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Composites of Copper Nanowires in Polyethylene: Preparation and Processing to Materials with NIR Dichroism

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ABSTRACT: Agglomeration of copper nanowires (aspect ratios on the order of 1000) in polyethylene, commonly a major problem, could be prevented by modification of the nanowires with a surface layer of oleylamine. Nanocomposite films were prepared by mixing nanowire dispersions in organic solvents with polyethylene solutions followed by casting, drying, and sometimes hot pressing. Orientation of the copper nanowires by solid-state drawing of the composites at elevated temperatures led to preferential alignment of the nanowires in the drawing direction. This arrangement gave rise to a uniform dichroism in the near-infrared (NIR) region, which is uncommon in the case of the hitherto reported dichroic nanocomposites. The NIR dichroism is ascribed to the high aspect ratio of the metal wires. Hence, drawing of isotropic nanocomposites with metal wires may serve for the manufacture of NIR polarization filters.

INTRODUCTION

While nanocomposites of polymers and isotropic (essentially spherical or cubical) metal particles have been in the focus of a plethora of studies, relatively few publications deal with nanocomposites comprising anisotropic metal nanoparticles, in particular, nanorods.1–9 In these materials, mostly nanorods with an aspect ratio below 10 were applied, while larger aspect ratios (up to the order of 100) have rarely been reported.1 Importantly, composites with metal nanorods can feature particular optical properties after drawing because of orientation of the nanorods in the drawing direction.1–4 Nanorods are characterized by optical anisotropy in two directions. As a consequence, the interaction of linearly polarized light with metal nanorods is different in two directions. When the nanorods embedded in a polymer matrix are preferentially uniaxially oriented by drawing, the optical anisotropy of the material leads to different absorption of light when the polarization plane of the light is oriented parallel or perpendicular, respectively, to the drawing direction, similar to parallel, linear aggregates of isotropic nanoparticles.10–19 Hence, the optical spectrum of such materials depends on the angle between the drawing direction and the polarization plane of the incident light. This phenomenon is designated as dichroism.

Dichroic nanocomposites were prepared essentially with rodlike silver and gold nanoparticles incorporated in poly(vinyl alcohol)1−4,6 or in cellulose triacetate.20 Notably, even nanorods with short aspect ratios (2−4) were oriented already at small draw ratios (about 2), although the orientation became more pronounced at a draw ratio of 4.4,6 Therefore, small draw ratios are sufficient to generate dichroic nanocomposites, and consequently draw ratios up to 5 have been commonly applied, while higher draw ratios (up to 8) were employed only occasionally.4 Gold nanorods (aspect ratios 3−4) were oriented in poly(ethylene oxide) during electrospinning, presumed by the effect of the flow field during fiber spinning.7,8 The resulting thin fibers (diameters 40 nm to 3 μm) also exhibited dichroism.

Dichroic nanocomposites were shown to act as polarization-dependent color filters.17–21 Moreover, such materials are envisaged as security features for documents and bank notes,20 and it was demonstrated that they operate as switchable chromophores in liquid crystal displays.17–19 Also, nanorods were converted to spherical nanoparticles by laser pulses, which caused selective melting of the nanorods.3,20 Upon irradiation of the nanocomposites through a grid, the dichroism vanished in the irradiated area, thus leading to a micropatterned dichroism.3,20 Instead of a laser, a hot embossing stamp was also used for this purpose.20

In the dichroic nanocomposites described so far, dichroism was typically observed in the visible region of the optical spectrum, and little attention has been paid to dichroism in the near-infrared (NIR) region, although a dominant dichroism in the NIR region was found in parallel aggregates of spherical gold nanoparticles.16 An increase in the aspect ratio of rodlike metal particles should shift dichroism to the NIR region.12,14

In this study, we describe the preparation of nanocomposites with nanorods of very high aspect ratio, around 1000 (also termed nanowires). Notably, this aspect ratio is an order of magnitude above the longest aspect ratio of metal nanowires applied so far in dichroic nanocomposites,1 to our knowledge. We employed copper as the metal and polyethylene as the
matrix. Note that prevention of agglomeration of copper nanowires in polyethylene is challenging because of the incompatibility of the hydrophilic copper surfaces and the hydrophobic polyethylene. These nanocomposites were subsequently drawn and the dichroism was investigated. With regard to drawing, polyethylene is particularly suited as a matrix, as poly(vinyl alcohol) often breaks already at a moderate draw ratio, and in addition, the drawing process of poly(vinyl alcohol) depends on the ambient humidity.

RESULTS AND DISCUSSION

Copper nanowires were synthesized according to the literature. The synthesis involves the reaction between copper(II) chloride and copper(II) acetylacetonate in a mixture of oleylamine and octadecene. The formation mechanism of the copper nanowires is based on three steps such as reduction of copper ions into metallic atoms, formation of nuclei, and finally anisotropic growth of the nuclei into one-dimensional structures. The nanowires were commonly around 100 nm thick and up to 100 μm long (aspect ratio about 1000), as evident from scanning electron microscopy (SEM) images (cf. Figure 1A,B). Although the nanowires were quite linear, wires with kinks also occurred (Figure 1A,B).

Figure 1. (A,B) SEM images of copper nanowires. The wires were deposited by evaporating a droplet of the dispersion resulting from the synthesis on a silicon wafer at ambient conditions. (C,D) Photographs of a composite with 5.5% m/m copper nanowires in linear LLD-PE before (C) and after (D) drawing (draw ratio = 5).

A linear low-density polyethylene (LLD-PE) was used in this study as a matrix for its good solubility and good drawability. As polyethylene is highly apolar and copper highly polar, the compatibility of these two materials is poor and as a consequence such systems strongly tend to become inhomogeneous. However, in general the compatibility can be improved in such cases by modification of the surface of the inorganic component with apolar organic moieties, such as alkyl groups. Gratifyingly, when copper nanowires are synthesized with a solution-phase procedure based on a reaction between copper(II) chloride and copper(II) acetylacetonate in a mixture of oleylamine and 1-octadecene, as-produced particles are functionalized with oleylamine at their surfaces. The amine group is coordinated to the copper surface and hence the alkyl group envelops the copper nanowires and renders them apolar toward the environment. Accordingly, the oleylamine-modified nanowires were readily dispersable in organic solvents such as hexane or chlorobenzene. In fact, it turned out that the oleylamine layer was crucial for nanowire dispersion; notably, it was even important to use fresh oleylamine or oleylamine stored in a glovebox, as otherwise poorly dispersible products were obtained. We attribute this effect to oxidation of oleylamine moieties as it is known for a long time that oleyl groups are sensitive toward oxidation. The underlying chemical processes are of complex nature and can also lead to dimerization and eventually to polymerization of oleyl groups.

The preparation of nanocomposites was aimed at fabricating them from polymer solutions containing dispersed copper nanowires. In order to obtain composites with well dispersed copper nanowires, the solvent has to first provide a homogeneous dispersion of the nanowires, which is stable toward sedimentation during processing. Second, the solvent must be able to dissolve polyethylene. Decahydropaphthalene (decalin), which is commonly used to dissolve polyethylene, did not yield stable dispersions of the copper wires. Therefore, toluene, chlorobenzene, hexane, and 1,2-dichlorobenzene were tested as dispersants, whereas the last two provided the most homogeneous dispersions. As the solvation of polyethylene proceeds best at high temperatures (since the polymer crystallizes melt at around 120 °C), 1,2-dichlorobenzene was chosen for its higher boiling temperature (179 °C compared to 68 °C of hexane).

Accordingly, LLD-PE was dissolved in hot copper nanowire dispersions, and the mixtures were subsequently cast and dried. In order to produce flat films of LLD-PE, a hot press was used. Temperature and pressure were optimized (the best parameters are indicated in the Experimental Section, the films became, for instance, less homogeneous at lower temperatures). An image of a film thus produced is shown in Figure 1C. The coloration of the film (5.5% m/m copper) is remarkably uniform and indicates a homogeneous macroscopic distribution of the copper nanowires in the film.

For the drawing experiments, small stripes were punched or cut out of the hot-pressed films. These stripes were subsequently stretched at elevated temperatures by means of a Kofer heating stage. The influence of the temperature on the stretching behavior is decisive. Best results were achieved at 120 °C, where large and uniform stretching without rupture was possible. Higher or lower temperatures resulted in preliminary ruptures of the films. The drawing of the films led to a reduction in thickness from about 100 to 25 μm, but not to an essential shrinkage in the lateral dimension (cf. Figure 1D). Therefore, because of the lower film thickness, the color of the sample is less intense in the drawn zone.

Compared to linear polyethylene, folding of the chains of LLD-PE is affected by the alkyl groups of the comonomer. Upon drawing of LLD-PE, the degree of crystallinity increases, promoted by strain-induced crystallization of amorphous chains. Also, the size distribution of the crystals becomes narrower as defective crystals are rearranged into crystals of improved quality. The orientation of the crystalline chains proceeds fast, in contrast to the amorphous chains which orient slowly and poorly.

Figure 2 shows SEM images recorded with a back-scattered electron (BSE) detector, before and after stretching of the
films. The BSE mode is sensitive to a heavier element like copper and is thus used as a straightforward way to detect copper nanowires. It should be remembered, however, that only objects in the vicinity of the surface of the films are detected with this method. The copper appears white in the images because the copper atoms scatter the electrons to a much higher extent than the carbon and hydrogen atoms of the polymer matrix because of the higher atomic number of copper. The copper wires appear somewhat larger in lateral size than they are because of the high acceleration voltage used in the BSE mode, corresponding to a large interacting volume of the beam with the sample.

The SEM image in Figure 2A reveals that the copper wires are, remarkably, well dispersed in the polyethylene matrix and not agglomerated. It seems, therefore, that the oleyl groups at the surface of the copper wires efficiently fulfill their function as a compatibilizer to the apolar organic polymer matrix. Further, Figure 2A displays that the copper wires are randomly oriented before drawing. However, by contrast, in the stretched state, the wires are orientedpreferentially along the drawing direction as shown in Figure 2B. Wires which are oriented perpendicular to the drawing direction are essentially absent. Accordingly, the drawing process led to an orientation of the copper wires.

It is expected that the orientation of the copper wires results in a dichroism, as reflected in vis−NIR spectra. The absorbance in the vis−NIR spectra depends on a number of factors. Besides the concentration of the nanowires, their lengths and diameters, their degree of orientation (which is also influenced by the fraction of nanowires with kinks), as well as the draw ratio of the films (and associated the film thickness) influence the absorbance. Note that in particular, the lengths and diameters of the nanowires as well as the fraction of nanowires with kinks may differ to some extent in different samples. A dichroism was observed indeed, as evident from Figure 3A, which presents the vis−NIR absorption spectrum of a sample containing copper nanowires in LLD-PE, recorded at different angles between polarization plane of the light and the drawing direction (φ). At φ = 0° the light is polarized parallel and at φ = 90° perpendicular to the drawing direction. Basically, optical absorption spectra of metallic, rodlike nanoparticles have two maxima, corresponding to the longitudinal (parallel to the long axis) and transverse (perpendicular to the long axis) surface-plasmon modes. The absorbance maximum around 575 nm for φ = 90°, shown in Figure 3A, is attributed to the absorption maximum of the transverse plasmon resonance. The absorption maximum at φ = 0° appears to rise beyond the detection limit of our spectrometer, that is, beyond 2000 nm because of the very long aspect ratios of the copper wires, similar to rodlike gold nanoparticles with even lower aspect ratios, which did not reveal a longitudinal absorption maximum either within the spectrometer range.

An isosbestic point arose at 650 nm. Isosbestic points are common in dichroic nanocomposites. They arise at wavelengths where the extinction coefficients of the longitudinal and transverse plasmon resonances are equal. The higher absorbance at φ = 90° at wavelengths below the isosbestic point in combination with the higher absorbance at φ = 0° at higher wavelengths implies an orientation of the nanowires parallel to the drawing direction, in line with the SEM image in Figure 2B. Notably, the dichroism is pronounced in particular in the NIR region, with relatively constant absorbances for a given φ between 1000 and 2000 nm. So far, such a feature has not been observed in this extent for drawn polymer−metal nanocomposites, to our knowledge.

Figure 2. SEM images of a composite of LLD-PE and 5.5% m/m copper nanowires. (A) Before drawing, (B) after drawing (the drawing direction is indicated by the red arrow, draw ratio = 11).
A dichroism in the NIR region was reported for drawn nanocomposites of poly(dimethylsiloxane) and elongated agglomerates of spherical gold nanoparticles, however, the absorbances strongly depended on the wavelength in those cases.16 Also, it appears that the absorbances of the drawn nanocomposites comprising silver nanowires of an aspect ratio of about 100 decreases linearly beyond wavelengths of 900 nm.1

The dichroism in the vis–NIR spectrum of samples with draw ratio 5 did not differ significantly from those of samples with draw ratio 10, in line with the observations in other systems with low-aspect-ratio nanorods where it was found that orientation was essentially established already at very low draw ratios (see Introduction).

For comparison, ultrahigh-molecular-weight polyethylene (UHMW-PE) was also employed as a matrix for the copper nanowires. UHMW-PE is more difficult to dissolve than LLD-PE because of its higher degree of crystallinity, but 1,2-dichlorobenzene was found to be a valuable solvent. As the method of solvent removal does not affect the hot-drawing behavior of UHMW-PE,25 in this study the solvent was simply evaporated by drying in air. When the initial UHMW-PE concentration is very dilute, for example 0.1% v/v or below, the resulting films may resemble a mat of single crystals and may become brittle after drying because of a large number of grain boundaries and cracks. This effect is reduced by formation of entanglements which become more pronounced at higher initial concentrations. Nearly constant nominal stress is obtained upon drawing of films prepared by casting from 1% v/v solutions, which is in the range of the concentration applied here.

Similar to LLD-PE, a 1,2-dichlorobenzene solution of the polymer could be mixed with a dispersion of the copper nanowires. In contrast to LLD-PE, however, films with UHMW-PE could not be processed by hot pressing because of the very high molar mass, and therefore the liquid comprising UHMW-PE and copper wires was cast and the gel-like matter which formed in the drying process was subsequently stapled onto an aluminum support to minimize shrinkage during drying. Thus, films with thicknesses in the range of 300–500 μm were obtained. After drying at 120 °C, the film thicknesses decreased to around 100 μm.

The drawn films with UHMW-PE showed a similar dichroic behavior as those with LLD-PE (Figure 3B), although the absorption maximum of the transverse plasmon resonance was less distinct with UHMW-PE. Nonetheless, an isosbestic point at 650 nm also emerged with UMMW-PE as the matrix. According to the results with LLD-PE as the matrix, the dichroism does not change significantly beyond draw ratios of 5. As the samples become thinner with increasing draw ratio, thus reducing their absorbance in vis–NIR spectra, a draw ratio of 6 was applied with UHMW-PE as the matrix polymer (Figure 3), although UHMW-PE is suited to achieve much higher draw ratios. Orientation of the UHMW-PE chains becomes pronounced upon drawing.33 During drawing, polymer chains are rearranged into single-phase crystalline segments, and accordingly highly crystalline UHMW-PE is obtained, with degrees of crystallinity around 90% or more.

The linear absorbance behavior in the NIR region of the materials comprising copper nanowires implies a high application potential as an improved NIR polarization filter, which could be expedient for suppression of undesirable polarization directions in integrated optical circuits. As NIR radiation is responsible for surface heating, these systems could also be useful for the development of intelligent surfaces able to minimize temperature rising during summer. Because heating in such materials is basically anisotropic,34 such materials can also serve as heat-shielding materials for space vehicles.35

## Conclusions

The surfaces of copper nanowires have to be modified with organic groups in order to achieve nanocomposites with randomly dispersed nanowires in polyethylene as the rather hydrophilic copper surfaces are not compatible with the apolar polymer matrix. Accordingly, copper nanowires (aspect ratio on the order of 1000) were coated with a layer of oleylamine. Thus, agglomeration of copper wires in the polyethylene is almost completely suppressed. The crucial role of oleylamine is underlined by the fact that only fresh oleylamine or oleylamine stored in a glovebox under inert gas atmosphere results in copper nanowires which can be dispersed in organic solvents. Such dispersions are a good basis for the preparation of nanocomposites because they can be mixed with polymer solutions, and films are subsequently obtained by casting and drying.

The copper nanowires in the polyethylene matrix were oriented by a simple process, namely, by solid-state drawing of the composite at 120 °C to ratios of 5 or more. During this process, the copper wires oriented preferentially along the drawing direction. This was reflected by a dichroism which was pronounced, in particular, in the NIR region because of the high aspect ratio of the copper nanowires. Notably, the results demonstrate that a rather constant dichroism can be achieved with long metal wires in the NIR region, which is atypical for dichroic systems established by drawing of nanocomposites reported so far. Thus, the results imply that polymer-embedded metal wires with high aspect ratio promote the preparation of NIR polarization filters by simple drawing processes.

## Experimental Section

**Materials.** The following chemicals were used without further purification. 1-Octadecene (90%, technical grade) and oleylamine (80–90%) were obtained from Acros Organics, New Jersey; Cu(acac)2 (99.99%), CuCl2 (99.999%), trioctylphosphine (97%), hexane (95%), 1,2-dichlorobenzene (99%), pentaerythritol tetrais(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate (98%), and tris(2,4-di-tert-butyl phenyl)phosphite (98%) from Sigma-Aldrich, Switzerland; linear LLD-PE (polyethylene no. 4, weight-average molar weight $M_w = 7.7 \times 10^4$, 0.3% mol/mol octene comonomer) from Dow Chemical, Midland; and UHMW-PE (GUR4120, $M_w = 5 \times 10^6$) from Ticona, Frankfurt.

**Synthesis of Copper Nanowires Coated with a Layer of Oleylamine.** The synthesis of oleylamine-coated copper nanowires was performed following the literature but with somewhat different quantities.24 Cu(acac)2 (0.168 g, 0.642 mmol) and CuCl2 (0.1076 g, 0.8 mmol) were placed in a 30 mL glass tube inside a glovebox. Octadecene (5 mL, 3.95 g, 16 mmol) and oleylamine (5 mL, 4.07 g, 15 mmol) were added (it was important that the oleylamine had not been exposed to the air previously). The vial was sealed with a cap and parafilm, and the reaction mixture was stirred with a magnetic stirring bar for 10 min at 300 rpm. After removing the sealed tube from
the glovebox, the vial was exposed to an ultrasonic bath (50 min, 37 kHz, 380 W, Elmasonic P 300H) until the compounds were completely dissolved and a dark blue solution was obtained. Subsequently, the tube was placed in an oil bath at room temperature and the reaction mixture was stirred for 10 min at 300 rpm. The temperature was increased to 120 °C, and held for 1 h under stirring. Afterward, the temperature was increased to 180 °C and held there for 1 h, again under stirring. The solution now appeared in a red-orange, transparent color. Trioctylphosphine (1 mL, 0.83 g, 2.2 mmol) was added with a syringe and the solution was stirred for another 15 min at 180 °C. The oil bath was removed and the solution was allowed to cool down to room temperature. Sample workup was performed by washing: hexane (10 mL) was added to the solution, shaken, and centrifuged (Hettich Universal 320) for 2 min at 1000 rpm. The supernatant liquid was decanted, fresh hexane (10 mL) was added, and the resulting mixture was shaken and again centrifuged at 1000 rpm for 2 min. This procedure was repeated twice. The nanowires were finally dispersed in 10 or 25 mL hexane for further use.

Preparation of Polymer Composites with LLD-PE. LLD-PE granulate (around 0.75 g) was dissolved in 1,2-dichlorobenzene (10 mL) in a 30 mL vial at 130 °C in an oil bath by stirring for 12 h. The copper nanowires dispersed in 25 mL hexane as described above were collected by centrifugation (1000 rpm, 5 min) and redispersed in 1,2-dichlorobenzene (10 mL) by exposure to an ultrasonic bath (3 min, 37 kHz, 380 W). This dispersion was subsequently added to the polymer solution and stirred for another 1 or 2 h at 130 °C. To prevent flocculation of polyethylene, the dispersion of the nanowires can be preheated to 130 °C. The polyethylene solution was then transferred to a vessel with flat bottom, allowed to cool down to room temperature and dried first in the air for 48 h and then in a desiccator for another 8 h at a pressure of 10⁻² mbar. The resulting composite was removed from the vessel and placed between two kapton foils. These foils were placed on an aluminum sheet and covered with a second aluminum sheet (Figure 4). This system was subjected to hot pressing at 180 °C for 5 min with a load of 10 kN, using two steel plates of dimension 14 cm × 14 cm. Aluminum is necessary to reach a homogeneous pressure while the kapton foil prevents the PE film from sticking to the aluminum. The thickness of the film was controlled with two metal stripes of known thickness between the kapton foils. Films with a nominal thickness of 100 μm were thus produced, with a copper content of 5.5% m/m [determined by inductively coupled plasma (ICP)—optical emission spectroscopy (OES)].

Preparation of the Polymer Composite with UHMW-PE. A dispersion of Cu nanowires in 10 mL hexane, produced as described above, was centrifuged at 1000 rpm for 5 min. The hexane was decanted and the solid redispersed in 1,2-dichlorobenzene (10 mL) by exposure to an ultrasonic bath (3 min, 37 kHz, 380 W). 1,2-Dichlorobenzene (250 mL) and the dispersed Cu nanowires were mixed in a 500 mL three-neck round-bottom flask, in order to avoid potential side reactions with oxygen during processing. Pentaaerythritol-tetrakis-(3,3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (30 mg, 25 μmol, “Irganox 1010”) and tris(2,4-di-tert-butylphenyl)phosphite (30 mg, 46 μmol, “Irgafos 168”) were dissolved each in approximately 2 mL of 1,2-dichlorobenzene and added to the round-bottom 3-neck flask. The flask was heated to 150 °C using an oil bath. UHMW-PE powder (3 g) was added and a slight flow of N₂ (1—2 L min⁻¹) was applied at the side necks. The solution was now stirred by hand using a PTFE crescent-shaped stirring rotor until the PE was completely dissolved and a clear, reddish, viscous liquid was received (the solution was too viscous to be stirred with a magnetic stirring bar). This liquid was poured into a self-made aluminum basket (dimensions approximately 15 cm × 15 cm), made by folding a thin aluminum sheet into a square shape with high walls at each side. After cooling down to room temperature, the composite was left to dry in air. Excess supernatant can be removed with a pipette occasionally to accelerate the drying process. In order to prevent complete constriction, the film was stapled to the bottom of the aluminum basket when the consistency was very viscous and before it dried completely. Thus, films with thicknesses in the order of 300—500 μm and a copper content of 0.65% m/m (determined by ICP−OES) were obtained.

Drawing of the Nanocomposites. The nanocomposites with LLD-PE or UHMW-PE as the matrix polymer were cut into strips of dimension 1 cm × 3 cm, and the strips were subsequently cleaned with ethanol. Thereafter, the strips were heated to 120 °C using a hot stage (Wagner and Munz, System Koller, Type WME) and manually drawn. The draw ratio (final length divided by initial length) was determined by measuring the elongation between two ink marks. Typically, draw ratios of about 5–10 were accomplished.

Characterization of the Films. UV-vis−NIR absorption spectroscopy was performed on a PerkinElmer Lambda 900 UV−vis−NIR spectrophotometer, equipped with polarizers. The baseline of each angle of the polarizer position relative to the sample was measured separately in presence of the empty sample holder and subtracted from the measurement of the sample at the respective angle. The curves were smoothed to reduce the noise in the lines by using the average over five subsequent measurement points. Enhanced noise around 850 nm arose from a change of the detector in the used device.

Film thicknesses were measured using a Mitutoyo thickness gauge. Elemental analysis of copper was carried out by the analytical laboratories of Bachema AG, Schlieren, by ICP−OES. X-ray powder diffraction (XRD) patterns were taken on an Empyrean (PANalytical B.V., Netherlands) powder diffractometer equipped with a Cu Kz tube, operating at 45 kV and 40 mA, and equipped with a PIXcel 1D detector. The range from 10° to 100° was scanned.

SEM images were taken on a LEO 1530 Gemini instrument. The nanowires were placed on a Si-wafer by evaporating a droplet of a dilute dispersion and sputtered with 3 nm platinum. The wafer was placed on a carbon tape to stick the nano
the sample holder. The composite sample was mounted on the carbon tape as well. To prevent charging of the sample, a layer of 5 nm Pt was sputtered on top. The composites were imaged using BSEs for image formation.

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The authors declare no competing financial interest.

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**Notes**

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