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Overcoming the Insolubility of Molybdenum Disulfide Nanoparticles through a High Degree of Sidewall Functionalization Using Polymeric Chelating Ligands**

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*Dedicated to Professor H. Schmöckel
on the occasion of his 65th birthday*

The covalent attachment of functional ligands such as photo- or redox-active molecular compounds to inorganic nanoparticle surfaces is an important first step in the design of new materials. These applications, however, usually require designated molecules to be immobilized on the nanoparticle. A wide variety of chemical linkages to the molecular surface have been devised for oxide surfaces by utilizing siloxane,^[1] carboxylic acid,^[2] acetyl acetate,^[3] phosphonate,^[4] and catecholate functional groups.^[5] Carbon nanotubes, which are chemically inert, can be surface-activated by oxidative treatment with anchor groups such as hydroxy (-OH), carboxy (-COOH), or carbonyl (>C=O),^[6] which are necessary to tether metal ions to the tube. Besides metal oxides and carbon nanotubes,^[7] metal chalcogenide nanoparticles^[8] and nanotubes,^[9] firstly reported by Tenne and co-workers in 1992, have opened up an exciting new area of research into nanomaterials with sheet structures, which—unlike single-layer graphite—are multiple layer structures. These MQ₂ (Q = S, Se, Te) species, termed inorganic fullerenes and inorganic nanotubes, are akin to carbon nanotubes in that they exhibit analogous mechanical^[10] and electronic^[11] properties. Their excellent lubrication properties^[12] can be explained on the basis of their crystal structures, which are characterized by weak van der Waals forces between the individual MQ₂ slabs which contain metal atoms sandwiched between two inert chalcogen layers. It is the inertness of the

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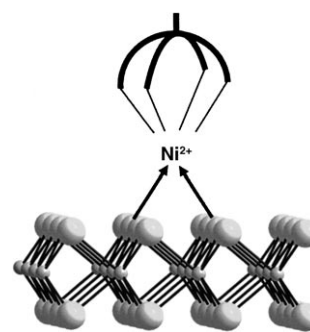
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chalcogen surface layer and the associated shielding of the molybdenum atoms from nucleophilic attack by organic ligands which are the main obstacles for the functionalization of MoS₂ nanoparticles.^[13]

In principle, a functional surface ligand consists of an anchor group that attaches to the nanocrystal, functional group, and a spacer in between. The purpose of the functional group is to render the particles soluble or to provide the proper reactivity when the inorganic fullerenes are to be used as chemical agents, for example, to disperse them in polymers or in oils. For example, aliphatic chains make the particles soluble in nonpolar solvents,^[14] while deprotonated carboxylic functions will lead to charged particles that are soluble in water.^[15] Some strategies employed for carbon nanotubes, but unsuccessful for metal chalcogenides, are polymer wrapping^[16] or coating with surfactants.^[17] A functionalization of chalcogenide nanoparticles and nanotubes can serve not only to improve their solubility, and therefore, dispersion, but also to create attractive van der Waals interactions between a nanotube and a polymer addend, or transfer the properties of functional ligands to the chalcogenide nanoparticle.

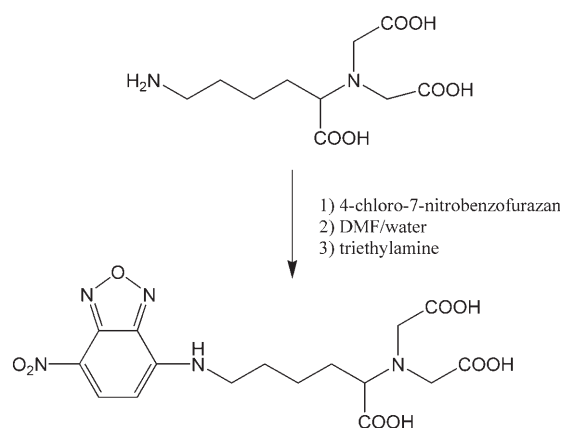
While thiolated organic molecules serve as excellent anchors to link the functional molecules on metallic nanoparticles such as Au, Pt, or Co,^[18,19] amines and/or thiols are prototypical organic anchor groups for inorganic semiconductors such as CdSe, ZnS, or ZnO which have reasonable affinities to nanoparticle surfaces with vacant metal cation (M²⁺) sites.^[19] Catechol-type chelating ligands^[19,20] (for example, dopamine), on the other hand, are robust anchor groups for most early transition metal oxide particles such as TiO₂,^[21] ZrO₂,^[22] Al₂O₃,^[23] Cr₂O₃,^[24] or Fe₂O₃,^[25] where the catechol group preferentially binds to the edges of the oxide nanocrystals where the surface energy is higher. These general principles of coordination chemistry are not new and have been used extensively for many years in the classic scheme of qualitative inorganic analysis with organic dyes.^[19,20] The sandwich-type structure of the metal dichalcogenide particles, however, necessitates the use of a different strategy. As the established strategies proved unsuccessful to generate individually functionalized chalcogenide nanoparticles or nanotubes, we have employed functional surface ligands which can serve as linkers between the nanoparticles and an appropriate "metal docking site".

We report herein a facile method for the functionalization of inorganic fullerene/MoS₂ nanoparticles that employs nitrilotriacetic acid (NTA)^[26] as a robust anchor to immobilize functional molecules on the outer sulfur layer. Since a direct anchoring of organic ligands to the sulfur surface is not possible, a transition-metal cation with a high sulfur affinity and octahedral coordination is used, whose coordination sphere is blocked completely on one side with an umbrella-type chelating ligand,^[27] while the other part of the coordination sphere remains open for docking to the sulfur layer. Recently we have used a modified tetradentate NTA ligand for the immobilization of proteins to self-assembled monolayers.^[28] In this approach two vacant coordination sites of the transition-metal ion (Ni²⁺) were used for binding to the "histidine tag" of the protein, whereas in the present case they bind to the sulfur layer of the inorganic fullerene/MoS₂



nanoparticles. The resulting functionalized inorganic fullerene/MoS₂ particles can be dispersed in water and organic solvents, and they were characterized by high-resolution transmission electron microscopy (HRTEM), thermogravimetric analysis (TGA), FTIR and UV/Vis spectroscopy, and confocal laser scanning microscopy (CLSM).

The inorganic fullerene/MoS₂ particles were prepared as described previously by a metal organic chemical vapor deposition (MOCVD) method.^[29] Surface functionalization was achieved using an NTA ligand functionalized with a fluorescent 7-nitrobenzofurazan unit (Scheme 1) and using a



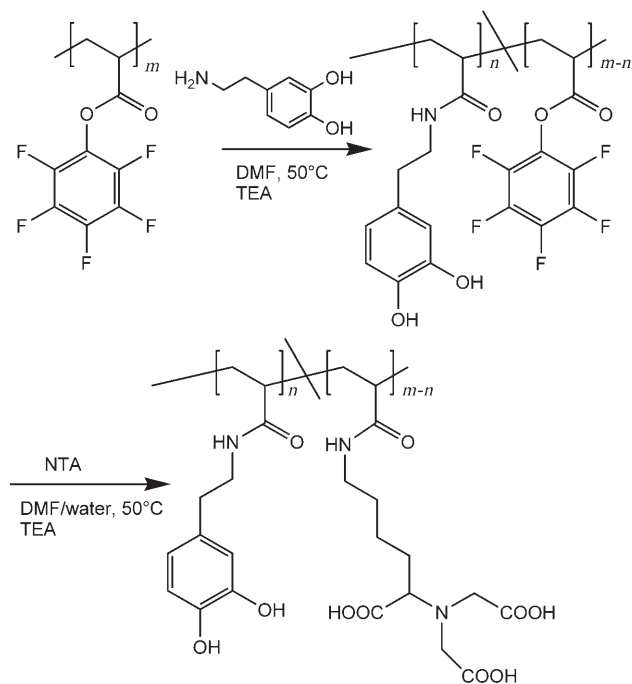
Scheme 1. Synthesis of the fluorescent ligand containing nitrilotriacetic acid (NTA) for binding to the MoS₂ surface.

polymeric ligand carrying an NTA group and a catechol type of ligand, which has been used as the anchor groups for the functionalization of metal oxides.^[21] The architecture of the polymeric ligand is of special importance, because it provides the basis of a toolbox to construct supramolecular assemblies of organic-inorganic hybrid nanomaterials.

The multifunctional polymers that are necessary to realize such systems can be prepared by a flexible synthetic route starting from reactive precursor polymers. Active ester polyacrylates can be used as such reactive precursor polymers. The fact that active ester polymers react quickly and quantitatively with amines to form the corresponding poly-(acrylamide)s opens up the possibility to obtain multifunctional polymeric materials.^[30] Compared to the commonly used poly(*N*-hydroxysuccinimide acrylate)s, active ester polymers based on pentafluorophenyl acrylates exhibit

better solubility and higher reactivity, as described by Eberhardt et al. recently,^[30b] thus opening up the possibility to work under mild conditions.

Free-radical polymerization of pentafluorophenyl acrylate yielded the polymeric active ester poly(pentafluorophenylacrylate) (PFA) with a molecular weight $M_n = 29.7 \text{ kg mol}^{-1}$ and $M_w = 58.5 \text{ kg mol}^{-1}$ (PDI = 1.96). This pre-polymer was then transformed into the multifunctional polymeric ligand by substitution with amino-functionalized molecules (Scheme 2). In the first step, 3-hydroxytyramine



Scheme 2. Synthesis of the block copolymer with catechol-type side groups for binding to metal oxides, and umbrella-type nitrilotriacetic acid ligands blocking the side of the coordination sphere of metals bonded to the S atoms of the MoS₂ surface layer, thereby preventing a precipitation of MoS₂ nanoparticles as a result of cross-linking.

(the anchor group for attachment onto TiO₂ nanowires) was covalently bound to the polymer backbone, and in the second step amino-functionalized nitrilotriacetic acid (NTA) was introduced. All the polymer-analogous reactions were carried out in a mixture of water, *N,N*-dimethylformamide (DMF), and triethylamine (TEA) at 50°C.

The resulting polymer exhibits two different features: 1) An NTA linker which can be used to coordinate to Ni²⁺ ions which, in turn, can use their vacant coordination sites for binding to the surface S atoms of inorganic fullerene/MoS₂ nanoparticles, and 2) 3-hydroxytyramine as an anchor group for attachment onto the surface of metal oxides. Analysis

of the obtained multifunctional polymer by ¹H NMR and FTIR spectroscopy as well as by GPC showed it had an NTA content of 80 mol %, with the remaining 20 mol % being 3-hydroxytyramine.

A first indication concerning the surface functionalization of inorganic fullerene/MoS₂ and based on the solubility of the functionalized nanoparticles in water and chloroform. Inorganic fullerene/MoS₂ is completely insoluble in water, because of its hydrophobicity, but can be dispersed in nonpolar solvents such as chloroform. After surface functionalization using the polymeric ligand containing NTA/Ni²⁺ (for surface binding) and polar (hydroxy, carbonyl) groups, the inorganic fullerene/MoS₂ nanoparticles could be transferred from apolar chloroform to the polar aqueous phase (Figure 1). The dark-brown color of the solution arises from

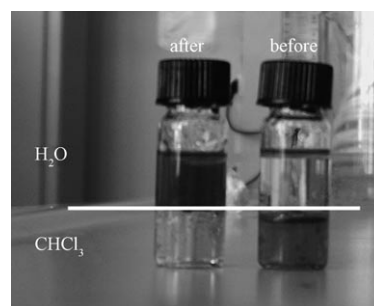


Figure 1. Photograph of a solution/dispersion of inorganic fullerene/MoS₂ before (right) and after (left) surface functionalization.

the ligand-to-metal charge-transfer interaction of the inorganic fullerene/MoS₂ nanoparticles and also between the ligand and surface-bound metal Ni²⁺ ions. The solubility properties of the functionalized inorganic fullerene/MoS₂ nanoparticles are mainly determined by the functional groups on the surface ligand.

Figure 2a shows the HRTEM image of a large functionalized MoS₂ particle with a diameter of approximately 70 nm. The energy-dispersive X-ray (EDX) spectrum of the circled area in Figure 2a shows the presence of a significant nickel content, thus validating the surface binding of NTA. Further

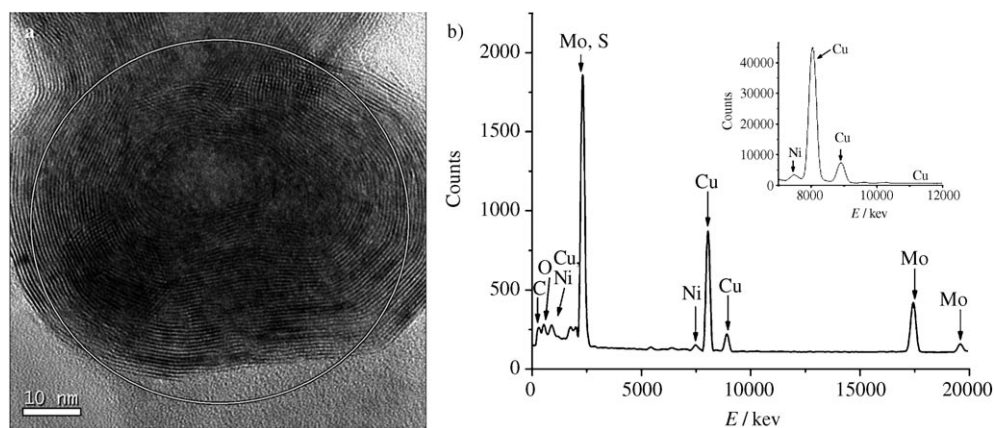


Figure 2. a) HRTEM image of a surface-functionalized inorganic fullerene/MoS₂ particle. b) EDX spectrum of the area marked by a circle in (a).

evidence of the sidewall functionalization was obtained by IR spectroscopy (Figure 3a,b) of polymer-functionalized inorganic fullerene/MoS₂ (Figure 3a) and inorganic fullerene/MoS₂ nanoparticles functionalized only with NTA ligands (Figure 3b). The most prominent bands in the 3500–3300 cm⁻¹ region arise from NH₂ stretching vibrations of the NTA ligand, the bands at 2920 (2917) and 2850 (2848) cm⁻¹ can be assigned to the stretching vibrations of the CH₂ groups, the absorption band at 1742 cm⁻¹ to the C=O stretches of the tricarboxylate anchor group, and the adsorption band at approximately 1632 cm⁻¹ to the aromatic ring of the 3-hydroxytyramine.

The UV/Vis spectrum of the functionalized MoS₂ particles (through catechol side groups attached to the polymer backbone) in water (Figure 3c) shows the characteristic broad absorption band of inorganic fullerene/MoS₂ at about 495 nm. The band at 280 nm for the polymer itself arises from the catechol side chains, while the strong absorption at 225 nm can be assigned to the C=O groups of the NTA moieties. The band corresponding to the inorganic fullerene/MoS₂ particles at 490 nm is still visible as a shoulder in the MoS₂ composite (inset in Figure 3c); the pronounced blue-shift of the C=O absorption from 225 nm to 205 nm in the inorganic fullerene/MoS₂/polymer composite indicates the surface binding of the NTA groups through the Ni²⁺ ions. A thermogravimetric (TG) analysis was performed to estimate the amount of polymer attached to the inorganic fullerene/MoS₂ surface. The inorganic fullerene/MoS₂/polymer composite exhibits

three thermal responses (Figure 3d): The thermal decomposition of the polymer begins at 150°C and is finished after 435°C, while the final step around 650°C may be related to a crystallization of the MoS₂ nanoparticles. The associated weight loss indicates that the amount of the polymeric ligand on the surface of MoS₂ is comparable to that of MoS₂ itself. An inorganic fullerene/MoS₂ particle, which has an average diameter of 30 nm and approximately 20 layers, has a mass of about 23×10^6 g per particle, which is 400 times the molar mass of a polymer molecule (58.5×10^3 g mol⁻¹). Therefore, each MoS₂ particle is covered by about 400 polymer molecules. We can assume that most of the NTA anchor groups are attached to the surface. From the approximate surface area of 5000 nm² for an inorganic fullerene/MoS₂ particle, we derive a surface area of approximately 13 nm² for a polymer molecule, if full surface coverage is assumed. For a polymer with about 250 monomer units, which carry an 80% NTA content, the surface volume covered by a single monomer unit can be estimated to be 6.5 Å². However, as the polymer is not likely to be wrapped smoothly around the surface, a somewhat lower coverage may be possible. In summary, the small surface area value obtained for a single monomer unit indicates a full surface coverage by the polymer.

Figure 4 shows the confocal laser scanning microscopy (CLSM) image of inorganic fullerene/MoS₂ nanoparticles after surface-functionalization with a benzofurazene derivative (NBD, see Scheme 1) of NTA exhibiting strong fluores-

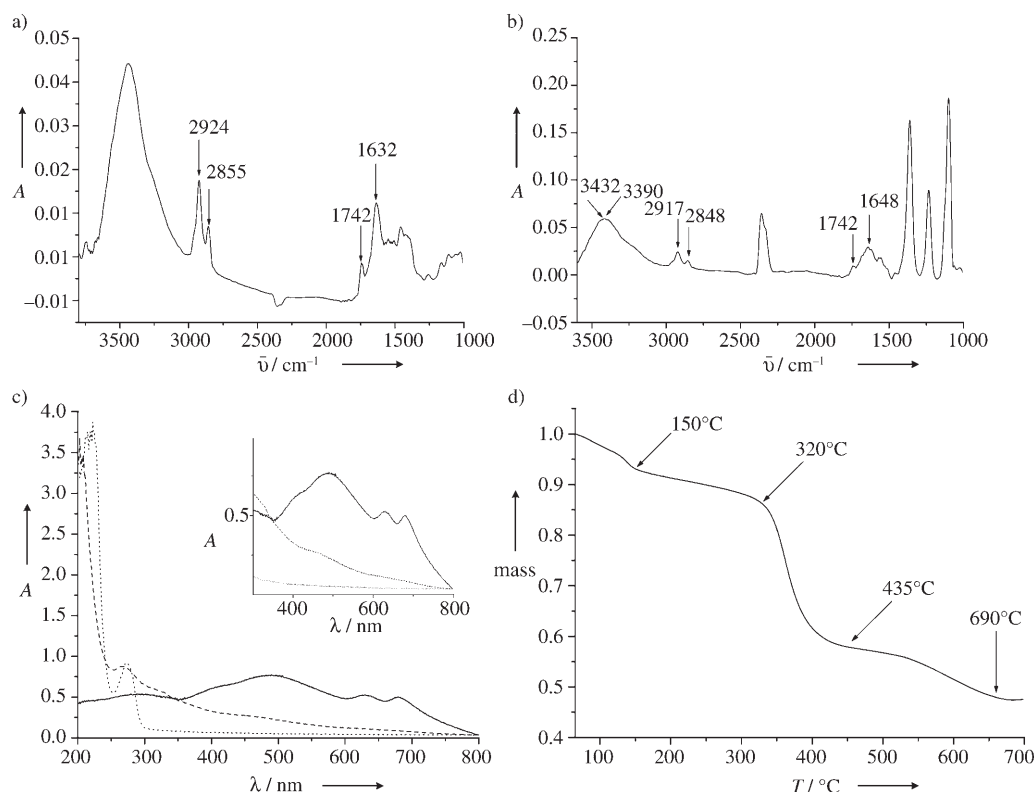


Figure 3. a) FTIR spectrum of polymer-functionalized inorganic fullerene/MoS₂ nanoparticles. b) FTIR spectrum of NTA-functionalized inorganic fullerene/MoS₂ nanoparticles. c) UV/Vis absorption spectrum of an inorganic fullerene/MoS₂ dispersion (solid line), the polymer (dotted line), and the functionalized inorganic fullerene/MoS₂ nanoparticles (dashed line). d) Determination of the mass ratio of inorganic fullerene/MoS₂ polymer by thermogravimetry.

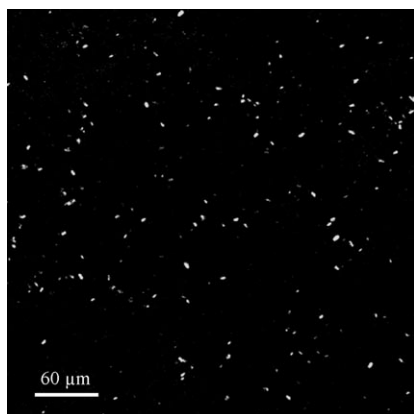


Figure 4. Fluorescence spectrum of inorganic fullerene/MoS₂ nanoparticles coated with an NBD fluorophore coupled to the NH₂ group of the NTA ligand. MoS₂ nanoparticles coated with NTA-NBD were excited at 488 nm.

cence when bound to primary or secondary amines. A 10 μL droplet of the sample was placed and dispersed carefully on a thin glass slide and the solvent was evaporated. The NBD dyes were excited at 488 nm and the fluorescence detected between 504 and 514 nm. A 40 \times (NA 1.25) oil immersion objective was used for the imaging. It is reasonable to conclude from the fluorescence images that the nanoparticles are fully coated by NTA ligands covalently bound to the inorganic fullerene/MoS₂ particle surface. It is, however, difficult to comment on the actual size of the functionalized nanoparticles because they are beyond the resolution limits of CLSM.

It is unclear so far as to whether the Ni²⁺/NTA units are bound to the close-packed sulfur surface layer of the MoS₂ nanocrystals or to defects present on the surface. The chemical reactivity of MoS₂ is associated with the edges of the sandwich layer, with the basal planes being less reactive. Therefore, the edges form the sites where gases adsorb on MoS₂ in hydro-desulfurization catalysis,^[31] and it seems logical to expect that the edges (because of their higher surface energy) are the seat of surface binding as well. Similarly, catechol is known to bind preferentially to the edges of the TiO₂ nanocrystals (which have a higher surface energy).^[32] However, full surface coverage, protection, and concomitant functionalization may be envisioned using the novel copolymer ligand containing a large number of NTA anchor groups covalently linked to the polymer backbone, thus forming a sheath around the nanoparticles—partly by surface-bound anchor groups and partly by steric shielding through the polymer ligand.

A final clue concerning the surface functionalization of inorganic fullerene/MoS₂ is based on the decoration of TiO₂ nanorods with inorganic fullerene/MoS₂ particles using the catechol groups to bind to the TiO₂ nanorods. In the first reaction step both the polymer ligand immobilized on the inorganic fullerene/MoS₂ nanoparticles and free catecholate groups were used to bind to undercoordinated surface sites of the TiO₂ nanorods. Figure 5 shows TEM images of a TiO₂ nanorod with several inorganic fullerene/MoS₂ particles attached; no unbound inorganic fullerene/MoS₂ particles

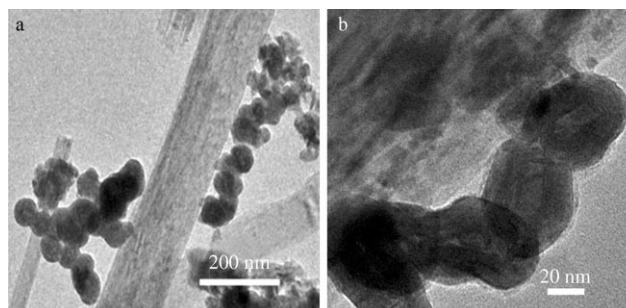


Figure 5. a) TEM image of inorganic fullerene/MoS₂ particles immobilized on a TiO₂ nanorod by functionalization of the surface wall. b) Magnified image of the rectangle marked in (a).

were detectable in the sample. Without the presence of reactive ligands, the wetting properties of TiO₂ and MoS₂ would preclude an aggregation of the hydrophobic MoS₂ particles on the hydrophilic TiO₂ surfaces. We note the aggregation behavior of inorganic fullerene/MoS₂ particles at the TiO₂ surface, which may be rationalized by the simultaneous binding of several MoS₂ particles to a single multifunctional polymer ligand (as a consequence of the high NTA content of 80%).

In summary, we have used the principles of coordination chemistry and multidentate ligand design to functionalize highly inert MoS₂ nanoparticles through a high degree of surface binding. For this purpose we have used the tetradentate NTA ligand which was coupled either to a fluorescent ligand for detection purposes or to a reactive polymer, which simultaneously serves as an anchor to the sulfide (through the NTA groups) and the oxide surfaces (through the catecholate groups) of inorganic fullerene/MoS₂ and TiO₂. We believe that this functionalization protocol can be generalized for various layered chalcogenide nanoparticles.

The functionalization of fullerene-type chalcogenide nanoparticles allows access to several fields which have been pursued actively during the past few years for the related carbon nanotubes and various oxide materials: 1) the functionalization of chalcogenide nanotubes for the attachment of electronically active components (metal and semiconductor nanoparticles, light-harvesting ligands for solar-cell applications) to the sidewalls of the tubes; 2) dispersion of nanotubes, for example, for the integration in composites, which is of interest because of their exceptional mechanical properties; and 3) fabrication of thin films by surface-binding of chalcogenide particles to oxide surfaces, which might allow their use as lubricants on seemingly incompatible ceramic materials.

Experimental Section

Synthesis: Inorganic fullerene/MoS₂ nanoparticles were synthesized according to the method recently reported by us.^[29] The active ester polymer PFA was prepared by free-radical polymerization as reported earlier.^[30b] The obtained polymer had a molecular weight of $M_n = 29.7 \text{ kg mol}^{-1}$; $M_w = 58.5 \text{ kg mol}^{-1}$, where the number of repeating units (246) is based on the M_w value. These data were obtained by gel-permeation chromatography (GPC) analysis in THF (light-scattering detection). The functional polymeric ligand was

synthesized by stirring a mixture of PFA (110 mg, 0.46 mmol repeating units) in dry DMF (3 mL) and 3-hydroxytyramine hydrochloride (10.5 mg, 0.055 mmol) in DMF (1.5 mL) and triethylamine (0.1 mL) at 50°C for 1 h. A solution of amino-functionalized NTA (120 mg, 0.46 mmol) in MilliQ water (0.9 mL) and triethylamine (2.1 mL) were introduced and the resulting mixture heated at 50°C for an additional 6 h. NTA was added in a slight excess to ensure complete quenching of the polymeric active ester groups. DMF was removed and the obtained polymeric product cleaned by dialysis in MilliQ water. Finally the ligand was isolated and dried in a vacuum oven at 40°C for 1 h and afforded 64 mg of a white polymeric powder.

¹H NMR ([D₆]DMSO): δ = 7.50–6.50 ppm (3H, brm), 6.50–4.00 ppm (1H, brs), 3.96–3.19 (5H, brm), 3.17–2.66 (5H, brs), 1.87–0.34 ppm (8H, brm); ¹⁹F NMR ([D₆]DMSO): no signals found; FTIR (ATR mode): 3200–2400 cm⁻¹: COOH (NTA), 3045 cm⁻¹: arom. C–H (dopamine); 1639 cm⁻¹: N–H (1° amide), 1199 cm⁻¹: C–N (1° amide).

For the functionalization, inorganic fullerene/MoS₂ nanoparticles (3 mg) were dispersed in ethanol (2 mL) and sonicated for 15 min. In a separate vial, polymer ligand (20 mg) or lysine nitriloacetic acid (NTA; 20 mg) was dissolved in H₂O (10 mL) and then 0.01 M NaOH (2 mL) and a 40 mmol aqueous solution of NiSO₄ (2 mL) added. Both the suspension and solution were mixed under inert conditions and stirred at 60°C for 4 h. The polymer-functionalized inorganic fullerene/MoS₂ particles were isolated and purified by repeated washing with H₂O, using centrifugation to remove the unbound polymer and water-soluble salt. To immobilize the inorganic fullerene/MoS₂ onto TiO₂ nanowires, a solution of inorganic fullerene/MoS₂ functionalized with polymer ligands in H₂O (1 mL) were mixed under inert conditions in a glove box with presuspended TiO₂ nanorods (1 mg mL⁻¹) in H₂O. The TiO₂ nanowires coated with functionalized inorganic fullerene/MoS₂ nanoparticles were then centrifuged and dried under vacuum. The product was used as such for characterization.

Instrumental analyses: The products obtained after functionalization and binding onto nanowires were analyzed by IR and UV/Vis spectroscopy as well as CLSM and HRTEM. The morphology of the MoS₂ nanoparticles and onions was characterized by high-resolution transmission electron microscopy (FEI Tecnai F30 ST operated at an extraction voltage of 300 kV, equipped with an energy-dispersive X-ray spectrometer) and by selected area electron-diffraction techniques (SAED). For TEM studies, carbon-film-coated copper grids containing a drop of a suspension of the sample in ethanol was used. A laser scanning microscope (Leica TCS SL, Leica Microsystems, Bensheim, Germany) with inverted laser was used for recording fluorescence images. UV/Vis absorption spectra were recorded on an Omega-10 spectrometer (Bruins Instruments).

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