Nanotechnology

DOI: 10.1002/ange.200503770

From Single Molecules to Nanoscopically Structured Functional Materials: Au Nanocrystal Growth on TiO_2 Nanowires Controlled by Surface-Bound Silicatein**

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Dedicated to Professor Hans-Georg von Schnering on the occasion of his 75th birthday

The chemical construction of organized inorganic matter by using inorganic nanoparticles as building blocks offers a new and promising approach to functional materials with complex architectures and properties.[1] The multiscale ordering, interlinking, and interfacing of preformed nanoparticles may be directed by using artificially structured synthetic templates or through a programmed assembly based on self-encoding elements such as streptavidin–biotin[2] and antibody–antigen complexes,[3] complementary DNA strands,[4] or electrostatic self-assembly.[5] Alternatively, artificial structuring can be achieved by using (meso)porous templates such as silica, synthetic opals,[6] foams,[7] emulsions,[8] or polymers.[9] The exploitation of these strategies remains a significant challenge as the properties and functions of materials are controlled not only by the nature of their building blocks, that is, atoms, molecules, and nanoparticles, but also through their organization into complex assemblies on various length scales.

Recently there has been much interest in the fabrication of ordered two- and three-dimensional devices by using nanotubes/wires as building blocks.[10] Nanotubes/wires with various electronic and mechanical properties can be synthesized by a variety of methods, depending on the nature of the constituent material. Nanotube/wire–nanoparticle hybrid materials, in which nanoparticles are attached to the walls of nanotubes/wires, may combine the unique structural and electronic properties of nanotubes/wires and the outstanding properties of nanoparticles which can tune their electronic structures through their size and morphology. In the past, most efforts towards such hybrid materials focused on carbon nanotubes, with prototype guest particles being Au[11] or Pt[11a,c] as well as semiconductors such as CdSe.[12] This observation is surprising, as carbon nanotubes are very inert and therefore difficult to functionalize. Nanotubes/wires from compounds other than carbon (e.g. TiO_2,[13] V_2O_5,[14] or WS_2[15]) can be expected to exhibit unique properties depending on the constituent compounds and their morphologies. In particular, oxidic nanotubes/wires would combine the versatile physical and chemical properties of ceramic materials and the tube/wire morphology.

A straightforward procedure to attach colloids onto the surface of nanotubes/wires is to grow the nanoparticles stabilized with capping ligands in solution and to anchor them to the outer tube/wire surface by chemical interactions in the final step.[16] Whereas this synthetic approach has to rely on sophisticated stabilizing ligands to control nanoparticle size and binding to the surface,[17] biological systems are able to control nucleation processes highly precisely and reproducibly to produce an amazing diversity of nanostructured particle morphologies.[18] Therefore, it is a logical approach to use "biological surfaces", for example, biofunctionalized nanowires, as templates for the growth of nanoparticles on the wire surface. Biological methods using bacteria or proteins for the synthesis of metal[19] and semiconductor[20] nanoparticles still represent a relatively unexplored and underexploited alternative. The use of polypeptides or proteins seems advantageous because some bacteria and peptides have been shown to form and bind metal or semiconductor nanocrystals. Recently we reported the immobilization of silicatein, an enzyme involved in the biosilicification processes in marine sponges, onto self-assembled monolayers, and we demonstrated the catalytic activity of surface-bound silicatein for the formation of SiO_2 from tetraethoxysilane (TEOS)[21] and ZrO_2 from ZrF_6^{2-}.[22]

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (DFG). We are grateful to S. Faiß for help with the CLSM studies.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Herein, we report a facile procedure for the surface functionalization of TiO_2 nanowires by immobilization of a His-tagged enzyme and the fabrication of Au nanoparticles onto the TiO_2 nanowires as a result of the bioreduction of $HAuCl_4$ that is mediated by the immobilized enzyme. The enzyme under consideration is versatile in its catalytic functions, as reported by Morse and co-workers[23,24] and us.[22] The methodology can be further extended to make core–shell materials of metal and metal oxide.

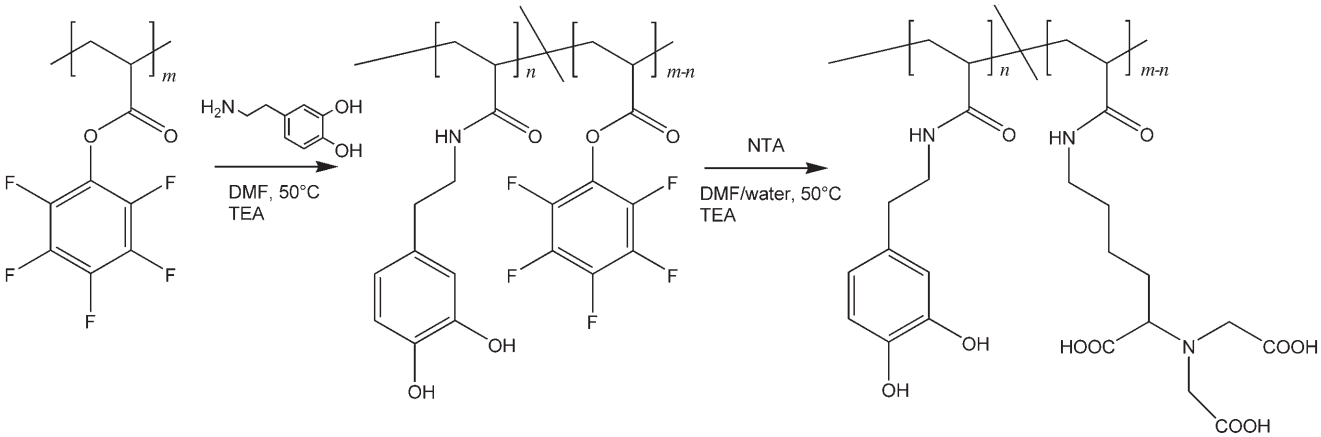
Surface functionalization was achieved using a polymeric ligand which can be used for the in situ and postfunctionalization of TiO_2[25] as well as for other metal oxides such as Fe_2O_3.[26] The architecture of the polymeric ligand is of major importance, because it provides the basis of a comprehensive toolbox to construct supramolecular assemblies of organic–inorganic hybrid nanomaterials. Polymeric ligands offer an enhanced binding efficiency over low-molecular-weight ligands as a consequence of their multifunctional interaction with the surface, as demonstrated by Whitesides and coworkers.[27] 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.[28] Compared to the commonly used poly(*N*-hydroxysuccinimide acrylate)s, active ester polymers based on pentafluorophenyl acrylates exhibit better solubility and higher reactivity.[28b]

The synthesis of the multifunctional polymeric ligand starting from this precursor polymer is illustrated in Scheme 1. The active ester polymer was prepared by free-radical polymerization to yield a polymer with a molecular weight of $M_n = 29.7\ kg\,mol^{-1}$ and $M_w = 58.5\ kg\,mol^{-1}$ (PDI = 1.96). This precursor polymer was then transformed into the multifunctional polymeric ligand by substitution with amino-containing functionalities. The polymeric ligand was prepared by a stepwise substitution of the active ester groups: in the first step, 3-hydroxytyramine was added as an anchor group for the attachment onto TiO_2 nanoparticles, and in the second step amino-functionalized nitrilotriacetic acid (NTA) in water and triethylamine were added and the resulting mixture was kept at 50 °C for 6 h and then the solution was adjusted to pH 2 with H_2SO_4. Characterization of the polymeric ligand by ^1H NMR and FTIR spectroscopy as well as GPC (see the Supporting Information) showed the composition to be 80 mol % NTA and 20 mol % 3-hydroxytyramine. The resulting polymer exhibits two different features: 1) An NTA linker to immobilize the His-tagged protein[29] 2) 3-hydroxytyramine as an anchor group for attachment to the TiO_2 nanoparticle surface.[30]

Functionalization of TiO_2 nanowires was achieved by sealing a mixture of TiO_2 nanowires and polymeric ligand in benzyl alcohol (10 mL) under inert conditions and stirring the mixture at 60 °C for 4 h. The product was repeatedly washed with CH_2Cl_2 to remove any remaining ligand. The functionalized TiO_2 nanowires were characterized by TEM as well as FTIR, ^1H NMR, and UV/Vis spectroscopy.

The binding of silicatein to the surface of the TiO_2 nanowires functionalized with polymeric ligand incorporating NTA in the backbone of the polymer was confirmed by confocal laser scanning microscopy (CLSM, Leica TCS SL with an argon laser) using fluorophore-labeled antibodies against silicatein.[31]

The dye molecules were excited at 488 nm and the resulting fluorescence detected from 504–514 nm using a 20× dry objective. The advantages of CLSM are that: 1) the detection of protein using fluorophore-labeled antibodies is very specific, that is, this antibody does not bind to any other component, and 2) a large surface area can be seen. Figure 1 a illustrates the identification of surface-bound silicatein. Figure 1 b, c show the CLSM images of immobilized silicatein after exposing the surface to fluorophore-labeled antibodies. Monoclonal antibodies raised against the silicatein immobilized onto the functionalized TiO_2 nanowires were used.[31] The functionalized nanowires with immobilized silicatein were treated with solutions containing the antibody (mAb-aSilic); the immunocomplexes were then stained with fluorophore-labeled (Cy2-label) secondary goat anti-rabbit antibodies. The surface-bound silicatein reacted strongly with the antibodies as illustrated in Figure 1 b, c. The presence of Cy2 resulted in the silicatein appearing green and fluorescing at 520 nm. The high magnification image in Figure 1 c indicates that several silicatein molecules are immobilized onto the backbone of functionalized TiO_2 nanowires and shows the globular morphology of silicatein, as already reported using AFM and CLSM.[21,22,32] It is difficult to comment on the



Scheme 1. Synthesis of a functional polymeric ligand containing nitrilotriacetic acid (NTA) and dopamine units. TEA = triethylamine.

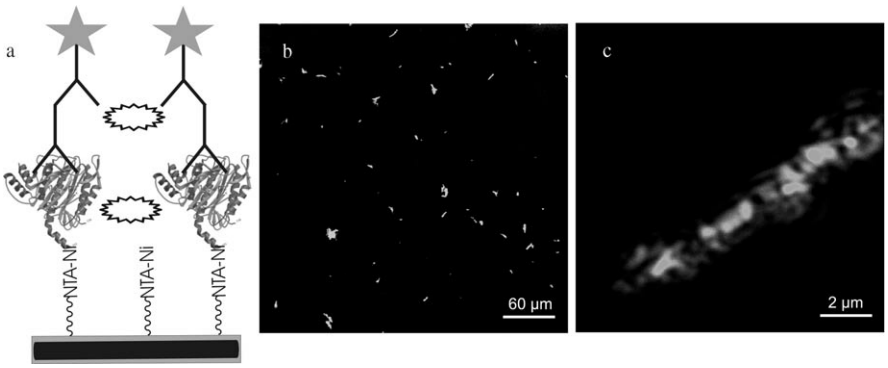


Figure 1. a) Antigen capture assay. a) TiO_2/silicatein complex (globular symbol = silicatein, oval dentate symbol = nonspecific bovine serum albumin (BSA), and **Y** symbol = specific monoclonal anti-silicatein of *Suberites domuncula*. The assay is visualized by recognition of the antigen/antibody by fluorophore Cy2 coupled to antibodies detecting the mouse F_{AB}. Upon immobilization of fluorophore-labeled antibodies (Ab) onto the TiO_2/polymer/silicatein surface, the surface-bound silicatein can be visualized by using confocal laser scanning microscopy (CLSM). b) Overview image showing many functionalized and immobilized silicatein TiO_2 nanowires. c) HRCSLM image showing the presence of several adjacent fluorescence spots which indicates the binding of several silicatein molecules onto a TiO_2 nanowire.

actual size of the silicatein because it is beyond the resolution limits of CLSM. In our control experiment where functionalized TiO_2 nanowires were exposed to fluoro-labeled antibodies, no fluorescence was observed.

The fabrication of TiO_2 nanowires decorated with Au nanocrystals is illustrated in Figure 2. In the first step the surface of the TiO_2 nanowire (white) is functionalized with the multifunctional polymer ligand (gray) by complexation through the hydroxy groups of dopamine, thus tailoring the surface of the TiO_2 nanowires with the NTA tripod ligand attached to the polymer. In the second step, silicatein containing the His-tag was immobilized onto the NTA ligand by complexation with Ni^{2+} ions. Finally, tetrachloroauric acid was reduced by the surface-bound silicatein. The growing Au nanocrystals were thus chemically bonded to the protein through complexation/surface binding.

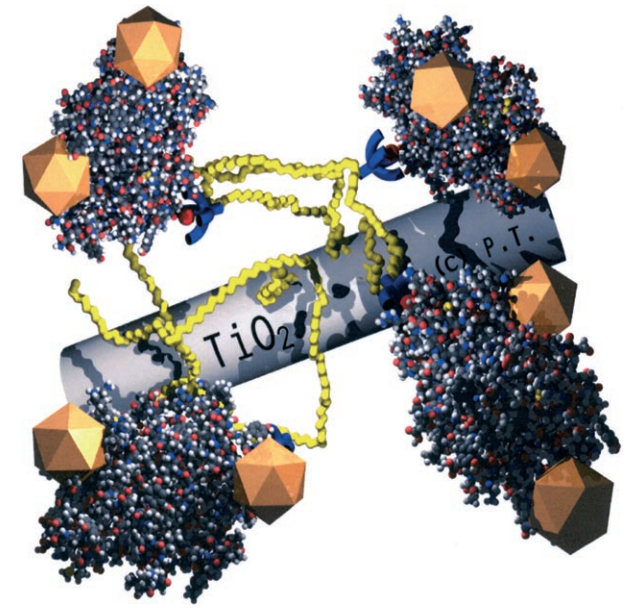


Figure 2. Schematic presentation of the fabrication of the TiO_2 nanowire/Au nanocrystals. In the first step the TiO_2 nanowire is functionalized with the multifunctional polymer ligand (gray) by complexation through the catechol groups. The NTA tripod ligand is bound to the side groups of the polymer. In the next step, the silicatein-containing HIS-tag is attached to the NTA ligand by complexation of Ni^{2+} ions through the His-tag. Finally, tetrachloroauric acid is reduced by the sulfhydryl groups of the immobilized silicatein. The Au nanocrystals are chemically bonded to the amino groups at the protein periphery.

The addition of aqueous chloroauric acid to a solution of the silicatein-functionalized TiO_2 nanowires resulted in the color of the solution changing from pale yellow to red, which indicates the formation of gold nanoparticles by the reductive action of the protein. The UV/Vis spectrum (Figure 3) recorded 3 h after mixing the solutions at room temperature

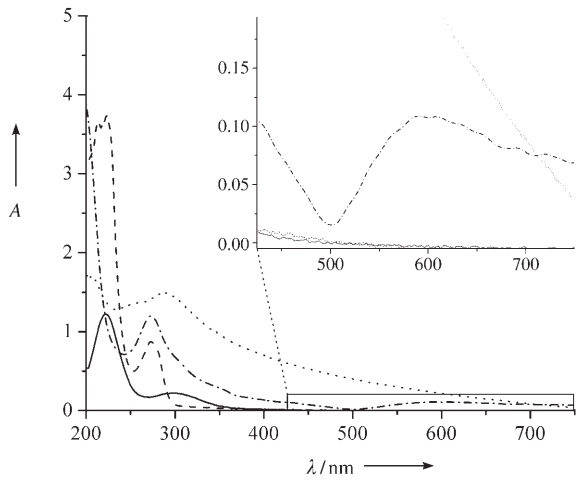


Figure 3. UV/Vis absorption spectrum of: synthesized TiO_2 nanowires (••••), polymeric ligand (----), $HAuCl_4$ solution (——), and polymer-functionalized TiO_2 nanowires with immobilized silicatein and bioreduced Au nanoparticles (–•–•).

showed the appearance of a surface-plasmon resonance band at about 570 nm which shifted to longer wavelength with time. This shift is accompanied by an increase in the near-infrared (NIR) region of the electromagnetic spectrum. Clearly, the absorption at 275 nm for the polymeric ligand (dashed line) shows the presence of aromatic catechol groups and the absorption at 220 nm shows the presence of carbonyl groups. The blue shift of 15 nm in the absorption of the carbonyl groups (dashed line) indicates the His-tagged binding of the protein through Ni complexation by the NTA groups. A broad plasmon absorption band ranging from 520–700 nm for the composite (see inset of Figure 3) indicates the aligned attach-

ment of Au nanoparticles in the TiO_2/Au nanocomposites. The UV/Vis absorption of the functionalized TiO_2 nanowires carrying no protein and $AuCl_4^-$ did not show any plasmon absorption band, which indicates that polymer-functionalized TiO_2 nanowires alone cannot reduce tetrachloroauric acid. In contrast, the polymeric ligand reduces $AuCl_4^-$ in solution at the expense of the free hydroxy groups of dopamine, whereas the surface-bound polymeric ligand exhibits no reducing properties because all the hydroxy groups are involved in surface binding. Moreover, free silicatein can reduce $AuCl_4^-$ efficiently to Au nanoparticles (see the Supporting Information). These results indicate that Au reduction is restricted to protein-functionalized TiO_2 nanowires only.

Our findings are compatible with the formation of anisotropic particles whose aspect ratio increases with time[19c,e] as a result of a uniaxial plasmon coupling or indicate the formation of spherical gold nanoparticles that aggregate with time (or a combination of both processes). Since recombinant silicatein does not contain any reducible saccharide groups, the SH groups of cysteine or OH groups of tyrosine within the protein mantle are considered to be involved in the reduction of $AuCl_4^-$ to Au^0 and the subsequent growth of Au nanoparticles. As electron transfer can occur easily over distances of 20 Å and more,[33] this reduction does not require the SH groups to be located at the periphery of the protein. The amino groups arranged at the outer surface of silicatein may be assumed to act as coordinating centers for the surface binding of the gold colloids.

The HRSEM image of TiO_2 nanowires decorated with Au nanocrystals (Figure 4, inset top left) shows that the TiO_2/Au hybrid is composed of hierarchically templated assemblies of Au nanoparticles and TiO_2 nanowires. The individual TiO_2/Au nanocomposites with a uniform TiO_2 backbone are clearly seen with a high aspect ratio in Figure 4. A high-resolution view in the inset (bottom right) reveals a triangular or hexagonal morphology of the Au nanoparticles, with a uniform statistical distribution across the TiO_2 nanowire.

The morphology of the TiO_2/Au composite was confirmed by TEM. Figure 5a shows a TEM image of the as-synthesized TiO_2 nanowires. It reveals TiO_2 nanowires with diameters of 25–50 nm and wire lengths of up to a few micrometers. Figure 5b shows an overview image of several TiO_2 nanowires decorated homogeneously over their entire length with Au nanoparticles. The corresponding EDX spectrum in Figure 5c clearly confirms the presence of Au, along with Ti and O. The TEM image of nanocrystals in Figure 5d, however, appears to be composed of triangular platelets inverted with respect to each other, which is in agreement with the results from the HRSEM image in Figure 4, where some of the nanocrystals grown in the presence of surface-bound silicatein exhibited triangular morphology of Au nanocrystals. The HRTEM image of one particle (see Figure 5e) exhibits the view down ⟨110⟩ with grain boundaries clearly visible. A typical electron

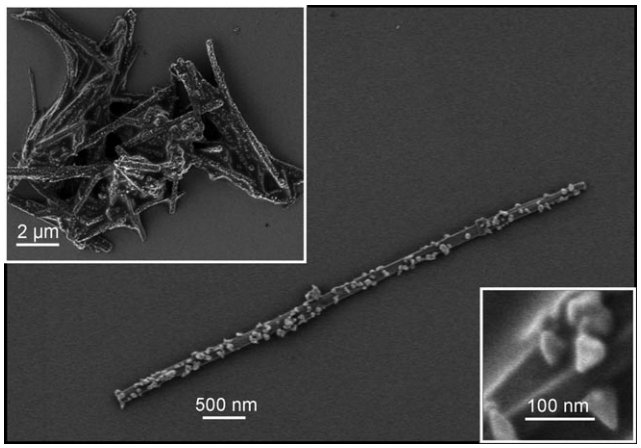


Figure 4. HRSEM image demonstrating the hierarchical structure of the TiO_2 nanowire/Au nanoparticle composite. Overview images of the TiO_2/Au nanocomposites (top left) and a magnified view (right bottom) are given.

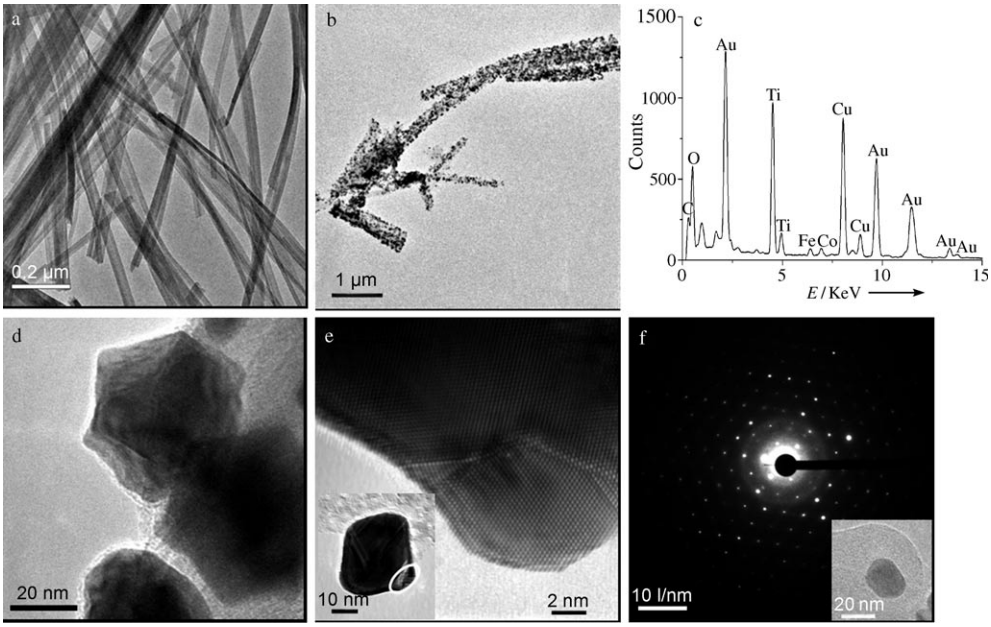


Figure 5. a) TEM image of TiO_2 nanowires. b) Overview image of TiO_2 nanowires decorated with Au nanocrystals, obtained by reduction with surface-bound silicatein. c) EDX spectrum of a TiO_2 nanowire decorated with Au nanocrystals, thus indicating the presence of Ti, O, and Au. d) Magnified view of a single TiO_2 nanowire with Au nanocrystals attached. e) HRTEM of a crystal edge, (marked by a circle in the inset) which shows the polycrystalline nature of the nanocrystal. f) Nano-electron diffraction (NED) spectrum of an Au nanocrystal shown in the inset.

diffraction pattern of a 20-nm-sized gold nanocrystal viewed along ⟨110⟩ is given in Figure 5 f. This triangular crystal shape[19e,34] is very unusual; except for one case[19e] the limited number of examples reported so far have been obtained by chemical/photochemical methods. Shape control of inorganic materials in biological systems is achieved either by growth in constrained environments such as membrane vesicles,[35] or through functional molecules such as polypeptides that bind specifically to inorganic surfaces.[36] Specific polypeptide repeating sequences in proteins secreted by the bacterium *Escherichia coli* have been shown to induce the growth of flat, triangular gold nanocrystals in low yield relative to the total formation of nanoparticles.[36] Therefore, a possible explanation for the formation of the surface-bound nanotriangles is based on the chirality of the nucleation centers at the surface of the protein. Whereas hexagonal crystals are achiral, because they have an inversion center in the center of the Au hexagons, triangular crystals are chiral, because the inversion symmetry is lost during the formation of the triangular crystal. An S_3 axis of the hexagon is maintained as the high symmetry element, that is, chiral information contained in the silicatein structure is transmitted to the nucleating gold nanocrystals during the $AuCl_4^- \rightarrow Au$ reduction and the subsequent Au nucleation at the outer surface of the protein, and maintained during the growth of the nanocrystal. This scenario is compatible with the observation that triangular nanocrystals were also formed by reduction of $AuCl_4^-$ in the presence of lemon grass extract,[19e] which presumably contains a multitude of as yet unidentified proteins. In contrast, no triangular (or even pronounced) Au nanocrystal morphologies were observed when Au precursor compounds were reduced chemically and attached to histidine-rich peptides on the surface of carbon nanotubes.[16,37] These findings suggest that the morphology of the Au nanocrystals is determined by the coordination and simultaneous reduction during the nucleation process in the presence of the protein rather than by the chemical reduction in solution and subsequent binding to the polypeptide chain.

In summary, we have fabricated a functional nanocomposite of immobilized silicatein—a hydrolytic protein involved in the biomineralization of SiO_2—on the surface of TiO_2 nanowires with the aid of a reactive polymeric ligand, which simultaneously serves as an anchor to the oxide surface and as a chelating ligand for the binding of the protein. The strategy of using such polymeric multifunctional ligands offers at least two advantages over the use of small (low-molecular-weight) molecules as ligands: Our polymeric ligand can be prepared by a two-step synthesis, whereas a multistep synthesis is required for a low-molecular-weight ligand which is compatible in function to our polymeric ligand,[38] and polymeric ligands provide multidentate properties for binding, whose surface bonding is much stronger than that of monodentate low-molecular-weight ligands.

The surface-bound protein not only retains its original hydrolytic properties,[21,22] but also acts as a reductant for $AuCl_4^-$ in the synthesis of hybrid TiO_2/Au nanocomposites. The fabrication of hybrid materials with functional nanobiocomposites is without precedence. The advantage of applying biological and chiral "recognition" to the synthesis of metal nanoparticles on one-dimensional building blocks such as nanowires/nanotubes is not only the efficient and reproducible production of nanoparticles, it may be viewed also as an environmentally friendly alternative to chemical methods for the synthesis of nanoparticles.

We believe that this procedure can be generalized for various metals and semiconductors and other nanotube/nanowire materials such as WS_2. The biofunctionalization of the highly rigid oxide/chalcogenide wires/tubes also opens up possibilities for the programmed assembly of strictly one-dimensional building blocks based on self-encoding elements such as streptavidin–avidin and antibody–antigen complexes, complementary DNA strands, or electrostatic self organization.

Experimental Section

PFA was prepared as reported earlier.[28b] GPC analysis of the obtained polymer (THF, light-scattering detection) gave the following values: $M_n = 29.7\ kg\,mol^{-1}$; $M_w = 58.5\ kg\,mol^{-1}$, where the number of repeating units (246) is based on the M_w value.

For the synthesis of the multifunctional poly(acrylamides), PFA (110 mg, 0.46 mmol repeating units) was dissolved in dry DMF (3 mL). A solution of 3-hydroxytyramine hydrochloride (10.5 mg, 0.055 mmol) in DMF (1.5 mL) and triethylamine (0.1 mL) were added and the clear mixture stirred for 1 h at 50 °C. A solution of amino-functionalized NTA (120 mg, 0.46 mmol) in MilliQ water (0.9 mL) and triethylamine (2.1 mL) were then added and the resulting mixture kept at 50 °C for 6 h. The slight excess of NTA was used to ensure complete conversion of the remaining active ester groups. After removal of the DMF, the solution was adjusted to pH 3 and the crude viscous product was cleaned by dialysis in MilliQ water, isolated, and finally dried in a vacuum oven at 40 °C for 1 h to give 64 mg of a white polymeric powder. Recombinant silicatein was prepared as described.[39]

The TiO_2 nanowires were synthesized following a modified procedure reported by Bruce and co-workers.[40] In brief, titanium isopropoxide (1 g; ACROS) was placed in a teflon vessel and analytical grade ethanol (99.8%, 6 mL) was added. The teflon vessel was kept in a desiccator. The precipitation of TiO_2 was initiated under a moist atmosphere induced by placing a petri dish filled with water at the bottom of the desiccator. The diffusion experiment was stopped after 12 h, and then a 10 M aqueous solution of NaOH (25 mL) added. The reaction vessel was then sealed in a stainless-steel hydrothermal bomb, which was placed in an oven maintained at 180 °C for 20 h. The obtained sample was filtered and repeatedly washed with 0.1 M HNO_3, 1 N HCl, and de-ionized water. The product was dried under vacuum for 3 h.

TiO_2 nanowires (5 mg) were then dispersed in benzyl alcohol (10 mL) and sonicated for 15 min. In a separate vial, polymer ligand (10 mg) was dissolved in benzyl alcohol (10 mL). Both the suspension and solution were mixed under inert conditions and stirred at 60 °C for 4 h. Then polymer-functionalized nanowires were isolated and purified by repeatedly washing them with CH_2Cl_2 using centrifugation, followed by drying them under vacuum and dispersing under water. To immobilize the silicatein, Ni^{2+} ions were bound to NTA group, and the TiO_2 nanowires functionalized with the polymeric ligand containing NTA in the backbone were treated with 1 mmol aqueous solution of NaOH for 10 min using continuous stirring. The mixture was then centrifuged, washed with 18.2 $M\Omega\,cm^{-1}$ MilliQ water, and the TiO_2 nanowires rotated in a solution of $NiSO_4$ (40 mmol) for 1 h. The TiO_2 nanowires containing complexed Ni^{2+} ions were then removed, washed with a solution of NaCl and deionized water (150 mmol), and dried in a stream of N_2. A solution of silicatein (30 nmol) in 3-(*N*-morpholino)propane sulfonic acid

(MOPS) buffer was then added to the Ni^{2+}-bound TiO_2 nanowires and the mixture left for 1 h. Then silicatein-immobilized TiO_2 nanowires were washed with MOPS buffer and deionized water to remove unbound protein. The immobilization of silicatein was monitored by CLSM. To monitor the specific immobilization or activity of the enzyme, silicatein-immobilized TiO_2 nanowires in water were added to an aqueous solution of $HAuCl_4$ (10^{-3} M, 1 mL) in a polyethylene vial (2 mL). The suspension of silicatein-coated TiO_2 nanowires and acidic gold solution was immediately placed on a rotator (biocentrifuge). The suspension of the protein-immobilized TiO_2 precursor was mixed on the rotator at a speed of 1000 rpm for 24 h under normal conditions. The "bioreduction" of tetrachloroauric acid was monitored by UV/Vis spectroscopy. The biomass was then centrifuged at 3000 rpm for 10 min and repeatedly washed with sterile distilled water before carrying out all subsequent characterization.

Received: October 24, 2005
Revised: March 1, 2006
Published online: June 23, 2006

Keywords: biofunctionalization · hybrid nanocomposites · nanotechnology · nanowires · titanium oxides

[1] S. Mann, S. A. Davis, S. R. Hall, M. Li, K. H. Rhodes, W. Shenton, S. Vaucher, B. Zhang, *J. Chem. Soc. Dalton Trans.* **2000**, 3753 – 3753.
[2] a) S. Connolly, D. Fitzmaurice, *Adv. Mater.* **1999**, *11*, 1202 – 1205.
[3] W. Shenton, S. A. Davis, S. Mann, *Adv. Mater.* **1999**, *11*, 449 – 452.
[4] a) C. A. Mirkin, R. L. Lesinger, R. C. Mucic, J. J. Storhoff, *Nature* **1996**, *382*, 607 – 609; b) P. Alivisatos, K. P. Johnsson, X. Peng, T. E. Wilson, C. J. Loweth, M. Bruchez, P. G. Schultz, *Nature* **1996**, *382*, 609 – 612; c) E. Dujardin, L.-B. Hsin, C. R. C. Wang, S. Mann, *Chem. Commun.* **2001**, 1264 – 1265; d) A. N. Shipway, I. Willner, *Chem. Commun.* **2001**, 2035 – 2045.
[5] A. K. Boal, T. H. Galow, F. Alhan, V. M. Rotello, *Adv. Funct. Mater.* **2001**, *11*, 461 – 465.
[6] a) Y. A. Vlasov, N. Yao, D. J. Morris, *Adv. Mater.* **1999**, *11*, 165 – 169; b) B. T. Holland, C. F. Blanford, T. Do, A. Stein, *Chem. Mater.* **1999**, *11*, 795 – 805; c) G. Subramania, V. N. Manoharan, J. D. Thorne, D. J. Pine, *Adv. Mater.* **1999**, *11*, 1261 – 1265; d) F. Fleischhaker, A. C. Arsenault, Z. Wang, V. Kitaev, F. C. Peiris, G. von Freymann, I. Manners, R. Zentel, G. Ozin, *Adv. Mater.* **2005**, *17*, 2455 – 2458.
[7] a) F. Carn, F. A. Colin, M. F. Achrad, H. Deleuze, Z. Saadi, R. Backov, *Adv. Mater.* **2004**, *16*, 140; b) S. Mandal, S. K. Arumugam, S. D. Adyanthaya, R. Pasricha, M. Sastry, *J. Mater. Chem.* **2004**, *14*, 43 – 47.
[8] B. zu Pulitz, K. Landfester, H. Fischer, M. Antonietti, *Adv. Mater.* **2001**, *13*, 500 – 503.
[9] M. Breulmann, S. A. Davis, S. Mann, H. P. Hentze, M. Antonietti, *Adv. Mater.* **2000**, *12*, 502 – 507.
[10] a) M. R. Diehl, S. N. Yaliraki, R. A. Beckman, M. Barahona, J. R. Heath, *Angew. Chem.* **2002**, *114*, 363 – 366; *Angew. Chem. Int. Ed.* **2002**, *41*, 353 – 356; b) A. Bachthold, P. Hadley, T. Nakanishi, C. Decker, *Science* **2001**, *294*, 1317 – 1320; c) Y. Cui, Q. Q. Wie, H. K. Park, C. M. Lieber, *Science* **2001**, *293*, 1289; d) W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, *Science* **2002**, *295*, 2425 – 2427; e) P. G. Collins, M. S. Arnold, P. Avouris, *Science* **2001**, *292*, 706 – 708.
[11] a) B. C. Satishkumar, M. G. Chapline, E. M. Vogl, A. Govindaraj, C. N. R. Rao, *J. Appl. Phys D* **1996**, *29*, 3173 – 3176; b) S. Fullam, D. Cottell, H. Rensmo, D. Fitzmaurice, *Adv. Mater.* **2000**, *12*, 1430 – 1432; c) H. Shoi, M. Shim, S. Bangsaruntip, H. Dai, *J. Am. Chem. Soc.* **2002**, *124*, 9058; d) K. Jiang, A. Eitan, L. S. Schadler, P. M. Ajayan, R. W. Siegel, N. Grobert, M. Mayne, M. Reyes-Reyes, H. Terrones, M. Terrones, *Nano Lett.* **2003**, *3*, 275 – 278; e) A. V. Ellis, K. Vijayamohanan, R. Goswami, N. Chakrapani, L. S. Ramanathan, P. M. Ajayan, G. Ramanath, *Nano Lett.* **2003**, *3*, 279 – 282.
[12] a) S. Banerjee, S. S. Wong, *Nano Lett.* **2002**, *2*, 195 – 199; b) J. M. Haremza, M. A. Hahn, T. D. Krauss, S. Chen, J. Calcines, *Nano Lett.* **2002**, *2*, 1253 – 1256.
[13] a) G. Armstrong, A. R. Armstrong, J. Canales, P. G. Bruce, *Chem. Commun.* **2005**, 2454 – 2456; b) Z. V. Saponjic, N. M. Dimitrijevic, D. M. Tiede, A. J. Goshee, Z. Zuo, L. X. Chen, A. S. Barnard, P. Zapol, L. Curtiss, T. Rajh, *Adv. Mater.* **2005**, *17*, 965 – 971.
[14] a) M. E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, H.-U. Nissen, *Angew. Chem.* **1998**, *110*, 1339 – 1342; *Angew. Chem. Int. Ed.* **1998**, *37*, 1263 – 1266; b) F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, R. Nesper, *J. Am. Chem. Soc.* **1999**, *121*, 8324 – 8331.
[15] a) A. Rothschild, G. L. Frey, M. Homyonfer, R. Tenne, M. Rappaport, *Mater. Res. Innovations* **1999**, *3*, 145 – 149; b) A. Rothschild, J. Sloan, R. Tenne, *J. Am. Chem. Soc.* **2000**, *122*, 5169 – 5179; c) H. A. Therese, J. Li, U. Kolb, W. Tremel, *Solid State Sci.* **2005**, *7*, 67 – 72.
[16] H. Matsui, S. Pan, G. E. Douberly, Jr., *J. Phys. Chem. B* **2001**, *105*, 1683 – 1686.
[17] O. Masala, R. Seshadri, *Annu. Rev. Mater. Res.* **2004**, *34*, 41 – 81.
[18] a) S. Mann, *Biomineralization*, Oxford University Press, New York, **2001**; b) E. Bäuerlein, *Biomineralization*, Wiley-VCH, Cambridge, **2004**.
[19] a) M. Field, C. J. Smith, D. D. Awschalom, N. H. Mendelson, E. L. Mayes, S. A. Davis, D. Mann, *Appl. Phys. Lett.* **1998**, *73*, 1739 – 1741; b) T. Klaus, R. Joerger, E. Olsson, C.-G. Granqvist, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 13611 – 13614; c) E. Dujardin, L.-B. Hsin, C. R. C. Wang, S. Mann, *Chem. Commun.* **2001**, 1264 – 1265; d) R. R. Naik, S. J. Stringer, G. Agarwal, S. E. Jones, M. O. Stone, *Nat. Mater.* **2002**, *1*, 169 – 172; e) S. S. Shankari, A. Rai, B. Ankamwar, A. Singh, A. Ahmad, M. Sastry, *Nat. Mater.* **2004**, *3* 482 – 488; f) S. Senapati, A. Ahmad, M. I. Khan, M. Sastry, R. Kumar, *Small* **2005**, *1*, 517 – 520.
[20] a) W. Shenton, T. Doughlas, M. Young, G. Stubbs, S. Mann, *Adv. Mater.* **1999**, *11*, 253 – 256; b) J. D. Hartgering, E. Beniash, S. I. Stupp, *Science* **2001**, *294*, 1684 – 1688; c) S.-W. Lee, C. Mao, C. E. Flynn, A. M. Belcher, *Science* **2002**, *296*, 892 – 895; d) C. Mao, D. J. Solis, B. D. Reiss, S. T. Kottmann, R. Y. Sweeney, A. Hayhurst, G. Georgiou, B. Iverson, A. M. Belcher, *Science* **2004**, *303*, 213 – 217; e) D. Rautaray, A. Ahmad, M. Sastry, *J. Mater. Chem.* **2004**, *14*, 2333 – 2340; f) V. Bansal, D. Rautaray, A. Ahmad, M. Sastry, *J. Mater. Chem.* **2004**, *14*, 3303 – 3305.
[21] M. N. Tahir, P. Théato, W. E. G. Müller, H. C. Schröder, A. Janshoff, J. Zhang, J. Huth, W. Tremel, *Chem. Commun.* **2004**, 2848 – 2849.
[22] M. N. Tahir, P. Théato, W. E. G. Müller, H. C. Schröder, A. Borejko, S. Faiß, A. Janshoff, J. Huth, W. Tremel, *Chem. Commun.* **2005**, 5533 – 5535.
[23] a) K. Shimizu, J. N. Cha, G. D. Stucky, D. E. Morse, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 6234 – 6238; b) J. N. Cha, K. Shimizu, Y. Zhou, S. C. Christianssen, B. F. Chmelka, G. D. Stucky, D. E. Morse, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 361 – 365.
[24] a) J. N. Cha, K. Shimizu, Y. Zhou, S. C. Christianssen, B. F. Chmelka, G. D. Kisailus, J. H. Choi, J. C. Weaver, W. Yang, G. D. Stucky, D. E. Morse, *Adv. Mater.* **2005**, *17*, 314 – 318.
[25] a) M. Niederberger, G. Garnweitner, F. Krumeich, R. Nesper, H. Cölfen, M. Antonietti, *Chem. Mater.* **2004**, *16*, 1202 – 1208; b) N. M. Dimitrijevic, Z. V. Saponjic, B. M. Rabatic, T. Rajh, *J. Am. Chem. Soc.* **2005**, *127*, 1344 – 1345.
[26] M. Nawaz Tahir, M. Eberhardt, P. Theato, S. Faiß, A. Janshoff, T. Gorelik, U. Kolb, W. Tremel, *Angew. Chem.* **2006**, *118*, 922 – 926; *Angew. Chem. Int. Ed.* **2006**, *45*, 908 – 912.

[27] a) J. L. Dalsin, L. Lin, S. Tosatti, J. Vörös, M. Textor, P. B. Messersmith, *Langmuir* **2005**, *21*, 640 – 646; b) M. Mammen, S.-H. Gu, Z. Yang, J. Gao, C. K. Choi, G. M. Whitesides, *Angew. Chem.* **1998**, *110*, 2908 – 2953; *Angew. Chem. Int. Ed.* **1998**, *37*, 2754 – 2794.
[28] a) I. Potavova, R. Mruk, S. Prehl, R. Zentel, T. Basche, A. Mews, *J. Am. Chem. Soc.* **2003**, *125*, 320 – 321; b) M. Eberhardt, R. Mruk, P. Theato, R. Zentel, *Eur. Polym. J.* **2005**, *41*, 1569 – 1575.
[29] a) G. B. Sigal, C. Bamdad, A. Barberis, J. Strominger, G. M. Whitesides, *Anal. Chem.*, 1996, **68**, 490 – 497; b) I. T. Dorn, K. R. Neumaier, R. Tampe, *J. Am. Chem. Soc.* **1998**, *120*, 2753 – 2763.
[30] T. Rajh, L. X. Chen, K. Lukas, T. Liu, M. C. Thurnauer, D. M. Tiede, *J. Phys. Chem. B* **2002**, *106*, 10543 – 10552.
[31] W. E. G. Müller, M. Rothenberger, A. Borejko, W. Tremel, A. Reiber, H. C. Schröder, *Cell Tissue Res.* **2005**, *321*, 285 – 297.
[32] A. Pisera, *Microsc. Res. Tech.* **2003**, *62*, 312 – 326.
[33] a) *Electron Transfer in Biology and the Solid State* (Eds.: M. K. Johnson, R. B. King, D. M. Kurtz, C. Kutal, M. L. Norton, R. A. Scott), *Adv. Chem. Ser.* 226, American Chemical Society, Washington, **1990**.
[34] a) A. Ahmad, S. Senapati, M. I. Khan, R. Kumar, M. Sastry, *Langmuir* **2003**, *19*, 3550 – 3553; b) Y. Sun, Y. Xia, *Science* **2002**, *298*, 2176 – 2179; c) Y. Sun, B. Mayers, Y. Xia, *Nano Lett.* **2003**, *3*, 675 – 679; d) S. Chen, D. L. Carroll, *Nano Lett.* **2002**, *2*, 1003 – 1007; e) R. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **2001**, *294*, 1901 – 1903; f) R. Jin, Y. C. Cao, E. Hao, G. S. Metraux, G. C. Schatz, C. A. Mirkin, *Nature* **2003**, *425*, 487 – 490.
[35] N. Kröger, R. Deutzmann, M. Sumper, *Science* **1999**, *286*, 1129 – 1132.
[36] S. Brown, M. Sarikaya, E. A. Johnson, *J. Mol. Biol.* **2000**, *299*, 725 – 735.
[37] R. Djalali, Y.-F. Chen, H. Matsui, *J. Am. Chem. Soc.* **2002**, *124*, 13660 – 13661.
[38] H. W. Gu, P.-L. Ho, K. W. Tsang, L. Wang, B. Xu, *J. Am. Chem. Soc.* **2003**, *125*, 15702 – 15703.
[39] W. E. G. Müller, A. Krasko, G. Le Pennec, R. Steffen, M. S. A. Ammar, M. Wiens, I. M. Müller, H. C. Schröder, *Prog. Mol. Subcell. Biol.* **2003**, *33*, 195.
[40] A. R. Armstrong, G. Armstrong, J. Canales, P. G. Bruce, *Angew. Chem.* **2004**, *116*, 2336 – 2338; *Angew. Chem. Int. Ed.* **2004**, *43*, 2286 – 2288.

