Multiscale Plasmonics for Energy and Environment

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Abstract

Plasmonics is one of the cutting-edge fields of science to which nanotechnology has been making an evident contribution. Discovery of an interaction of collective oscillations of electrons on a metal surface with electromagnetic radiation has opened up new perspectives in a variety of areas where the outcome of the interaction, such as electromagnetic field enhancement, acts importantly. Two representative fields which benefit from strong field enhancement are surface enhanced Raman spectroscopy (SERS) and broadband light absorption. The light absorption and the SERS enhancement are correlated in theory with the second and fourth powers of the electric-field enhancement, respectively. Therefore, a plasmonic platform that could embody strong field enhancements has been of great demand in both areas.

The field of plasmonics has seen a fascinating progress in the last two decades. The advent of nanomanufacturing technologies as well as the development of strong computational techniques has enabled the engineering of complex plasmonic architectures. Numerous studies have unveiled the mechanism of surface-plasmon mediated field enhancement and the effects of geometry, material and dielectric environment. In spite of the level of physical understanding, active commercialization of the plasmonic substrates has not been realized. The challenges lie in the fabrication of low-cost and high-performance substrates. The main goal of this Ph.D. thesis is to design and manufacture such plasmonic substrates to bring the field closer to real-world applications.

Our main strategy to accomplish this task is to avoid expensive nanolithographic techniques. Therefore, we would not design a structure composed of a periodic array of a well-defined nanometer-scale geometry. Conversely, we make use of the
random geometries. Randomness in plasmonic structure does not only reduce the cost, but also broadens the resonance bandwidth effectively. Obviously, the broadband resonance is necessary for the light absorption purposes. SERS also benefits from the broad resonance bandwidth because it can effectively enhance both incident and scattered fields.

It should be noted that the broadband absorption phenomenon can stem from several factors. Overlapping multiple resonances can lead to a broad, single resonance peak. Similarly, non-resonant coupling of light to geometric singularities does not depend significantly on the excitation frequency. Regardless of the mechanism, we name such substrates showing the broadband light interaction as non-resonant. For either of the applications, we design and fabricate non-resonant substrates.

In this thesis, femtomolar sensitivity is demonstrated using a non-resonant SERS substrate. The SERS substrate is a composite structure built at the top of a forest of vertically aligned carbon nanotubes (VA-CNT) by coating individual CNTs with a few-nm-thick dielectric material conformally and then depositing a few nanometers of metal at the canopy of the forest. The resultant useful structure is a canopy of densely intertwined nanowires (NW). The intermediate dielectric layer has a critical role in accomplishing great chemical-detection sensitivity because it helps eliminate possible surface plasmon quenching by CNTs. It is this sensitive SERS substrate that allows potential sensor applications of SERS in two areas: environmental monitoring and biodetection.

Using the substrate out of concentric metal-dielectric-CNT nanowires, we detect characteristic micropollutants found in freshwater resources: e.g., Ibuprofen (Ibu) and Benzotriazole (BTAH). The femtomolar detection sensitivity is once again demonstrated for BTAH having a strong affinity to the NW metal surface. We can also achieve picomolar detection of the weakly binding Ibu if adopting a proper surface-functionalization
technique. We draw a relation of the binding-energy-dependent surface adsorption of molecules with concentration-dependent SERS signal. In addition, the multiplex detection capability of SERS is discussed.

The second application of our SERS substrate is the biological detection. We can detect microRNAs as low as subfemtomolar in concentration. This biodetection part of the SERS performance investigation begins with comparing synthetic microRNA with ones extracted from a human blood sample. The selectivity of SERS on three different solutions comprising distinct blends of microRNAs is then determined. We show that both SERS and the state-of-the-art RT-qPCR methods achieve similar sensitivities. Immediacy in biodetection is a key feature of SERS, which bears great potential in clinic applications.

Following, we provide a mechanistic understanding of field enhancement of our SERS substrate based on a simplified model: a NW dimer. By use of the finite element method, we find out multiple resonant and non-resonant enhancement modes that our SERS substrate poses. Enormous field enhancement can take place for “kissing nanowire” configurations in which one of the NWs is obliquely oriented against a horizontal one.

For the broadband light absorption, we design a novel architecture that places a nanoporous-spacer in between random islands of plasmonic absorber atop a perfect reflector. The nanoporous spacer is formed by using a block copolymer (BCP) self-assembly technique. Here again, based on the mechanistic understanding and prediction, the tunability and angular dependence of an absorption spectrum is verified experimentally.

Finally, we demonstrate the nanoporous polymer film coated on a flat metal surface. This porosity design is achieved by use of energetic ion beams through pores of a BCP etch mask. By producing an ultradense array (50 nm in pitch) of metallic nanopores over a 10-cm-diameter wafer via simple minimization
of the roughness of the underlying metal thin film, this technique embodies the concept of manufacturing over many length scales.

**Zusammenfassung**


um dieses Forschungsgebiet näher in Richtung kommerzieller Anwendungen zu führen.


In dieser Dissertation wird femtomolare Sensitivität durch ein nichtresonantes SERS-Substrat demonstriert. Das SERS-Substrat ist eine Verbundstruktur, welche auf der Oberfläche eines Waldes aus vertikal ausgerichteten Kohlenstoffnanoröhrchen (VA-CNT) hergestellt wird indem das Baumkronendach der individuellen Kohlenstoffnanoröhrchen konform mit einer weniger Nanometer dicken Schicht dielektrischen Materials und anschliessend einer wenigen Nanometer dicken Schicht Metall beschichtet wird. Die daraus entstehende nützliche Struktur ist ein Baumkronendach aus eng verwobenen Nanodrähten (NW). Die zwischengelagerte dielektrische Schicht ist besonders wichtig um hohe chemische Detektionssensitivität zu erreichen, da sie hilft mögliche Oberflachenplasmonenlöschung durch die CNTs zu


Anschliessend bieten wir eine mechanistische Erklärung der Feldverstärkung unseres SERS-Substats basierend auf einem vereinfachten Modell: einem NW-Dimer. Durch Nutzung der Finite-Elemente-Methode bestimmen wir mehrere resonante und nichtresonante Verstärkungsmoden die unser SERS-Substrat besitzt. Enorme Feldverstärkung resultiert für die
„küssender Nanodraht“-Konfiguration in welcher ein NW schräg zu einem horizontalen NW orientiert ist.

Für Breitbandlichtabsorption entwickeln wir eine neue Struktur, in welcher ein nanoporöser Distanzhalter zwischen zufälligen Inseln plasmonischer Absorber und einem perfekten Reflektor platziert ist. Der nanoporöse Distanzhalter wird durch eine Blockcopolymer (BCP) Selbstanordnungstechnik hergestellt. Erneut liefern wir mechanistisches Verständnis und Vorhersagen und das einstellbare, winkelabhängige Absorptionsspektrum wird experimentell verifiziert.