x\) involves the modulation of the energy levels of the semiconductor: Ti\(^{3+}\) defects that enhance visible-light photoactivity by introducing band-gap energy states\(^2\),\(^4\). In addition, the distorted TiO\(_x\) shell on TiO\(_2\) creates an additional energy “tail” from the valence band into the band gap\(^1\),\(^2\). Thus, the engineering of TiO\(_x\) phase on crystalline TiO\(_2\) opens new opportunities for visible-light active TiO\(_2\). Most of the above synthesis techniques, however, require extreme processing conditions offering limited control of the suboxide phase formation so their applicability to mass production is not straightforward.

On the other hand, TiO\(_2\) and specific metals (e.g. Pt, Pd, Ni or Ag) exhibit an abnormal interaction\(^8\)-\(^11\), the so-called strong metal-support interaction (SMSI). Under H\(_2\) reduction at high temperatures, the TiO\(_2\) surface is reduced. The so-formed Ti\(^{3+}\) can either interact with the metal phase, thereby forming weak covalent bonds\(^9\) or receive electrons from it\(^12\). Then the Ti\(^{3+}\) can diffuse to the surface of noble metal or TiO\(_2\) and surround them, thereby forming TiO\(_x\)\(^8\),\(^9\). Indeed, the formation of Ti\(^{3+}\) on the Pt-TiO\(_2\) surface by SMSIs has been observed with X-ray photoelectron spectroscopy\(^13\). Such a distorted TiO\(_x\) has been seen also by transmission electron microscopy (TEM) in Pd-TiO\(_2\).\(^14\) The chemical structure of TiO\(_x\) depends on reducing conditions. Above 600 °C in H\(_2\), Ti\(_4\)O\(_7\) can be formed\(^15\) whereas further reduction to Ti\(_3\)O\(_5\) may require a radical structure\(^9\) reorganization.

Here “black” composite TiO\(_2\) nanoparticles (NPs) consisting of TiO\(_2\), TiO\(_x\) and nanosilver are prepared in one-step by a continuous gas-phase method, flame spray pyrolysis (FSP)\(^16\) that is scalable to kg/h\(^17\): Titanium and silver precursors in flammable solvents are sprayed and dispersed by O\(_2\) in fine mists that are combusted resulting in TiO\(_x\) onto nanosilver on predominantly anatase TiO\(_2\) NPs. This flame aerosol technology produces rapidly in one step high purity materials (e.g. optical fibers) without liquid byproducts and any post-
processing. As a result, it is used in large scale manufacture (tons/h) of carbon black, pigmentary titania and fumed oxides\textsuperscript{18}. The structural profiles of these TiO\textsubscript{2}-Ag/TiO\textsubscript{x} NPs are investigated by TEM, diffuse reflectance spectroscopy and X-ray diffraction (XRD). Their photoactivity is monitored by electron paramagnetic resonance (EPR) spectroscopy. Finally, the photocatalytic performance of the NPs with respect to Cr\textsuperscript{6+} and methylene blue (MB) degradation are examined under visible light ($\lambda > 400$ nm).

### 4.2 Materials and methods

#### 4.2.1 Catalyst preparation and characterization

TiO\textsubscript{2}-TiO\textsubscript{x} (“black” TiO\textsubscript{2}) NPs loaded with 10 or 20 wt.% of Ag (10Ag/TiO\textsubscript{2} or 20Ag/TiO\textsubscript{2}) were prepared by single step FSP and collected on glass-fiber filters\textsuperscript{19}. Silver acetate (Aldrich, purity > 99%) and titanium isopropoxide (TTIP, Aldrich, purity > 97%) were used as silver and titanium precursors, respectively. The total precursor (TTIP and silver acetate) concentration in a 1:1 mixture of 2-ethylhexanoic acid (Aldrich, purity > 99%) and acetonitrile (Aldrich, purity > 99.5%) was 0.16 M. The precursor solution was fed through the FSP nozzle at $X = 3$ or 8 mL/min, dispersed to a fine spray by $Y = 5$ L/min oxygen (Pan Gas, purity > 99%), hereafter referred to as the FSP $X/Y$ feed ratio, and combusted to produce high-purity NPs. Additionally, 20Ag/TiO\textsubscript{2} NPs was prepared at $X/Y = 8/5$ with additional 20 L/min sheath O\textsubscript{2} flowing through an annulus surrounding that for O\textsubscript{2} dispersion\textsuperscript{19}.

Scanning transmission electron microscopy (STEM) images were recorded with a high-angle annular dark-filed detector (Hitachi, HD 2700-Cs, 200 kV, point resolution ~1.4 Å). The concentration of each element at selected spots in the STEM images was determined by energy-dispersive x-ray (EDX) analysis (EDAX detector, Genesis, Hitachi). High-resolution TEM was performed with a Tecnai F30-ST microscope (FEI, 300 kV, point resolution ~2 Å). As-prepared particles were dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid.

XRD patterns were obtained by a Bruker AXS D8 Advance diffractometer (Cu K\textsubscript{\alpha}, 40 kV, 40 mA) at $2\theta = 20^\circ$ - $50^\circ$ with a step size of 0.03°. The exposure time for each step was 2.5 s for high-quality XRD patterns. Crystalline mass fractions were calculated from the integral intensities of each peak (OriginPro, 8.6). A background signal corresponding to amorphous phases was corrected in the spectra by software (EVA). As the Ti\textsubscript{4}O\textsubscript{7} peaks at 28.5° and 29.5° overlap, its integral intensity was set to be half the peak area at 29.5°. Raman spectroscopy was performed (Renishaw InVia Reflex Raman) with a 514 nm diode (Ar-ion laser, 25 mW) laser as excitation source focused with a microscope (Leica, magnification
The samples were pressed into tablets and placed on a glass plate. The spectra were recorded for 10 s with 20 accumulations to obtain sufficient signal-to-noise ratio with a CCD camera after being diffracted by a prism (1800 lines per millimeter) using 3.75 mW laser energy.

4.2.2 Characterization of visible light activity and photocatalysis

Diffuse-reflectance spectra of the catalysts were measured by a Varian Cary 500 UV–Vis spectrophotometer equipped with an integrating sphere. EPR spectra were recorded at 77 K with a Bruker ER200D spectrometer equipped with an Agilent 5310A frequency counter. For each experiment, 10 mg of NPs are placed inside a quartz EPR tube (Suprasil, Willmad Glass) with an outer diameter of 3 mm. The EPR signals presented herein were recorded at 9.49 GHz, using a modulation amplitude of 4 G, a field modulation of 100 kHz and 4 mW microwave power. Adequate signal-to-noise ratios were obtained with 10 scans. A solar-light-simulating Xe light source (Oriel model 66929, 450 W) equipped with a water IR filter was used to investigate photogeneration of electrons and holes. Visible-light illumination ($\lambda > 400$ nm) was performed using a longpass 400 nm filter (Edmund Optics 85754). The same light source was used for photocatalytic experiments.

Photocatalytic degradation of Cr$^{6+}$ and methylene blue (MB) was performed in a Pyrex glass container. For Cr$^{6+}$ degradation, 9 mg of NPs was dispersed in 90 mL of Milli-Q water ($C_{\text{catalyst}} = 100$ mg/L) in a water-bath sonicator. The solution pH was adjusted to 3.5 with HNO$_3$. K$_2$Cr$_2$O$_7$ (Aldrich) was added at an initial concentration of $C_{\text{Cr}} = 0.5$ mM. Salicylic acid (SA) (Aldrich) was added at a concentration of $C_{\text{SA}} = 5$ mM to optimize the photocatalytic kinetics. For MB degradation, 22.5 mg of NPs were dispersed in 90 mL of Milli-Q water ($C_{\text{catalyst}} = 250$ mg/L) in a water-bath sonicator. Methylene blue (Aldrich) was added at an initial concentration of $C_{\text{MB}} = 0.01$ mM. The solution pH was adjusted to 9.0 with NaOH. The solutions were mixed with the appropriate amount of photocatalyst and magnetically stirred before and during the illumination. The suspensions were kept in the dark for 30 min prior to illumination to reach adsorption equilibrium on the semiconductor surface. As the reaction progressed, samples were withdrawn from the reactor at specific time intervals. The MB suspension was centrifuged for 15 min at 4000 rpm using a Hettich Universal 16A centrifuge for further analysis. The MB decolorization was determined by monitoring the change in optical absorption at 660 nm using a Perkin Elmer Lambda 35 double-beam UV-Vis spectrophotometer. The Cr$^{6+}$ ions in each solution were determined by the diphenylcarbazide method using the UV-Vis spectrophotometer.
4.3 Results and discussion

4.3.1 Catalyst properties

Figure 4.1 (a) Commercial (P25) and FSP-made TiO$_2$ loaded with Ag (10 or 20 wt.%) prepared at low (X/Y = 3/5) and high (8/5) temperature and Ti concentration. (b) STEM image and EDX analysis of 20Ag/TiO$_2$ made at X/Y = 3/5. Positions (c-e) for EDX analysis are marked in the STEM image. (f) TEM image of 20Ag/TiO$_2$ made at X/Y = 8/5 with selected (g) high-resolution images. The blue arrows and red broken lines indicate disordered TiO$_x$ onto nanosilver and TiO$_2$. (e) Schematic of TiO$_x$ onto nanosilver and TiO$_2$ created by strong metal-support interactions (SMSI).

By controlling the FSP feed ratio of the Ti/Ag precursor solution flow to that of dispersion O$_2$, appropriate conditions for particle synthesis are selected$^{19}$. Figure 4.1a shows images of P25 (commercial TiO$_2$) and FSP-made TiO$_2$ NPs loaded with Ag (10 or 20 wt.% of composite Ag/TiO$_2$ particles) prepared at X/Y feed ratio of 3/5 and 8/5. A high Ag loading (e.g. 20 wt.%)
and a high FSP feed ratio (e.g. 8/5) resulted in the darkest particles (Fig. 4.1a). These dark colors are similar to H$_2$-reduced TiO$_2$ and do not come from incomplete combustion products remaining on the particle surface. Thermogravimetric analysis showed < 2% of organic loading and EPR showed zero carbon-based radicals. The color changes correspond to formation of TiO$_x$ which exhibits an absorption band in the visible range$^{22}$.

Figure 4.1b shows a STEM image of the 20Ag/TiO$_2$ NPs prepared at X/Y = 8/5 with EDX analysis at different points (c-e). The darker and lighter parts in the STEM image correspond to titanium oxide and silver, respectively, (e.g. points c and d). At point (c), Ti/O are dominant and Ag hardly appears as its signal is less than that of the Cu support (not shown here). At point (d), the titanium peak practically does not appear, indicating predominantly Ag NP. On the other hand, both Ag and titanium are detected at the weakly bright point (e) indicating that Ag NPs might be embedded or coated (fully or partially) by TiO$_x$.

Figure 4.1f shows a TEM image of the 20Ag/TiO$_2$ NPs prepared at X/Y = 8/5 with its higher resolution and magnification at Fig. 4.1g. In contrast to STEM (Fig. 4.1b), the lighter and darker parts correspond to titanium oxide and silver, respectively. This image reveals that the darker Ag NPs are embedded and fully or partially coated or decorated (Fig. 4.1g) by layered titanium oxide (indicated by broken red lines). Similar morphologies have been observed with strongly interacting Co$^{23}$ and Pt$^{24}$ nanostructures on TiO$_2$ produced by H$_2$ reduction at high temperatures. This morphology indicates SMSI that result in embedding or partial encapsulation or coating of noble metal clusters by TiO$_x$$^{8,14,23}$ indicated here by blue arrows in Fig. 4.1g similar to Pt-CeO$_2$ made by SMSI$^{25}$. Figure 4.1h shows schematically such distorted TiO$_x$ onto Ag/TiO$_2$ partially encapsulating and exposing the nanosilver.

Silver does not form independently SMSI because it cannot dissociate H$_2$ and generate Ti$^{3+}$ states; Ag, however, can create SMSIs in the presence of Pt, which facilitates hydrogen dissociation$^{10}$. Here, abundant intermediate combustion products are present during flame synthesis of TiO$_2$ that can reduce it similarly to dissociated hydrogen$^{4}$ and induce SMSI on Ti-Ag that facilitate crystallization of TiO$_x$ and/or prevent complete oxidation of the newly formed TiO$_x$. 

Figure 4.2 (a) XRD patterns and (b) mass fractions of 10Ag/TiO₂ & 20Ag/TiO₂ prepared at FSP feed X/Y = 3/5 and 8/5 and 20Ag/TiO₂ prepared at X/Y = 8/5 with 20 L/min of sheath O₂. Diffraction patterns are marked for TiO₂ anatase (diamonds) and rutile (circles) as well as for Ag⁰ (squares), Ti₄O₇ (up triangles) and Ti₃O₅ (down triangles).

Figure 4.2a shows the XRD patterns of 10 and 20Ag/TiO₂ NPs prepared at X/Y = 3/5 or 8/5, respectively. A higher FSP feed ratio (e.g. X/Y = 8/5) results in stronger and sharper peaks indicating larger crystals. Increasing the X/Y ratio increases particle mass concentration
and residence time at high temperatures that lead to larger particles by enhanced coagulation and sintering. The peaks at 25.5° and 48° correspond to anatase TiO$_2$ (diamonds) that are dominant in all particles. Only particles prepared at X/Y = 8/5 (blue, black and purple spectra) contain a small peak around 27.5° corresponding to rutile (circles). The Ag$^0$ peaks (squares) at 44° are distorted more than those of flame-made Ag$^0$ NPs supported on SiO$_2$ indicating the SMSI between Ag and TiO$_2$ here.

Most interestingly, TiO$_x$ were resolved by XRD: Ti$_3$O$_5$ (down triangles) at 33° and Ti$_4$O$_7$ (up triangles) at 28.5° and 29.5° in Fig. 4.2a. Note, however, that the Ti$_4$O$_7$ peaks might correspond also to other TiO$_x$, especially Ti$_3$O$_{2x-1}$ (e.g. Ti$_3$O$_6$) that have similar connectivity and diffraction features. Analogous features, however, have been reported for Ti$_3$O$_5$ and Ti$_4$O$_7$ formed by SMSI, supporting the present assignment of the 28.5° and 29.5° peaks to Ti$_4$O$_7$. Here, the TiO$_x$ peaks are broad, indicating small crystals and/or low crystallinity, consistent with their layered morphology (Fig. 4.1g). The peak intensities increased with increasing Ag loading and FSP feed ratio (reducing flame conditions) corresponding to the darkening of these particles (Fig. 4.1a).

Figure 4.2b shows the XRD-mass fractions of anatase (red diamonds), rutile (black circles), Ag$^0$ (orange squares), Ti$_3$O$_5$ (blue down triangles), and Ti$_4$O$_7$ (green up triangles) phases for the particles in Figure 4.2a. The mass fraction of anatase decreased with increased nominal mass fraction of Ag (from 10 to 20%) and reducing flame conditions (X/Y from 3/5 to 8/5). This was accompanied by increases in the mass fractions of rutile, Ti$_3$O$_5$ and Ti$_4$O$_7$. Highly reducing conditions result in SMSIs of Pd and Pt with TiO$_2$ that lead to formation of Ti$_4$O$_7$. For further reduction to Ti$_3$O$_5$, a radical reorganization of the structure may be required.

The Ag$^0$ mass fraction in all particles was slightly lower than its nominal value (10 or 20 wt.%) and decreased with reducing flame conditions similarly to anatase mass fraction. This reduction in Ag$^0$ mass fraction could be attributed to the interaction of Ti$^{3+}$ with isolated Ag atoms created by electron transfer from Ag to titanium. The use of additional O$_2$ as a sheath gas during FSP made the flame more oxidative and affected TiO$_x$ formation (Fig. 4.2a, purple spectrum). The mass fraction of Ti$_4$O$_7$ decreased whereas that of Ti$_3$O$_5$ slightly increased compared to those in the absence of sheath O$_2$ (Fig. 4.2a, black spectrum) as shown in Fig. 4.2b. The use of O$_2$ sheath during FSP increases the conversion of the precursor solution, flame temperature and subsequently the high temperature residence time of the particles.
Figure 4.3 (a) XRD patterns and (b) mass fractions of 20Ag/TiO$_2$ prepared at X/Y = 8/5 (Fig. 4.2a) and annealed at 350 or 550 °C in air for 2 h. Diffraction patterns are marked for TiO$_2$ anatase (diamonds) and rutile (circles) & for Ag$^0$ (squares), Ti$_4$O$_7$ (up triangles) and Ti$_3$O$_5$

Figure 4.3 shows (a) the XRD patterns and (b) mass fractions of 20Ag/TiO$_2$ prepared at X/Y = 8/5 (black spectrum) and annealed at 350 (pink spectrum) and 550 °C (brown spectrum) in air for 2 h. These patterns indicate that the TiO$_x$ phases are stable, at least, up to 350 °C but transformed to rutile at 550 °C$^{29}$ with remnant Ti$_3$O$_5$ and Ti$_4$O$_7$$^{28}$ as shown
quantitatively in Figure 3b. Moreover, during this annealing, isolated Ag atoms\textsuperscript{12} with Ti\textsuperscript{3+} sinter with exposed Ag particles (by the decomposition of TiO\textsubscript{x}) increasing the Ag mass fraction back to its nominal 20\%. This provides further indication to promotion of TiO\textsubscript{x} formation during FSP by the presence of silver.

Figure 4.4 Raman spectra of “black” TiO\textsubscript{2} NPs loaded with Ag (10 or 20 wt.\%) and prepared at X/Y = 3/5 or 8/5. For comparison, the Raman spectra of commercial TiO\textsubscript{2} (P25, Degussa) and FSP-made Ag (95 wt.\%) supported on SiO\textsubscript{2} NPs (95Ag/SiO\textsubscript{2}) are also included.

Figure 4.4 shows Raman spectra of black TiO\textsubscript{2} NPs loaded with Ag (10 or 20 wt.\%) and made at X/Y = 3/5 or 8/5. Most notably, no Raman peak for silver was detected in contrast to FSP made 95Ag/SiO\textsubscript{2} particles\textsuperscript{30} (dashed line). The Raman spectra of all Ag/TiO\textsubscript{2} show new peaks at 246 and 361 cm\textsuperscript{-1} and a stronger one at 199 cm\textsuperscript{-1} than that of commercial TiO\textsubscript{2}, P25. Analogous features have been observed in the Raman spectra of “black” TiO\textsubscript{2}\textsuperscript{1}. However, some peaks (294, 690, 765, 849 and 938 cm\textsuperscript{-1}) from amorphous TiO\textsubscript{x}\textsuperscript{1} are not seen here. Chen et al.\textsuperscript{1} suggested that their reduced TiO\textsubscript{2} phase was distorted, so, several TiO\textsubscript{x} structures were present but could not be detected by XRD. Most importantly, when the Ag loading was increased from 10 to 20 wt.\% in our samples and/or the flame conditions became more reducing (by increasing the precursor/fuel flow from 3 to 8 mL/min or changed the FSP feed ratio, X/Y, from 3/5 to 8/5), the anatase peaks at 514 and 639 cm\textsuperscript{-1} were broadened indicating distortion of the TiO\textsubscript{2} lattice\textsuperscript{1,2}.

The formation of “black” TiO\textsubscript{2} here is based on a different physical mechanism than
wet-made “black” TiO$_2$\cite{1,2}: SMSIs between Ag$^0$ and TiO$_2$ result in a crystalline TiO$_{x}$ (i.e. Ti$_4$O$_7$ and Ti$_3$O$_5$) that forms around the silver NPs on the TiO$_2$ support. As pointed out by Chen et al.\cite{1}, distortion of the reduced phases could be responsible for the distribution of the density of states creating the so-called energy tails that extend into the band-gap energies of the semiconductor. This phenomenon is responsible for light absorbance at visible wavelengths, rendering the black color of the as prepared Ag/TiO$_2$ NPs. Here the distorted phase of TiO$_{x}$ is attributed to crystalline Ti$_4$O$_7$ and Ti$_3$O$_5$ as detected by XRD (Fig. 4.2a, 4.3a).

### 4.3.2 Visible light activity and photocatalysis

Figure 4.5a shows UV-Visible light absorption spectra of commercial TiO$_2$ (P25, green line) and various “black” TiO$_2$ (Fig. 4.1a) and 20Ag/TiO$_2$ prepared at FSP X/Y = 8/5 in the presence of 20 L/min O$_2$ sheath gas (from red to purple lines). The 20Ag/TiO$_2$ particles show significant absorption from 360 to 800 nm, which is the origin of their characteristic black color (Fig. 4.1a). However, the absorption band of Ag$^0$ around 550 nm in the solid state\cite{31} or 400 nm in the liquid phase\cite{30} was not observed. Its absence is attributed to a strong electron interaction between Ag and Ti\cite{32} induced by SMSI\cite{9}. Thus, the improved light absorbance at visible wavelengths (400 - 800 nm) of all TiO$_{x}$/Ag/TiO$_2$ over commercial TiO$_2$ is attributed to the presence of TiO$_{x}$ on the surface of the former.

Interestingly, “black” TiO$_2$ prepared at high Ag loading (20Ag/TiO$_2$) and high precursor concentration (X/Y = 8/5, black spectrum) exhibits greater absorption intensity in the visible range but lower in the UV than “black” TiO$_2$ prepared at more oxidative conditions, either at lower fuel concentration (X/Y = 3/5, orange spectrum) or with sheath O$_2$ (X/Y = 8/5, purple spectrum).

Figure 4.5b shows the absorption spectra of 20Ag/TiO$_2$ NPs “as prepared” at X/Y = 8/5 (black spectrum) and annealed at 350 (pink spectrum) or 550 °C (brown spectrum) in air for 2 h. A 350 °C, the UV absorption of 20Ag/TiO$_2$ increases but in the visible decreases. Note that the mass fraction of the TiO$_{x}$ does not change (Fig. 4.2b and 4.3b). This indicates surface oxidation of TiO$_{x}$ similar to 20Ag/TiO$_2$ NPs prepared at X/Y = 8/5 in the presence of sheath O$_2$ (Fig. 4.5a, purple spectrum). By annealing at 550 °C, the UV absorption further increases, compared to that at 350 °C as further conversion of TiO$_{x}$ and anatase to rutile took place (Fig. 4.3a). Furthermore, the plasmonic absorption of Ag around 550 nm\cite{31} was revealed. This is attributed to removal of the TiO$_{x}$ (Fig. 4.3b, triangles at 550 °C) followed by Ag$^0$ sintering and crystal growth (Fig. 4.3a).
Figure 4.5 Diffuse reflectance absorption spectra of (a) commercial TiO$_2$ (P25, green spectrum) and “black” TiO$_2$ NPs loaded with 10 and 20 wt.% Ag prepared at FSP feed ratios of X/Y = 3/5 and 8/5 in the absence or presence of 20 L/min sheath O$_2$ (red to purple spectra) (b) 20Ag/TiO$_2$ NPs “as prepared” at FSP feed ratio X/Y = 8/5 (black spectrum) and annealed at 350 °C (pink spectrum) or 550 °C (brown spectrum) in air for 2 h.
Figure 4.6 Electron paramagnetic resonance (EPR) spectra for the 20Ag/TiO₂ NPs prepared at X/Y = 8/5 and recorded at 77 K in the dark (black; prior to illumination), after illumination with UV-Vis radiation (red; λ > 240 nm), or Vis radiation (blue; λ > 400 nm).

Figure 4.6 presents low-temperature EPR spectra (77 K) of 20Ag/TiO₂ prepared at X/Y = 8/5. In the dark (black line), the NPs contain two types of paramagnetic centers:

(I) A sharp axial signal with $g = 1.998$ assigned to lattice electrons of anatase. This g-component is attributed to the perpendicular g-tensor component of anatase Ti³⁺ bulk centers. Its sharp lineshape is characteristic of a well-defined local environment, which corresponds to Ti³⁺ centers localised inside the anatase nanocrystal. Thus both EPR and XRD show that the 20Ag/TiO₂ particles made at X/Y = 8/5 contain a well-ordered crystalline phase where Ti³⁺ centers are localised.
A broad signal extending from 3400 to 4000 Gauss corresponding to Ti\textsuperscript{3+} electron trapping sites\textsuperscript{34}. Typically, surface Ti\textsuperscript{3+} electron trapping sites are characterized by EPR signals much broader than those in Figure 4.6. Recently Naldoni et al.\textsuperscript{35} showed that broad EPR signals from surface Ti\textsuperscript{3+} can be photoinduced in Pt-loaded TiO\textsubscript{2} or Au-loaded TiO\textsubscript{2} as in the case of P25\textsuperscript{33}. The narrower linewidth of the surface Ti\textsuperscript{3+} signals in Figure 4.6 indicates restricted mobility of the trapped Ti\textsuperscript{3+} electrons; therefore, it is assigned to Ti\textsuperscript{3+} states localized at the interface of TiO\textsubscript{2}. In parallel with the Ti\textsuperscript{3+} signals at \( g < 2 \), photoinduced h\textsuperscript{+} centers are detected under illumination at \( g = 2.0016 - 2.0024 \).\textsuperscript{33}

TiO\textsubscript{x} are rich in Ti\textsuperscript{3+} electron trapping sites which are easily detected by EPR spectroscopy\textsuperscript{36}. In pure Ti\textsubscript{4}O\textsubscript{7} or Ti\textsubscript{3}O\textsubscript{5} crystals, the Ti\textsuperscript{3+} centers belong to lattice oxygen vacancies\textsuperscript{28} of the type Ti\textsuperscript{3+}–\( V_{o} \)–Ti\textsuperscript{4+}. Here, the Ti\textsuperscript{3+} EPR signals are broader than Ti\textsuperscript{3+} in Ti\textsubscript{4}O\textsubscript{7} indicating strain/distortion of the local environment around the Ti\textsuperscript{3+} centers. Irradiation under visible-light wavelengths (Fig. 4.6: blue line; \( \lambda > 400 \text{ nm} \)) rapidly photoinduces (< 30 s) three signals in Figure 4.6: A strong narrow axial signal appears at \( g = 1.980 \) that is attributed to lattice electron (Ti\textsuperscript{3+}) trapping sites at the interior of the crystal phase\textsuperscript{33,34,37}. The broader trough-like signal at \( g = 1.913 \) is a characteristic of surfacial electron-trapping Ti\textsuperscript{3+} sites\textsuperscript{33}. Most importantly, the photogenerated e\textsuperscript{−} and h\textsuperscript{+} signals can be induced at high yield (> 80%) under visible-light irradiation at \( \lambda > 400 \text{ nm} \) (Fig. 4.6). This high visible-light photoactivity is consistent with the enhanced UV-Vis absorbance (Fig. 4.5), which can be attributed to the generation of sub-band-gap energy tails from the TiO\textsubscript{x}.\textsuperscript{1}

Plasmonic nanoparticles such as Ag\textsuperscript{0}, Au\textsuperscript{0} attached on TiO\textsubscript{2} can enhance its photoactivity when excited at wavelengths matching their plasmonic resonance\textsuperscript{38,39}. Here the plasmonic resonance peak of Ag is largely absent or weak in our Ag/TiO\textsubscript{x} particles (Fig. 4.5) probably because of a strong electron interaction between Ag and Ti\textsuperscript{32}. Thus the observed strong visible-light activity should originate primarily from the generation of sub-band-gap energy tails from the TiO\textsubscript{x}, while the plasmonic contribution is minimal, if any. The absorption spectrum of Ag becomes strongly apparent after annealing at 550 °C for 2 hours (Fig. 4.3a). Then Ag particles have sintered to 51 nm crystals and TiO\textsubscript{x} have been fully oxidized.

Finally, Figure 4.7a shows the visible-light photocatalytic activity of commercial TiO\textsubscript{2} (P25, circles) and present 20Ag/TiO\textsubscript{2} particles made at X/Y = 3/5 (triangles) and 8/5 (squares) for reduction of Cr\textsuperscript{6+}, a priority toxic pollutant\textsuperscript{20}. The half-life of Cr\textsuperscript{6+} was 30 and 55 min by 20Ag/TiO\textsubscript{2} NPs made at X/Y = 3/5 and 8/5, respectively. Furthermore, both photocatalysts are highly active also for methylene blue degradation under visible light irradiation with even
shorter half lives of 15 and 25 min for the same NPs respectively (Fig. 4.7b). The faster kinetics of the NPs made at X/Y = 3/5 are consistent with their higher specific surface area (SSA) of 208 m²/g, which is almost twice that (113 m²/g) of the NPs made at X/Y = 8/5. In comparison, the P25 (reference TiO₂) exhibited the well known minor catalytic efficiency under visible light. Even though nanosilver on TiO₂ might slightly enhance the visible light photodegradation of phenol⁴⁰ and Alizarin Red S⁴¹ by pure TiO₂ (P25), the present TiO₂/Ag/TiOₓ nanostructures exhibit a much stronger photoactivity due to TiOₓ presence¹,². This photoactivity is comparable to that of P25 for methylene blue under UV light.

![Figure 4.7](image)

**Figure 4.7** Photocatalytic reduction of (a) Cr⁶⁺ ions and (b) methylene blue by pure TiO₂ (commercial P25, circles) and 20Ag/TiO₂ prepared by flame spray pyrolysis at X/Y = 3/5 (triangles) or 8/5 (squares) under visible-light irradiation (λ > 400 nm).

### 4.4 Conclusions

Crystalline TiOₓ onto Ag nanoparticles supported on nanostructured titania exhibit strong photoactivity under visible light. These composite particles were made by scalable flame spray pyrolysis. Silver nanoparticles supported on TiO₂ catalyze the formation of crystalline TiOₓ on the Ag/TiO₂ surface by strong metal-support interactions (SMSI) during their combustion synthesis as shown by microscopy, XRD, EPR and diffuse reflectance.
These suboxides could be assigned to $\text{Ti}_4\text{O}_7$ and $\text{Ti}_3\text{O}_5$. Controlling their synthesis conditions provides an easy method to fine tune the composition of these “black” titania NPs and as a result, their photophysical and photocatalytic performance. Such heterostructural “black titania” is stable under ambient conditions and highly photoactive under UV and visible light as shown by EPR and rapid photodegradation of Cr$^{6+}$ and methylene blue (down to 15 min half life for MB). As a result, these nanocomposite materials are attractive for photocatalytic and solar energy applications.

### 4.5 Acknowledgments

This research was supported in part by the Swiss National Science Foundation (grant no. 200021_149144) and the European Research Council under the European Union’s Seventh Framework Program (FP7/2007-2013, ERC grant agreement no. 247283).

### 4.6 References


Chapter 5

Enhanced Ag⁺ ion release from aqueous nanosilver suspensions by absorption of ambient CO₂

Abstract
Nanosilver with closely controlled average particle diameter (7 - 30 nm) immobilized on nanosilica is prepared and characterized by X-ray diffraction, N₂ adsorption and transmission electron microscopy. The presence of Ag₂O on the as-prepared nanosilver surface is confirmed by UV-vis spectroscopy and quantified by thermogravimetric analysis and mass spectrometry. The release of Ag⁺ ions in de-ionized water is monitored electrochemically and traced quantitatively to the dissolution of a preexisting Ag₂O monolayer on the nanosilver surface. During this dissolution, the pH of the host solution rapidly increases, suppressing dissolution of the remaining metallic Ag. When however a nanosilver suspension is exposed to a CO₂-containing atmosphere, like ambient air during its storage or usage, then CO₂ is absorbed by the host solution decreasing its pH and contributing to metallic Ag dissolution and further leaching of Ag⁺ ions. So the release of Ag⁺ ions from the above closely-sized nanosilver solutions in the absence and presence of CO₂ as well under synthetic air containing 200 - 1800 ppm CO₂ is investigated along with the solution pH and related to the antibacterial activity of nanosilver.

Published in part in Langmuir. 2015;31(19):5284-5290.
5.1 Introduction

Nanosilver is attractive for medical\(^1\), textile\(^2\) and water treatment\(^3\) applications for its exceptional antibacterial properties.\(^4\) Nanosilver is one of the most commercialized nanomaterials in health care.\(^5\) Such broad and frequent usage of nanosilver makes inevitable its exposure to humans, increasing risks for public health.\(^6\)-\(^9\)

The bactericidal activity of nanosilver depends predominantly on the Ag\(^+\) ions released or leached from it, especially for rather small Ag particles (up to about 10 nm)\(^10\),\(^11\). These Ag\(^+\) ions originate from dissolution of a preexisting Ag\(_2\)O surface layer\(^12\) followed by \textit{in situ} oxidation of the metallic Ag core and its subsequent dissolution.\(^13\),\(^14\) The dissolution of preexisting Ag\(_2\)O dominates the rapid Ag\(^+\) ion release in water,\(^15\) that corresponds to one or two Ag\(_2\)O surface layers depending on Ag size regardless of Ag preparation method.\(^12\) Small nanosilver releases more Ag\(^+\) ions than large because of its high specific surface area and particle curvature (Kelvin effect).\(^10\),\(^12\) For increasing nanosilver size, however, the ion release decreases and therefore, a particle-specific antibacterial effect and toxicity is observed.\(^10\),\(^16\),\(^17\) The particle-specific toxicity can be associated also to further particle dissolution upon nanosilver-cell interaction.\(^16\),\(^18\)

After completion of the preexisting Ag\(_2\)O dissolution, Ag\(^+\) ions are slowly released by dissolution of the metallic Ag core\(^19\) depending on particle size\(^10\),\(^12\),\(^14\) and host solution conditions (pH\(^13\), oxygen\(^11\),\(^13\) sulfide\(^20\) and/or organics\(^19\) concentrations in solution). The effect of host solution composition on Ag\(^+\) ion release from differently sized nanosilver and host solution conditions, however, has not been fully understood. For example, for increasing pH, the Ag\(^+\) ion release can either increase\(^21\) or decrease\(^13\). Most importantly, the relationship between ion release and solution conditions is not clear as most studies on Ag\(^+\) ion release have been investigated in buffer solutions\(^11\),\(^13\),\(^21\),\(^22\) that are quite different than ambient water. For example, after dissolution of preexisting Ag\(_2\)O, metallic Ag continues to dissolve in acidic buffer solutions\(^19\) but not in enclosed air-saturated deionized (DI) water.\(^12\) This indicates that the host solution pH increases from rapid dissolution of preexisting Ag\(_2\)O that forms\(^23\) OH\(^-\) that react with any H\(^+\) in solution hindering thus dissolution of the remaining metallic Ag core. On the other hand, metallic Ag (without surface Ag\(_2\)O) continuously dissolves for prolonged (> 100 h) water exposure to ambient air.\(^14\),\(^24\) Although metallic Ag dissolution consumes protons\(^13\), the pH of the solution exposed to ambient air was constant because of CO\(_2\) absorption.\(^14\) Therefore the acidification of nanosilver suspensions by ambient CO\(_2\) absorption\(^25\) could affect metallic Ag dissolution and needs to be better understood. This
is important both for the prolonged performance of nanosilver products as well as their long-term environmental impact.

Here, first the release of Ag\(^+\) ions from nanosilver is quantified electrochemically, thermogravimetrically, by UV-Vis and mass spectroscopy and traced to a monolayer of preexisting Ag\(_2\)O on its surface. Then, the pH and Ag\(^+\) ion release from nanosilver of controlled size suspended in de-ionized (DI) water are monitored under synthetic and laboratory air containing different CO\(_2\) concentrations (200-1800 ppm) to identify and quantify, for the first time to our knowledge, the effect of CO\(_2\) absorption on metallic Ag dissolution after preexisting Ag\(_2\)O dissolution.

### 5.2 Materials and methods

#### 5.2.1 Particles synthesis

Silver nanoparticles immobilized or supported on nanostructured SiO\(_2\) (Ag/SiO\(_2\)) and containing 50 wt.% Ag were made by flame spray pyrolysis (FSP) of appropriate solutions of silver acetate (Aldrich, purity >99%) and hexamethyldisiloxane (HMDSO, Aldrich, purity >97%) and collected on glass fiber filters.\(^{10}\) The precursor solution was fed through the FSP capillary nozzle at X = 5-16 mL/min, dispersed to a fine spray by Y = 3-5 L/min oxygen (Pan Gas, purity >99%), and combusted to produce high purity Ag/SiO\(_2\) nanoparticles of controlled nanosilver size through the FSP feed X/Y ratio.\(^{16}\) Additionally, pure SiO\(_2\) nanoparticles were prepared at the same molarity of HMDSO precursor solution (without Ag-acetate) as reference/control.

#### 5.2.2 Characterization

Particles were characterized by X-ray diffraction (XRD) with a Bruker AXS D8 Advance diffractometer (Cu K\(_\alpha\), 40 kV, 40 mA) at 2\(\theta = 15-70^\circ\) with a step size 0.03\(^\circ\). Crystal sizes were obtained by Rietveld analysis on the (111) Ag peak (2\(\theta = 38^\circ\)). High-resolution transmission electron microscopy (TEM) was performed with a Tecnai F30-ST microscope (FEI, operated at 300 kV, point resolution ~2 Å). Particles were dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid. Nanosilver size distributions were obtained from TEM images by counting at least 280 particles with the software ImageJ.\(^{26}\)

UV-Vis optical absorption spectra of the nanosilver dispersed in DI water or methanol were obtained at Ag concentration of 10 mg/L by sonication (SANDELIN DT106, 480 W, 35 kHz) for 3 min with a Cary Varian 500 spectrometer. Peak positions were determined by
parabolic spectra fitting at 375 to 425 nm\(^{10,12}\). Thermogravimetric analysis (TGA) on as-prepared Ag/SiO\(_2\) powder was performed on a Netzsch STA 449 C Jupiter coupled to a Netzsch QMS 403C mass spectrometer (MS). Pure SiO\(_2\) or Ag/SiO\(_2\) nanoparticles were heated from 25 to 800 °C at 10 °C/min under 50 mL/min of Ar. For each experiment, at least 40 mg of sample (20 mg of nanosilver) was weighed in an alumina crucible (0.9 cm\(^3\)) and the sample weight was normalized at 25 °C. The mass loss (%) of nanosilver was calculated by accounting for the mass loss of SiO\(_2\) nanoparticles made at the same FSP X/Y and HMDSO concentration. From the nanosilver size distribution\(^{26}\), the preexisting Ag\(_2\)O fraction and released Ag\(^+\) ions corresponding to one molecular layer of Ag\(_2\)O (density \(\rho = 7.14 \text{ g/cm}^3\), Ag\(_2\)O molecular diameter 0.46 nm\(^{12}\)) were calculated for comparison to electrochemically measured Ag\(^+\) ion concentration, [Ag\(^+\)], in solution.

### 5.2.3 Evaluation of Ag\(^+\) ion release

The pH and [Ag\(^+\)] of DI water containing 100 mg/L of nanosilver (or 200 mg/L of Ag/SiO\(_2\)) were measured with a pH meter (Metrohm), an ion selective electrode and an ion meter (both Metrohm).\(^{10}\) For the measurement of [Ag\(^+\)], nanosilver suspensions (5 mL) were mixed with an aqueous ionic medium (1 M KNO\(_3\)) for 3 min before measurement. A standard Ag\(^+\) solution (Aldrich, 100 mg/L) diluted with deionized water in the [Ag\(^+\)] range of 1 to 100 mg/L resulted in a linear calibration with a slope of 59.1 mV/log[Ag\(^+\)]. The reliability of the ion-selective measurement in deionized water has been confirmed by ICP-Mass Spectrometry combined with a diffusive gradients in thin films (DGT) measurements.\(^{22,27}\) The error bars for pH and [Ag\(^+\)] were obtained from, at least, three measurements. The Ag/SiO\(_2\) particles were dispersed in deoxygenated DI water (pH 7.5) by sonication (as above) for 3 min and then, magnetically stirred at 200 rpm to keep the particles suspended and the solution well-mixed under a) synthetic air (79% N\(_2\) and 21% O\(_2\)) with 200, 600 or 1800 ppm CO\(_2\) in a glove box and b) laboratory air (CO\(_2\): 580 ± 60 ppm). The uniformity of the solution was proven by measuring identical [Ag\(^+\)] and pH values at 1 and 5 cm below the surface of a 100 mg/L suspension of nanosilver (d\(_{\text{TEM}} = 8.2\) nm) under laboratory air for four days. The CO\(_2\) concentration was monitored by a CO\(_2\) sensor (HygiNed B.V., AQ-5000UA-Q). As a control, the evolution of pH was monitored in water containing 100 mg/L of pure SiO\(_2\) made at the same FSP X/Y and HMDSO concentration.
5.3 Results and Discussion

5.3.1 Nanosilver morphology, plasmonics and composition

Figure 5.1 (a) Counted nanosilver size distributions at three different FSP feed X/Y ratios from TEM images with TEM image of 50Ag/SiO$_2$ nanoparticles made at X/Y = 9/3 (insert). N and $\sigma_g$ are the number of the counted particles and geometric standard deviation respectively. The nanosilver size distributions were fitted as a lognormal function (dotted line). (b) Ag crystal size (open triangles) and count-mean average diameter by TEM images (filled triangles) of 50Ag/SiO$_2$ nanoparticles as a function of FSP feed X/Y ratio.
Figure 5.1a shows a TEM image of Ag/SiO$_2$ nanoparticles made at FSP X/Y = 9/3, and nanosilver size distributions made at X/Y = 5/5 (green), 9/3 (red) and 16/3 (blue) by counting N = 280-520 particles. The nanoparticles (dark spots) are rather spherical and well dispersed on the amorphous (gray) nanostructured SiO$_2$ support. Their geometric standard deviation, $\sigma_g$, ranges from 1.47 to 1.73 consistent to nanosilver made at similar conditions$^{16}$. Figure 5.1b shows the Ag crystal size (open triangles), $d_{\text{XRD}}$, as a function of X/Y to be in agreement with the corresponding count-mean average nanosilver diameter (filled triangles) from TEM, $d_{\text{TEM}}$. (Fig. 5.1a). This indicates monocrystalline silver nanoparticles consistent with the corresponding literature.$^{10}$ Both sizes increase with increasing X/Y that induces higher nanosilver aerosol concentration and longer residence time at high temperatures.$^{28}$

Figure 5.2 shows optical absorption spectra of nanosilver suspensions (10 mg/L) with $d_{\text{TEM}}=$ (a) 8.2 and (b) 28.5 nm made at X/Y = 5/5 and 16/3, respectively, in DI water (black solid line) and methanol (red broken line). The plasmon absorption band of silver$^{29}$ at about 400 nm is normalized by the maximum intensity of each spectrum. The nanosilver peaks in DI water are at shorter wavelengths than those in methanol. This is attributed to the rapid water dissolution of the preexisting Ag$_2$O surface layer of nanosilver$^{23}$:

$$\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Ag}^+ + 2\text{OH}^- \quad (5.1)$$

In contrast, Ag$_2$O is insoluble in methanol$^{30}$ and remains on the nanosilver surface. As a result, when nanosilver is suspended in methanol, the Ag/Ag$_2$O interface is responsible for the observed plasmon shift. When, however, nanosilver is suspended in H$_2$O, the preexisting Ag$_2$O is dissolved rapidly so the Ag/H$_2$O interface becomes responsible for the plasmon shift. Since the refractive index of Ag$_2$O is higher than that of water$^{31}$, the plasmon band of suspended nanosilver shifts more in methanol than in water. Therefore, the observed plasmon shift is not attributed to the difference of the refractive indexes of water and methanol$^{29}$ but to the differing surface properties of suspended nanosilver in these solvents. Figure 5.2c shows that the difference of peak position (determined by a parabolic fitting) between DI water and methanol, $\Delta\lambda$, decreases with increasing nanosilver size.
Figure 5.2 Optical absorption spectra of nanosilver suspensions (10 mg/L) with $d_{\text{TEM}} = (a)$ 8.2 and (b) 28.5 nm made at $X/Y = 5/5$ and 16/3, respectively in DI water (black solid line) and methanol (red broken line). The particles were suspended in each solution by 3 min sonication. (c) Difference of the peak position of the plasmon absorption band between DI water and methanol, $\Delta \lambda$, as a function of the $X/Y$ ratio. The peak position was determined by a parabolic fitting of the absorption bands ranged from 375 to 425 nm.

\begin{itemize}
  \item $d_{\text{TEM}} = 8.2$ nm
  \item $d_{\text{TEM}} = 28.5$ nm
\end{itemize}
$d_{XRD} = 28.5 \text{ nm}$

$\Delta T$ (decomposition of Ag$_2$O)

Mass of nanosilver, wt.%

Thick line: Ag/SiO$_2$
Thin line: SiO$_2$

Ion current (O$_2$), A

Temperature, °C

Ion current (CO$_2$), A

$\Delta T$ (decomposition of Ag$_2$O)
Figure 5.3 (a) Mass of nanosilver with $d_{\text{TEM}}$ of 8.2 (green), 16.9 (red) and 28.5 (blue) nm under Ar by TGA as a function of temperature. (b) $O_2$ ($m/z = 32$) and (c) $CO_2$ ($m/z = 44$) mass spectrometer signals from nanosilver of Fig. 5.3a (thick lines) and pure SiO$_2$ of similar size with the SiO$_2$ support of nano-Ag (thin lines) as a function of temperature. (d) Calculated mass fraction of Ag$_2$O over nanosilver from the TGA mass loss of nanosilver (circles) from Fig. 5.3a and electrochemically measured mass fraction of Ag as Ag$^+$ ions in DI water after 3 min sonication (triangles) as a function of nanosilver size. Red line shows theoretical mass fraction of Ag$_2$O over nanosilver and Ag as Ag$^+$ ions in DI water assuming Ag$_2$O monolayer on its nanosilver surface.

Figure 5.3a shows the mass of nanosilver having $d_{\text{TEM}}$ of 8.2 (green), 16.9 (red) and 28.5 nm (blue) under Ar by TGA as a function of temperature. All three samples were heated up to 800 ºC that is slightly below the melting point of bulk silver$^{32}$. The vertical dashed line shows the decomposition temperature of Ag$_2$O at 330 ºC under inert gas at 1 atmosphere. With decreasing nanosilver size, more mass of nanosilver is lost with increasing temperature.

Figure 5.3 shows also the (b) $O_2$ ($m/z = 32$) and (c) $CO_2$ ($m/z = 44$) MS signals from Ag/SiO$_2$ (thick lines) and pure SiO$_2$ (thin lines) of similar silica particle size as a function of temperature. For Ag/SiO$_2$, there are sharp and broad $O_2$ peaks around 420 and 700 ºC. In contrast, $O_2$ was not released from SiO$_2$ as seen from the MS of pure SiO$_2$ (thin lines). The mass loss of pure SiO$_2$ was comparable to that of vapor-fed flame-made SiO$_2$ nanoparticles$^{34}$ and was caused by decomposition of silanols on the SiO$_2$ surface or any products of incomplete combustion that are detected as CO and CO$_2$ (note that there is no detectable CO signal for all particles here).
For Ag/SiO$_2$ (thick line), there is a sharp CO$_2$ peak around 200 °C (Fig. 5.3c) that could be attributed to incomplete combustion of the precursor solution while there is no significant difference on the CO$_2$ signals above 330 °C among the three nanosilver samples. The intensity of the O$_2$ peaks for the smallest nanosilver (d$_{TEM}$ = 8.2 nm) is higher than that of larger nanosilver (Fig. 5.3b: d$_{TEM}$ = 16.9 and 28.5 nm). Thus, the enhanced release of O$_2$ from the smaller nanosilver above 400 °C (Fig. 5.3b) could be attributed to decomposing Ag$_2$O preexisted on its surface$^{33}$. This is consistent with Fig. 5.3a showing that the mass loss of the smallest nanosilver is steeper than that of the larger consistent also with the higher surface-to-volume ratio and preexisting Ag$_2$O fraction of the smallest nanosilver$^{12}$ (Fig. 5.2c).

Figure 5.3d shows the calculated mass fraction of preexisting Ag$_2$O on the nanosilver surface (left axis) from the TGA mass loss of nanosilver (circles) from Fig. 5.3a as a function of nanosilver size. This reduction of the Ag$_2$O mass fraction with increasing nanosilver size is consistent with the decreasing O$_2$ intensity of the MS spectra (Fig. 5.3b) and Ag plasmon absorption shift (Fig. 5.2c). Fig. 5.3d (right axis) shows also the electrochemically measured mass fraction of Ag as Ag$^+$ ions in DI water after 3 min sonication (triangles) as a function of nanosilver size to be in excellent agreement with the above TGA mass fraction of preexisting Ag$_2$O (circles). These measurements closely follow the theoretically predicted Ag$_2$O monolayer (red line) on the surface of nanosilver$^{12}$ from its size distributions (Fig. 5.1a).

5.3.2 Ag$^+$ ion release during nanosilver solution acidification by atmospheric CO$_2$ absorption

Figure 5.4 shows the evolution of [Ag$^+$] in DI water from nanosilver (100 mg/L of Ag) of d$_{TEM}$ = 8.2 (triangles), 16.9 (circles) and 28.5 (squares) nm under ambient laboratory air containing 580 ppm of CO$_2$ (open symbols) and CO$_2$-free synthetic air (79% N$_2$ and 21% O$_2$, filled symbols). For both air compositions, the [Ag$^+$] almost instantly (t = 0 days) reaches the level that corresponds to the dissolved preexisting Ag$_2$O layer from the nanosilver surface for that particle size$^{12}$ (Fig. 5.3d triangles). Under synthetic air (filled symbols), the [Ag$^+$] levels for all nanosilver sizes do not change for seven days indicating that the remaining metallic Ag, after Ag$_2$O dissolution (0 days), does not further dissolve, similarly with identical nanosilver suspensions in enclosed, air-saturated water$^{12}$. In contrast, under laboratory air containing 580 ppm of CO$_2$, the [Ag$^+$] of all three nanosilver suspensions (open symbols) slowly increases analogous to the evolution of [Ag$^+$] in acidic buffer solutions.$^{19}$ This is higher than that corresponding to preexisting Ag$_2$O dissolution in DI water for a given nanosilver size$^{12}$ (Fig. 5.3d), indicating additional Ag dissolution here. After removal of the surface Ag$_2$O from as-
prepared nanosilver here, the additional release of Ag\(^+\) ions comes from the metallic Ag core\(^\text{19}\):

\[
4\text{Ag} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Ag}^+ + 2\text{H}_2\text{O}
\]  \hspace{1cm} (5.2).

This reaction does not contribute significantly to the release of Ag\(^+\) ions in basic pH solutions.\(^\text{13}\) According to Eq. 5.1, the pH increases during preexisting Ag\(_2\text{O}\) dissolution by the released OH\(^-\) species along with Ag\(^+\) ions resulting in weak basic pH solutions. When these solutions are exposed to CO\(_2\)-containing atmospheres, absorption of CO\(_2\) in the host solution leads to its acidification and facilitates metallic Ag dissolution (Eq. 5.2). This Ag dissolution would not be observed in air-saturated, basic buffer solutions\(^\text{13,14,35}\) that maintain a constant pH regardless of any CO\(_2\) absorption.

**Figure 5.4** Evolution of Ag\(^+\) ion concentration in DI water from nanosilver (100 mg/L of Ag) of \(d_{\text{TEM}} = 8.2\), 16.9 and 28.5 nm under laboratory air containing 580 ppm of CO\(_2\) (open symbols) and synthetic air (79% N\(_2\) and 21% O\(_2\), filled symbols). All suspensions are magnetically stirred at 200 rpm over time to suspend the nanoparticles in water.
**Figure 5.5** (a) pH of nanosilver suspensions containing 25 (blue), 50 (red) and 100 (green) mg/L of Ag in DI water attained just after 3 min sonication (Fig. 5.4: \( t = 0 \) days) as a function of the corresponding Ag\( ^+ \) ion concentration in solution. The nanosilver average diameter are 8.2 (triangles), 16.9 (circles) and 28.5 (squares). (b) Evolution of pH in DI water containing nanosilver (100 mg/L of Ag) of \( d_{\text{TEM}} = 8.2, 16.9 \) and 28.5 nm under laboratory air containing 580 ppm of CO\(_2\) (open symbols) and synthetic air (79\% N\(_2\) and 21\% O\(_2\), filled symbols).
Figure 5.5a shows the pH of suspensions with average nanosilver diameter of 8.2 (triangles), 16.9 (circles) and 28.5 (squares) containing 25 (blue), 50 (red) and 100 (green) mg/L of Ag in DI water attained just after 3 min sonication (Fig. 5.4: $t = 0$ days) as a function of the corresponding [Ag$^+$] in solution. This initial, rapidly attained pH increases almost linearly with increasing [Ag$^+$] (Fig. 5.5a) and is traced to OH$^-$ formation by preexisting Ag$_2$O dissolution (Eq. 5.1). When extrapolating this linear relation to zero [Ag$^+$], it gives pH = 8 that nicely corresponds to the initial pH of the DI-water suspension of flame-made, pure SiO$_2$ support (inverse triangle, 100 mg/L of SiO$_2$ made at X/Y = 5/5). Note that the initial pH of the suspension of flame-made pure SiO$_2$ does not depend on FSP X/Y and SiO$_2$ concentration (not shown here).

Under CO$_2$-free synthetic air, the pH of all nanosilver suspensions (100 mg/L of Ag) is stable (alkaline) over time (Fig. 5.5b filled symbols). This prevents metallic Ag dissolution by further Ag$^+$ ion release$^{13}$ resulting in the corresponding constant [Ag$^+$] in Fig. 5.4 (filled symbols). On the other hand, under CO$_2$-containing laboratory air (Fig. 5.5b, open symbols), the pH of all nanosilver suspensions continuously decreases for four days reaching nearly a steady state after seven days. The pH of DI water (diamonds) reaches a true steady state after 4 days as the dissolved CO$_2$ attains its solubility limit$^{25}$ in water with pH $\sim$ 5.8. The pH evolution of the nanosilver suspensions is analogous to that of DI water indicating that CO$_2$ absorption from air dominates$^{25}$ the change of the pH. After seven days exposed to laboratory air, the pH of all nanosilver suspensions is about 6.5. This is slightly higher than that of DI water (pH 5.8$^{13,14}$) and attributed to the buffering effect of SiO$_2$ by absorbing protons since its acid dissociation constant$^{36}$ is around 7.

So the pH of nanosilver solutions increases first rapidly by dissolution of preexisting Ag$_2$O and release of OH$^-$ (Eq. 5.1). Slow absorption of atmospheric CO$_2$ gradually acidifies these solutions promoting metallic Ag dissolution that allows additional release of Ag$^+$ ions and OH$^-$ resulting in higher pH than in DI water. Thus, metallic Ag dissolution in water exposed to CO$_2$-containing ambient air during its prolonged storage$^{24}$ could be enhanced by acidification resulting from atmospheric CO$_2$ absorption in solution.

In Fig. 5.4, the difference in [Ag$^+$] between nanosilver suspensions under laboratory (open symbols) and synthetic (filled symbols) air corresponds to the released Ag$^+$ ions solely by metallic dissolution. Decreasing nanosilver size, increases this difference and subsequently the metallic Ag dissolution. This is due to particle curvature (Kelvin effect)$^{10}$ and higher surface availability of metallic silver$^{19}$ with decreasing size as with surface Ag$_2$O.
Figure 5.6 (a) 7-day evolution of Ag mass fraction as Ag\textsuperscript{+} ions (open symbols) and pH (filled symbols) of nanosilver suspensions (100 mg/L of Ag of d\textsubscript{TEM} = 8.2 nm) under synthetic air containing 200 (triangles), 600 (circles) and 1800 (squares) ppm of CO\textsubscript{2} in a glove box. (b) Ag mass fraction as Ag\textsuperscript{+} ions from nanosilver (100 mg/L of Ag) of d\textsubscript{TEM} = 8.2 (triangles), 16.9 (circles) and 28.5 (squares) nm in DI water after 7 days as a function of the CO\textsubscript{2} concentration in the surrounding synthetic air (filled symbols) and under laboratory air containing 580 ppm of CO\textsubscript{2} (open symbols).
To better elucidate CO$_2$ absorption in solution and metallic Ag dissolution, the release of Ag$^+$ ions under synthetic air containing different CO$_2$ concentrations (200-1800 ppm) was investigated. So Figure 5.6a shows the 7-day evolution of Ag as Ag$^+$ ions (open symbols) and pH (filled symbols) of nanosilver (d$_{\text{TEM}}$ = 8.2 nm) suspensions (100 mg/L of Ag) under synthetic air containing 200 (triangles), 600 (circles) and 1800 (squares) ppm of CO$_2$. First of all, both pH and [Ag$^+$] evolutions for 600 ppm CO$_2$ are in excellent agreement with those of nanosilver under laboratory air containing 580 ppm CO$_2$ (Fig 5.4 and 5.5b, open triangles). Analogous with laboratory air (Fig. 5.4, open symbols), the [Ag$^+$] (open symbols) slowly increases while the pH decreases (filled symbols)$^{25}$ depending on the CO$_2$ concentration in air. This is in agreement with the pH dependence of metallic Ag dissolution in a buffer solution$^{13}$. The same trend was observed for larger nanosilver (d$_{\text{TEM}}$ = 14.1-28.5 nm).

Figure 5.6b shows the Ag mass fraction as Ag$^+$ ions after 7 days from nanosilver of d$_{\text{TEM}}$ = 8.2 (triangles), 16.9 (circles) and 28.5 (squares) nm in DI water (100 mg/L of Ag) as a function of CO$_2$ concentration in synthetic air (filled symbols). The release of Ag$^+$ ions agrees with that under laboratory air (580 ppm, open symbols) indicating that acidification by CO$_2$ absorption$^{25}$ plays a dominant role on metallic Ag dissolution in DI water. For all nanosilver sizes, the Ag mass fraction as Ag$^+$ ions increases with increasing CO$_2$ concentration.

This can have important implications in nanosilver applications as well as its environmental impact. For example, under ambient laboratory air (e.g. containing 580 ppm CO$_2$), the [Ag$^+$] in nanosilver (8.5-28.5 nm) suspensions rises 40-60% after 7 days by the additional Ag$^+$ ion release attributed to CO$_2$ absorption. This is important for the antibacterial applications of nanosilver. The Ag$^+$ ion release from nanosilver of d$_{\text{TEM}}$ = 16.9 nm increases by 43% after 7 days under CO$_2$-containing laboratory air (Fig. 5.4 open/filled circles). Such increase would correspond to 35% enhancement of bactericidal activity for similarly sized nanosilver (d$_{\text{TEM}}$ = 16.6 nm) when its [Ag$^+$] release was increased by 50%.$^{10}$

5.4 Conclusions

The effect of CO$_2$ content in the surrounding atmosphere of size-selected, buffer-free nanosilver suspensions on their released or leached [Ag$^+$] was systematically investigated, for the first time to our knowledge. The nanosilver size is closely controlled by the process conditions during its preparation. The as-prepared nanosilver was covered by a monolayer of Ag$_2$O as determined by optical spectroscopy, thermogravimetry and mass spectroscopy. This monolayer corresponds to the [Ag$^+$] in aquatic suspensions of nanosilver as determined
electrochemically and quantitatively confirming the rapid and complete dissolution of preexisting Ag₂O.

During the Ag₂O dissolution, the pH of the nanosilver suspensions increases forming moderately alkaline suspensions preventing dissolution of the remaining metallic Ag core (Eq. 2) and any Ag⁺ ion release. When, however, ambient CO₂ is absorbed in solution, its pH decreases resulting in metallic Ag dissolution and additional Ag⁺ ion release. Increasing the CO₂ content of the surrounding atmosphere decreases the nanosilver solution pH and increases the release of Ag⁺ ions. So if a nanosilver suspension is exposed to a CO₂ containing atmosphere, nanosilver slowly dissolves and releases Ag⁺ ions in solution over a much longer period than the initial dissolution of any Ag₂O layer on nanosilver. Although the pH of solutions in environmental systems may depend also on other buffers, solution acidification by CO₂ dissolution is often critical, as for example, on the pH of sea³⁷ and soil³⁸ water. Therefore, nanosilver’s antibacterial performance can be enhanced significantly while the risk to environment could increase by CO₂ absorption in aquatic nanosilver suspensions.

5.5 Acknowledgements

The research leading to these results has received funding from the Swiss National Science Foundation (grant no. 200021_149144 and PA00P2_145392) and the European Research Council under the European Union’s Seventh Framework Programme (FP7/2007-2013, ERC grant agreement no. 247283).

5.6 References


Chapter 6

Outlook and Research Recommendations

In this thesis metal-support interactions in various composites of metals and metal oxides produced using flame spray pyrolysis (FSP) technique and their photocatalytic activity as well as their environmental risks were investigated. The interactions enable to stabilize Pd atoms and subnano-clusters as well as form highly visible-light active crystalline titanium suboxides (TiO\textsubscript{x}). Such material strictures extensively boost their photocatalytic activity under solar and visible light. FSP technique offers high flexibility for controlling material properties such as size, surface area, crystallinity and morphology which in turn improves the (photo-)catalytic activity in a laboratory-level explorations\textsuperscript{1} and the manufacturing of promising materials brought from the scientific works can be easily scale-up to kg/h of production rate.\textsuperscript{2}

Although FSP-made Pd subnano-clusters and atoms are highly stable at high temperature (at least, 600 °C for 2h), mechanism of their high thermal-stability is unclear yet. Since the subnano-clusters are stable in the presence of oxygen while easily grow into nanoparticles in N\textsubscript{2} as discussed in Chap. 2, the presence of SOSIs is speculated.\textsuperscript{3} SOSIs are induced by the formation of metal-O-support bonding and the bonding strength can be characterized by extended X-ray absorption fine structure spectroscopy. According to Chap. 2, the photocatalytic NO\textsubscript{x} removal efficiency is degraded by Pd clusters growth to the nanoparticles by N\textsubscript{2} annealing but still significantly higher than that of wet-made Pd nanoparticles, although they have similar Pd size and oxidation state as well as TiO\textsubscript{2} crystallinity. According to Chap. 3, the most active site seems to be single Pd atoms on TiO\textsubscript{2} but these are hardly detected by STEM imaging and XPS spectroscopy. These facts deduce the stronger binding of Pd single atoms to TiO\textsubscript{2} than the clusters to it and the presence of the single atoms after N\textsubscript{2} annealing as the active sites. The understating of the size dependency in subnano-scale on the bonding
strength that is crucial parameter for some catalysis\(^4\) can facilitate the design of noble photocatalysts and catalysts.

Also the size effect of catalysts in subnano-scale is currently receiving much interest because the size reduction into that scale alters not only the SSA but also the electronic states,\(^5\) which drastically influence the catalytic activity, and the optimal cluster size seems to vary for different reactions: for instance, single-atom catalysts (e.g. Au, Pt) appear suitable for the water gas shift reaction\(^6\) while clusters of Au\(^7\) (2 - 3 nm) and Pd\(^8\) (~ 1 nm) are optimal for CO oxidation. The systematic study of the size effect in subnano-scale and single atom catalysts, however, is often challenging due to the difficulty in controlling the catalyst size from subnano-scale down to a single atom. FSP technology allows to control Pd cluster size on TiO\(_2\) from a few nano-meters to a single atom as presented in Chap. 3. This size controllability can be applied for different noble metals and metal oxides\(^1\), which opens opportunities to develop highly effective and selective catalysts.\(^5\)

SMSIs in Ag-TiO\(_2\) made in FSP forms crystalline TiO\(_x\) (x < 2) that is highly visible-light active as presented in Chap. 4. On the photocatalyst (TiO\(_x\)-Ag/TiO\(_2\)), Ag dissolution during photocatalysis\(^9\) might be undesirable for its durability. Crystalline TiO\(_x\) is stabilized though SMSIs in Ag-Ti and thus, leaching of Ag as Ag\(^+\) ions might cease the SMSIs resulting in TiO\(_x\) decomposition. Furthermore, unexpected Ag\(^+\) ion release from Ag nanoparticles in ambient conditions cause risks for the environment as presented in Chap. 5. These problems can be solved by hermetic coating of Ag particles by TiO\(_x\) layers formed by SMSIs. Based on classic SMSIs as highlighted in Chap. 1, reduced oxide layers completely encapsulate the noble metal surface depending on the treatment conditions (e.g. temperature, H\(_2\) concentration), which is confirmed by H\(_2\) or CO chemisorption. As presented in Chap. 4, the TiO\(_x\) layers on Ag surface formed by FSP, at least, partially cover the Ag. Indeed, the fraction of dissolved Ag as Ag\(^+\) ion from TiO\(_x\)-Ag/TiO\(_2\) is lower than Ag on SiO\(_2\) (Table C.1) where the Ag surface is fully exposed as discussed in Chap. 5. The hermetic coating could be achieved by tuning Ag/Ti ratio as well as flame and post-treatment conditions. Also functionalization of Ag surface by thiocyanate (SCN\(^–\))\(^10\) would be an potential option. These approaches limiting Ag leaching can facilitate the practical application of TiO\(_x\)-Ag/TiO\(_2\) photocatalysts that is highly active under visible and solar lights.

### 6.1 References

1. Koirala R, Pratsinis SE, Baiker A. Synthesis of catalytic materials in flames:


Appendix A

Supporting Information: Pd subnano-clusters on TiO$_2$ for solar-light removal of NO

A.1 Catalyst performance and characterization

<table>
<thead>
<tr>
<th>Performance, %</th>
<th>f-TiO$_2$</th>
<th>f-Pd/TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct deposition from a flame</td>
<td>53.0</td>
<td>63.5</td>
</tr>
<tr>
<td>Cold spray drying deposition</td>
<td>55.1</td>
<td>60.1</td>
</tr>
</tbody>
</table>

Table A.1. Average efficiencies of NO and NO$_x$ removals ($\eta_{NO}$ and $\eta_{NOx}$) as well as NO$_2$ formation ($\eta_{NO2}$) for 5 hours under artificial solar-light by f-TiO$_2$ and f-Pd/TiO$_2$ particle film prepared by different deposition methods.

<table>
<thead>
<tr>
<th>Powders</th>
<th>Anatase, wt%</th>
<th>Rutile, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>f-Pd/TiO$_2$</td>
<td>91.4</td>
<td>8.6</td>
</tr>
<tr>
<td>c-TiO$_2$</td>
<td>86.2</td>
<td>13.8</td>
</tr>
<tr>
<td>f-TiO$_2$</td>
<td>90.3</td>
<td>9.7</td>
</tr>
<tr>
<td>w-Pd/c-TiO$_2$</td>
<td>86.5</td>
<td>12.5</td>
</tr>
<tr>
<td>w-Pd/f-TiO$_2$</td>
<td>91.1</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table A.2. Mass fraction of TiO$_2$ anatase and rutile in total crystalline content for c-TiO$_2$, FSP-made (f-TiO$_2$ and f-Pd/TiO$_2$) and photodeposited Pd (w-Pd/c-TiO$_2$ and w-Pd/TiO$_2$). The Pd loading for all powders is 1 wt.%. 

<table>
<thead>
<tr>
<th>Powders</th>
<th>Anatase, wt%</th>
<th>Rutile, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>f-Pd/TiO$_2$</td>
<td>91.4</td>
<td>8.6</td>
</tr>
<tr>
<td>c-TiO$_2$</td>
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<tr>
<td>w-Pd/c-TiO$_2$</td>
<td>86.5</td>
<td>12.5</td>
</tr>
<tr>
<td>w-Pd/f-TiO$_2$</td>
<td>91.1</td>
<td>8.9</td>
</tr>
</tbody>
</table>
Figure A.1 XRD patterns of c-TiO$_2$, photodeposited Pd on commercially available (w-Pd/c-TiO$_2$) and FSP-made TiO$_2$ (w-Pd/f-TiO$_2$) and FSP-made powders as-prepared (f-TiO$_2$ and f-Pd/TiO$_2$) as well as annealed for 2 hours under air at 600 °C (f-Pd/TiO$_2$/air) and N$_2$ at 400 °C (f-Pd/TiO$_2$/r-N$_2$). Diffraction patterns are marked for TiO$_2$ anatase (diamonds) and rutile (circles) as well as for Pd (squares) and PdO (star).
Appendix A

Figure A.2 (a, b) Peak positions (3Pd$_{3/2}$ and 3Pd$_{5/2}$), (c) Area fraction and (d) FWHM of fitting peaks corresponding to metallic Pd (squares), intermediate Pd oxidation state (circles), PdO (triangles) and ionic Pd$^{2+}$ (diamonds) for XPS spectra of Pd in Fig. 2.3 and 2.7. The FWHM for all fitting curves was set at 1.1 except for that of intermediate Pd oxidation state indicating that the latter could consist of different oxidation states. Error bars were obtained from two powders produced separately.
Figure A.3 Evolution of the Raman peak of anatase TiO$_2$ for f-Pd/TiO$_2$ as prepared powders (circles) and pretreated under N$_2$ at 400 °C for 2 hours (diamonds) as a function of annealing temperature in air for 2 hours.
Appendix B

Supporting Information: Size effect of atomically dispersed Pd on TiO\textsubscript{2} for NO removal

B.1 Catalytic performance

![Graph showing NO removal efficiencies as NO\textsubscript{x} (NO + NO\textsubscript{2}) removal, \(\eta\text{NOx}\), and nitrate formation, \(\eta\text{NO3}\), of Pd/TiO\textsubscript{2} containing 0.1 (red) and 1 (blue) wt% Pd made in the cold flame as-prepared and annealed in air at 400 - 800 °C. Nitrate formation was obtained based on ISO standard (22197-1:2007).]
B.2 Catalyst characterization

Figure B.2 XRD patterns of Pd/TiO₂ containing 0.2 - 3 wt% Pd made in the cold flame and annealed in air at 800 °C for 2 hours. Below 0.5 wt% of Pd, there are no detectable Pd and PdO peaks because of the low Pd fraction.
Figure B.3 STEM images of Pd/TiO$_2$ containing 0.1 wt% made in cold flame (P = 3 mL/min) and annealed at 600 °C in air for 2 hours.
Figure B.4 $\text{H}_2\text{O} \,(m/z = 32, \text{black line})$ and $\text{CO}_2 \,(m/z = 44, \text{red line})$ mass spectrometer signals from Pd/TiO$_2$ containing 1 wt% of Pd made in cold flame ($P = 3 \text{ mL/min}$) in $\text{O}_2$ (20%) and $\text{N}_2$ (80%) mixture as a function of temperature (25 - 800 °C) with 10 °C/min of temperature ramp. Most of incomplete combustion products during flame synthesis are removed at 200 - 400 °C forming $\text{CO}_2$ and $\text{H}_2\text{O}$. 
Appendix C

Supporting Information: Visible-light active black

TiO₂-Ag/TiOₓ particles

C.1 Ag dissolution from TiO₂-Ag/TiOₓ particles

<table>
<thead>
<tr>
<th></th>
<th>As prepared particles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>samples</strong></td>
<td>10Ag/TiO₂</td>
</tr>
<tr>
<td>X/Y = 3/5</td>
<td>238</td>
</tr>
<tr>
<td>X/Y = 8/5</td>
<td></td>
</tr>
<tr>
<td>Specific surface area</td>
<td></td>
</tr>
<tr>
<td>of the particles [m³/g]</td>
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<tr>
<td></td>
<td>238</td>
</tr>
<tr>
<td>Crystal size of Ag</td>
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</tr>
<tr>
<td>at 44° [nm]</td>
<td>2.8</td>
</tr>
<tr>
<td>Observed Ag⁺ ion release</td>
<td></td>
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<tr>
<td>[wt.%]</td>
<td>34.9</td>
</tr>
<tr>
<td>Assumed Ag⁺ ion release</td>
<td></td>
</tr>
<tr>
<td>[wt.%]¹</td>
<td>90</td>
</tr>
</tbody>
</table>

The crystal size of Ag were obtained by Rietveld Analysis (TOPAS 4.0) on the XRD spectra at 44°. The Ag⁺ ion concentration in de-ionized water containing 100 mg/L of nanosilver was measured with an ion selective electrode and an ion meter (both Metrohm, working pH range 2–8).¹ The release of Ag⁺ ion release depends on Ag size benig enable to assume from Ag size¹ as shown in the bottom row.

Appendix D

Highly active TiO$_x$/TiO$_2$ photocatalyst under solar light

Abstract

Crystalline TiO$_x$ (e.g. Ti$_2$O$_7$, Ti$_3$O$_5$) onto Ag/TiO$_2$ nanoparticles is prepared by scalable flame spray aerosol technology. By selecting flame synthesis conditions, the mass fraction of crystalline TiO$_x$ varies from 0 to 12 wt.% with significant (up to 80 wt.%) amorphous TiO$_y$ ($y \leq 2$) that is not photocatalytic active. The TiO$_y$ fraction decreases with increasing precursor feed rate to the reactor but this is hindered at high Ag loading (40 wt.%) implying that a part of TiO$_x$ is formed and/or stabilized by Ag. Subsequent annealing ($< 500$ °C) in air for 2 h converts the amorphous TiO$_y$ into crystalline TiO$_x$ and anatase TiO$_2$. These phase transformations drastically improve the photocatalytic activity of these materials resulting in a 4-minute half-life for methylene blue (MB) under solar light. This is six times faster than that (24 min) of commercial photocatalytic titania (P25, Evonik). After annealing ($< 500$ °C) for 40Ag/TiO$_2$, however, significant TiO$_y$ (about 70 wt.%) still remains resulting in inferior activity. The quantum yield for phenol degradation shows that annealing these materials at 350 °C improves their activity under both UV and visible light, even though it decreases the intensity of their visible light absorption.
D.1 Materials and methods

D.1.1 Catalyst preparation and characterization

Crystalline TiO$_x$ onto Ag/TiO$_2$ NPs were prepared by FSP$^1$ of Ag acetate (Aldrich, purity > 99%) and titanium isopropoxide (TTIP, Aldrich, purity > 97%). The nominal Ag loading ratio (z = 0 - 40 wt.% in total Ag of Ag/TiO$_2$) was controlled by varying the ratio of the silver and titanium precursors. The total metal (Ti and Ag) concentration in a 1:1 mixture of 2-ethylhexanoic acid (Aldrich, purity > 99%) and acetonitrile (Aldrich, purity > 99.5%) was 0.16 M. Additionally, pure TiO$_2$ powders were prepared at 121 mM of TTIP and 39 mM of acetylacetone (Aldrich, purity > 99.5%) instead of Ag acetate that correspond to the morality of 30Ag/TiO$_2$ to investigate the effect of Ag in the solvent. The precursor solutions were fed (P = 3 or 8 mL/min) through the FSP capillary nozzle, dispersed by D = 5 L/min oxygen (Pan Gas, purity > 99%) though the surrounding annular and combusted to produce high-purity NPs. These NPs were annealed in air at 350 - 600 °C for 2 hours.

To measure the mass fraction of the component, the product NPs were mixed with NiO powder (Aldrich, size: -325 mesh) as an internal standard corresponding to 50 wt % of the mixture. High-quality XRD patterns of these mixtures were obtained by a Bruker AXS D8 Advance diffractometer (Cu K$_{\alpha}$, 40 kV, 40 mA) at 2θ = 20° - 50° with a step of 0.009 °/s. The XRD mass fractions of Ag, TiO$_2$ (anatase and rutile) and crystalline TiO$_x$ were calculated from the XRD pattern$^1$ and corrected by the fraction of NiO (50 wt.%). The mass fraction of amorphous TiO$_y$ was obtained by subtracting the above crystalline mass fractions from the nominal Ti fraction as TiO$_2$ (= 100-z %). The crystalline size of Ag and crystalline TiO$_x$ were obtained by Rietveld (EVA).

XPS was performed with X-ray photoemission spectrometer (PHOIBOS100-2D-CCD, SPECS) with an X-ray source (Al, K$_{\alpha}$; XR 50, SPECS). The background and spectrum shift by static electrical charge were corrected by the Shirley method and C 1s peak at 284.6 eV.$^2$

D.1.2 Photocatalytic evaluation under solar light

Photocatalytic degradation of MB was performed in a 150 mL cylindrical glass vessel (c.a. diameter: 5 cm) under magnetic stirring. A solar simulator (100 mW/cm$^2$ at the suspension surface, Solarsim 150) was used as a light source. 24 mg of NPs were dispersed in 80 mL of MB solution (C$_{MB}$: 10 ppm) by the sonicator. Suspensions were kept in dark for 30 min prior to irradiation to reach adsorption equilibrium on the NP surface. As the reaction progressed, suspensions (c.a. 1.5 mL) were withdrawn from the vessel at specific time intervals and NPs were removed by a PTFE filter (Aldrich, ≤ 0.2 µm) from the solution. The MB concentration was determined by monitoring the change in optical absorption at 664 nm$^3$ using the UV–Vis spectrophotometer (Varian 500).

The wavelength dependency of apparent quantum yield, $\Phi$, for photocatalytic degradation of phenol was determined according to Emeline et al.$^4$
In a spherical glass reactor (5.5 cm in a diameter), 0.3 g/L of NPs were dispersed in air-saturated aqueous phenol (Aldrich, purity > 99%) solution (0.23 mM) adjusted at pH 3 by HNO₃. The suspension was irradiated by Xe lamp (Oriel, model 66929: 450 W) whose radiation was filtered through a water filter (Oriel, model 66929) to remove IR radiation. Appropriate wavelengths of irradiation were selected by band pass filters (Edmonds, 84715, 84781, 84795, 84797) and the power of the irradiation was measured by a power meter (Oriel, 919P-040-50) placed behind the glass reactor to determine the number of photons irradiated to the reactor. During the photocatalytic reaction, 0.5 mL of the suspension was extracted at specific time intervals and was passed through a PTFE filter (≤ 0.2 µm) to remove NPs. The phenol in the sample was extracted by CH₂Cl₂ (0.5 mL) for 20 min and the extracted phenol in CH₂Cl₂ was analyzed by a gas chromatograph with a flame ionization detector (Thermo Finnigan, Trace GC). To determine the rate of the phenol degradation, the phenol concentration at the initial 10 min was analyzed to achieve the first order reaction.

D.2 Results and Discussion

D.2.1 Structural and chemical properties

![Figure D.1 XRD patterns of zAg/TiO₂ (z = 0 - 40) prepared at FSP feed P/D = 3/5 - 16/5). Diffraction patterns are marked for TiO₂ anatase (diamonds), rutile (squares) and Ag (stars) as well as for TiOₓ (Ti₄O₇, up triangles and Ti₃O₅, down triangles).]
Figure D.1 shows XRD patterns of zAg/TiO₂ (z = 0 - 40) made at FSP feed P/D = 2/8 - 16/5. For all powders anatase (squares) is the dominant phase while the rutile (diamonds) is negligible except for P/D = 16/5, which is consistent with flame-made TiO₂ in excess O₂ environment. At P/D = 2/8, the peak of anatase is quite sharper, which is attributed to the large TiO₂ anatase formed by droplet-to-particle conversion, precipitation in precursor droplets before their full evaporation and combustion. Except for P/D = 2/8, as the P/D ratio increases, the tᵣ and the particle concentration in a flame increase that may contribute to larger particles and larger crystals.

For all powders with Ag loading, a broad hump appears around 22-45° that is assigned to amorphous TiOₓ. With increasing Ag loading, the peak intensity of TiO₂ anatase (squares) decreases while that of TiOₓ (triangles) increases indicating crystalline TiOₓ formation by SMSI with Ag. As the Ag particles segregate from TiOₓ/TiO₂, the Ag peaks appear at 38° and 44° for Ag (111) facet and Ag (200), respectively. In the presence of SMSI, Ag is distorted resulting in inhibited growth of Ag (111) facet at 38°. At z = 40 for P/D 3/5 - 16/5, however, the Ag peak intensity at 38° is stronger than that at 44° implies spherical Ag in agreement with FSP-made Ag on SiO₂. Thus, spherical Ag with main (111) facet is preserved at z = 40, implying weak SMSI.

Figure D.2a shows the mass fraction of crystalline TiOₓ (triangles, Ti₃O₅ and Ti₄O₇) in zAg/TiO₂ (z = 10 - 40) made at FSP feed P/D = 2/8 - 16/5. The TiOₓ mass fraction increases with Ag loading up to z = 30 indicating that Ag induces TiOₓ formation by SMSI. Beyond that Ag content (e.g. z = 40), the crystalline TiOₓ fraction decreases in agreement with weak SMSIs suggested by the XRD patterns. Furthermore, more TiOₓ is formed at higher P/D (up to 8/5) that induces longer tᵣ and more reducing flame conditions to promote SMSI and TiOₓ crystallization. At P/D = 16/5, the TiOₓ fraction, however, is smaller than that at 8/5 because of Ag particle growth.

Figure D.2b shows the Ag crystal size in zAg/TiO₂ (z = 10 - 40) prepared at FSP feed P/D = 2/8 - 16/5. The Ag crystal size increases by the increases of P/D resulting in the long tᵣ and the high particle concentration in a flame. Interestingly, the Ag crystal size below P/D = 8/5 is almost independent from z, which is inconsistent with FSP-made Ag on SiO₂. This is attributed to Ag embedding by SMSI, which could prevent Ag sintering and subsequent Ag particle growth on TiOₓ/TiO₂ surface. At P/D = 16/5, Ag crystal size significantly increases from 5.8 to 9.7 nm for z = 10 to 40 indicating weak Ag-Ti SMSI in agreement with the XRD. Furthermore, the Ag particle growth is crucial for the formation of crystalline TiOₓ because it is formed by SMSI that takes place on Ag surface. Here, the Ag crystal size is almost
identical to the primary size, because of its high temperature process.\textsuperscript{26} Thus, larger Ag particles at P/D = 16/5 result in limited contact between Ag and Ti and subsequent less TiO\textsubscript{x} formation as shown in Fig D.2a.

**Figure D.2** Mass fractions of (a) crystalline TiO\textsubscript{x} in total Ti content and (b) Ag crystal size from XRD in as prepared zAg/TiO\textsubscript{2} nanoparticles made at different Ag loading (z = 0 - 40) and FSP feed P/D = 3/5 - 16/5.

Figure D.3 shows the mass fraction of amorphous TiO\textsubscript{y} in zAg/TiO\textsubscript{2} (z = 0 - 40) prepared at FSP feed P/D = 2/8 - 16/5. For FSP-made pure TiO\textsubscript{2} (z = 0), amorphous TiO\textsubscript{y} decreases with increasing, P/D ratio because of longer \( t_R \) that could induce its further crystallization. The crystallization at larger P/D ratio is, however, hindered by increasing Ag loading and especially, at z = 40, the fraction of amorphous TiO\textsubscript{y} remains the same level over the P/D ratio indicating that Ag creates amorphous TiO\textsubscript{y}. This could be due to SMSI\textsuperscript{27} and/or
the increase of a low volatile compound (Ag ions) in the precursor solvents which decreases burning rate of solvent droplet resulting in short residence time of particles in a flame.\textsuperscript{28}

**Figure D.3** Mass fractions of amorphous TiO\textsubscript{y} in total Ti content on as prepared zAg/TiO\textsubscript{2} nanoparticles made at different Ag loading (z = 10 - 40) and FSP feed P/D ratio (3/5 - 16/5).

Figure D.4 shows the mass fraction of (a) TiO\textsubscript{x}, (b) amorphous TiO\textsubscript{y}, TiO\textsubscript{2} (c) anatase and (d) TiO\textsubscript{2} rutile of P25 (squares) and Ag/TiO\textsubscript{2} (z = 0, 20 and 30) made at P/D = 3/5 (open symbols) and 8/5 (filled symbols) as a function of annealing temperature (350 - 600 °C) for 2h in air. Regardless of Ag content and P/D, up to 500 °C, the mass fraction of amorphous TiO\textsubscript{y} gradually decreases while one of anatase and crystalline TiO\textsubscript{x} increase because of TiO\textsubscript{x} stabilization by SMSI.\textsuperscript{6} The more increment of crystalline TiO\textsubscript{x} fraction is attained at higher Ag loading. Since Ag does not provoke SMSI in air, a part of TiO\textsubscript{y} is sub-stoichiometric, which could be formed by Ag. This crystallization along with removal of the TiO\textsubscript{y} could improve the photocatalytic performance. At 600 °C, most of amorphous TiO\textsubscript{y}, anatase as well as crystalline TiO\textsubscript{x} in Ag/TiO\textsubscript{2} are converted due to Ag\textsuperscript{29} while those in FSP-made pure TiO\textsubscript{2} and P25 are not as the phase transition temperature of pure TiO\textsubscript{2} anatase to rutile within 2 hours is about 700 °C\textsuperscript{30}. 
Appendix D

Figure D.4 Mass fraction of (a) crystalline TiO\(_x\), (b) amorphous TiO\(_y\), (c) anatase and (d) rutile at z = 0 (circles), 20 (triangles) and 30 (diamonds) and FSP feed ratio P/D = 3/5 (open symbols) and 8/5 (filled symbols) as well as P25 (squares) as a function of annealing temperature (350 - 600 °C) in air for 2 h.

D. 2.2 Solar and visible light photocatalysis

Figure D.5 shows the photocatalytic degradation of MB under solar light irradiation (100 mW/cm\(^2\)) by as-prepared (filled symbols) and annealed (open symbols) in air for 2 h pure titania (P25, Evonik) and zAg/TiO\(_2\) (P/D = 3/5 and 8/5) (b, d) for z = 20 (a, b) and 30 (c, d)). The half-lives of as prepared FSP powders (Fig. D.3a-c: filled triangles) are 15-32 min close to P25 (squares, 24 min). Annealing them in air at 350 °C (diamonds), however, drastically improves the photocatalytic activity under solar light of all FSP-made powders while that of P25 (open squares) remains unchanged. Especially the half-life of 30Ag/TiO\(_2\) (P/D = 3/5) drops to 4 min which is 6 times faster than that of P25 and the activity under UV-Vis light irradiation is comparable to that of hydrogenated “black” TiO\(_2\) \(^{31}\) and highly active Ag\(_3\)PO\(_4\) composite\(^{32}\). Additionally, the present annealed powders exhibit a much higher activity than that of wet-made\(^{16}\) Ag/TiO\(_2\) and Ag loaded P25\(^{17}\) as high Ag (z > ~ 2%) loadings typically diminish the photocatalytic activity\(^{33}\). Thus, this superior performance of annealed
30Ag/TiO\textsubscript{2} (P/D = 3/5) could be attributed to the crystallization of TiO\textsubscript{y} and crystal growth of TiO\textsubscript{x} and anatase. Annealing the particles to 500 °C, their half-lifes for MB photo-degradation increase slightly or stay comparable to those at 350 °C despite further crystallization of TiO\textsubscript{2}, TiO\textsubscript{x} and TiO\textsubscript{y} (Fig. D.2) as their SSA decreases from 110-170 to 70-80 m\textsuperscript{2}/g. Annealing at the highest temperature, 600 °C, degrades significantly the photocatalytic activity because of complete conversion of TiO\textsubscript{x} and anatase to rutile\textsuperscript{6} (Fig. D.4).

**Figure D.5** Photocatalytic degradation of methylene blue (MB) under artificial solar light irradiation (100 mW/cm\textsuperscript{2}) by as prepared (filled symbols) and annealed in air (open symbols) for 2 h pure TiO\textsubscript{2} (P25, Evonik), FSP-made 20Ag/TiO\textsubscript{2} (a, b) and 30Ag/TiO\textsubscript{2} (c, d) prepared at FSP feed P/D = 3/5 (a, c) and 8/5 (b, d).

Figure D.6 shows the apparent quantum yield, \(\Phi\), for photocatalytic degradation of phenol by pure TiO\textsubscript{2} (P25, squares), as prepared (filled triangles) 30Ag/TiO\textsubscript{2} (P/D = 3/5) and annealed in air at 350 °C for 2 h (open triangles). The P25 is active only under UV light (< 400 nm) and its present apparent quantum yield agrees to that by Emeline et al.\textsuperscript{21} as well as by the others\textsuperscript{34,35} measured under similar conditions. As-prepared FSP-made 30Ag/TiO\textsubscript{2} (P/D = 3/5) is active under visible light (up to 600 nm), exhibiting photocatalytic activity under solar
light. Its $\Phi$ under UV light (350 nm), however, is notably lower than that of TiO$_2$ (P25). Nevertheless by annealing, it increases nearly to that of P25. Most importantly, under visible light (400 - 600 nm), it is twice than that of as-prepared that exhibits a higher visible-light absorption. Thus, careful annealing of the catalyst plays an important role on its photocatalytic activity.

![Apparent quantum yield vs Wavelength](image)

**Figure D.6** Spectral dependence of apparent quantum yield, $\Phi$, for photocatalytic degradation of phenol by pure TiO$_2$ (P25, squares) and as prepared (filled triangles) 30Ag/TiO$_2$ (P/D = 3/5) and annealed at 350 °C (open triangles). For comparison, the apparent quantum yield of pure TiO$_2$ under similar conditions by Emeline et al. is shown.

Figure D.7 shows Ti 2p XPS spectra of pure TiO$_2$ (P25, black), as-prepared at P/D =3/5 (red) and annealed at 350 (green) and 600 °C (blue) 30Ag/TiO$_2$. For P25, there are two peaks at 464.1 and 458.3 eV corresponding to Ti$^{4+}$ of Ti 2p$_{1/2}$ and 2p$_{3/2}$ indicating fully oxidized TiO$_2$. The peaks of as-prepared powder shift to the lower binding energy at 462.9 and 457.3 eV, indicating reduced Ti phase (Ti$^{n+}$, n ≤ 3) in agreement with a shift of Ti 2p$_{1/2}$ by Ti$^{3+}$ with SMSI on Co/TiO$_2$. The Ti 2p$_{1/2}$ peaks for Ti$^{3+}$ and Ti$^{2+}$ are 457.2 eV and 455.3 eV: therefore, crystalline TiO$_x$ is assigned to Ti$^{3+}$ state in agreement with XRD.
By annealing at 350 °C (green broken line), the peak positions slightly shift to higher binding energy side indicating partial oxidation of TiO\(_x\). Under oxidative conditions, only the surface of TiO\(_x\) layer is oxidized until SMSI ceases\(^{40}\). Thus, the shift could be attributed to oxidation of surface TiO\(_x\) but crystalline TiO\(_x\) still remains\(^{40}\) in agreement with Fig. D.3. Annealing at 600°C (blue broken line), shifts more dramatically the peak to lower binding energy, so the XPS spectrum consists of only Ti\(^{4+}\) signal indicating complete oxidation of TiO\(_x\) (Fig. D.4) as it becomes identical to that of P25 TiO\(_2\) (solid black line).\(^{33}\)

![Ti 2p XPS spectra of pure TiO\(_2\) (P25, black), as prepared (red) 30Ag/TiO\(_2\) (P/D =3/5) and annealed in air at 350 (green), 500 (purple) and 600 °C (blue) for 2 h.](image)

**Figure D.7** Ti 2p XPS spectra of pure TiO\(_2\) (P25, black), as prepared (red) 30Ag/TiO\(_2\) (P/D =3/5) and annealed in air at 350 (green), 500 (purple) and 600 °C (blue) for 2 h.

## D. 3 Conclusions

Crystalline TiO\(_x\) on Ag/TiO\(_2\) were made by flame spray pyrolysis tuning the Ag/Ti ratio and flame synthesis conditions are investigated for solar photocatalysis. Less amorphous TiO\(_x\) is generated at higher FSP P/D because of longer \(t_R\) but at high Ag loading (\(z = 40\)), the mass fraction of amorphous TiO\(_y\) indicating amorphous TiO\(_y\) formation by SMSI. Particle annealing (< 500 °C) in air for 2 h where crystalline TiO\(_x\) is stabilized by SMSI crystallizes the amorphous TiO\(_y\) into crystalline TiO\(_x\) and anatase TiO\(_2\) with partial oxidation of the particle surface. These phase transformations dramatically improve the photocatalytic activity
of these materials for phenol degradation under both UV and visible light, even though annealing decreases the intensity of their visible absorption. This is attributed to the superior solar light activity that is six times better than that of commercial titania (P25). The annealing (< 500 °C), however, does not affect the Ag plasmon absorption of the powders.

D.4 References


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