

A facile route to a highly stabilized hierarchical hybrid of titania nanotube and gold nanoparticle

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A hierarchical hybrid of gold nanoparticles and titania nanotubes with high metal loading was prepared by a one-pot approach using a natural cellulosic substance as template. Gold nanoparticles were uniformly anchored onto titania nanotubes, and particle fusion at high temperature was suppressed by surface coating with an ultrathin titania layer.

Nanoparticle/nanotube hybrid materials in which certain nanoparticles are attached onto the wall of host nanotubes combine unique structural features of nanotubes and outstanding functionality of nanoparticles, and promise wide applications such as heterogeneous catalysis¹ and molecular sensors.² In the past, carbon nanotubes were mostly employed to fabricate such hybrid materials, and guest nanoparticles included metals such as Au³ and Pt,^{3a,3c} and semiconductors such as CdSe,⁴ SnO₂⁵ and TiO₂.⁶ Unfortunately, chemical routes to these hybrid materials have been rather restricted due to the surface inertness of carbon nanotubes and undesirable side-reactions in the employed methods. Uniform and high coverage by individual nanoparticles is not readily achieved, and this fact limits many practical applications.

Nanotubes other than those of carbon are also expected to show unique properties that are characteristic of their morphologies. In particular, ceramic nanotubes would combine versatile physical and chemical properties of ceramic materials and peculiarity of the nanotube morphology.

We have established very recently an efficient method to achieve nanoscale duplication of the hierarchical morphology of natural cellulosic substances (e.g. natural paper, cotton) with ceramic matrices.⁷ It was possible to fabricate ceramic replica (artificial fossil) of the template substance as hierarchical assemblies of metal oxide nanotubes. This procedure involves faithful coating of morphologically complex surfaces of the natural substance with ultrathin metal oxide layers, and the subsequent removal of the organic template by calcination.

In the present research, we took advantage of a unique hierarchical morphology of the metal oxide (titania) nanotube, and incorporated gold nanoparticles onto the individual nanotubes. The resultant hybrid nanomaterial is composed of gold nanoparticles and titania nanotubes with the morphological hierarchy of the template cellulosic substance faithfully duplicated from the macroscopic all the way down to the nanometer scale.

In a typical procedure, a piece of commercial filter paper (Advantec, Japan) was placed in a suction filtering unit, and 15-cycles of the surface sol-gel process was conducted with Ti(OⁿBu)₄ (100 mM in 1:1/v:v toluene/ethanol) *via* suction, to give cellulose fibers covered with thin titania gel layers.⁷ Ten milliliters of a suspension of cationic gold nanoparticles (0.5 mg mL⁻¹ in ethanol; the particles were capped with bis(11-trimethylammonioundecanoylaminoethyl)disulfide dibromide)⁸ were then added into the filter funnel, and the first 5 mL of the suspension was slowly suction-filtered through the filter paper. The remaining suspension was let to stand for 30 min, and then slowly suction-filtered. After thorough washing with ethanol and drying by air flow, 5-layers of the titania film were additionally deposited. The latter titania layers form an ultrathin shell that coats individual gold

nanoparticles. The as-prepared paper/titania/gold composite was subjected to calcination (6 h at 450 °C in air, heating rate 1 °C min⁻¹) to remove the original filter paper as well as the organic ligand on gold nanoparticles, giving a dark-brown gold/titania hybrid sheet (Fig. 1a inset, this sample is denoted as [(TiO₂)₁₅/Au-nanoparticle/(TiO₂)₅] hereafter). This gold/titania composite sheet is self-supporting and weighs ~2.4 mg. It contains as much as ~40% Au by weight.

An FE-SEM image displayed in Fig. 1a shows that the gold/titania hybrid sheet is composed of hierarchically templated assemblies of gold nanoparticles and titania nanotubes. The individual hybrid nanotube is clearly seen in Fig. 1b. It is uniform with an extremely high aspect ratio (length *vs* diameter), and possesses tube walls of *ca.* 10 nm thickness. An expanded view in Fig. 1c gives a detailed morphology of the hybrid tube with individual gold nanoparticles uniformly attached to titania nanotube as monolayer.

This unique morphology was also confirmed by TEM measurements. Fig. 2a and b visualize high coverage of the titania nanotube with uniform gold nanoparticle monolayers. Each gold nanoparticle is covered by an ultrathin titania shell. The interparticle distance of *ca.* 3 nm is apparently determined by presence of the long chain organic ligand on the gold nanoparticle employed.⁸ This unique nanoparticle/nanotube hybrid structure is schematically illustrated in Fig. 2c. We have found that properly modified gold nanoparticles

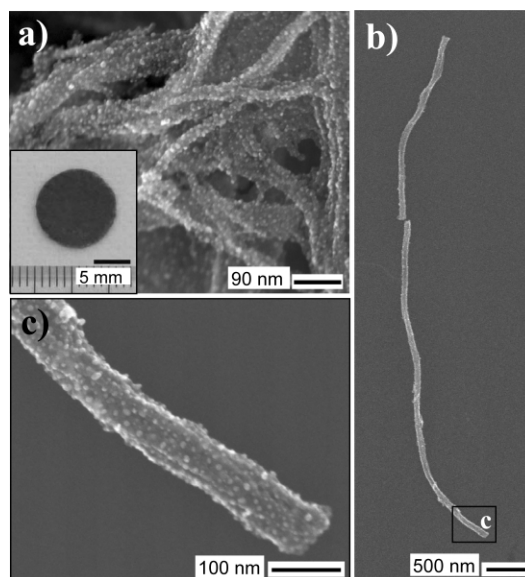


Fig. 1 A hierarchical hybrid of gold nanoparticles and titania nanotubes, [(TiO₂)₁₅/Au-nanoparticle/(TiO₂)₅], as derived from filter paper. (a) Field emission scanning electron micrograph (FE-SEM) image of the hybrid. The inset shows a macroscopic photograph of the hybrid. (b) FE-SEM image of an individual titania nanotube with gold nanoparticles attached onto it. (c) FE-SEM image of the details of the boxed area in (b). To prepare specimens for SEM observation, a small piece of the gold/titania hybrid sheet was crushed, and dispersed in ethanol by applying sonication. The resultant suspension was dropped onto a silicon wafer, and the sample was left to dry in air. The SEM micrographs were obtained on a Hitachi S-5200 instrument at an acceleration voltage of 25.0 kV.

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are active components in the surface sol-gel process.⁹ Titania nanotubes are first formed *via* the surface sol-gel process in the current approach, then positively-charged gold nanoparticles are anchored onto the negatively-charged titania surface. The titania thin layer is additionally deposited on the gold nanoparticle, so that the individual nanoparticles are wholly covered by the titania layer. Subsequent removal of the initial template substance results in the hierarchically ordered gold-titania hybrid.

Gold nanoparticles undergo melting at relatively low temperatures,¹⁰ and this facilitates fusion of the unprotected nanoparticle. In the case of gold nanoparticles (sizes, 6 ± 1 nm) on carbon nanotube, the fusion was observed after heating for 30 s at 300 °C.^{3b} We also found that the gold nanoparticles we employed underwent fusion on a solid substrate at room temperature through oxygen plasma treatment, due to prompt removal of the capping ligands.¹¹ The titania layers that surround individual gold particles should suppress fusion of adjacent gold particles even at higher temperatures. The gold nanoparticles are protected by coating with 5 titania layers (thickness ~ 2.5 nm) in the case of $[(\text{TiO}_2)_{15}/\text{Au}$ -

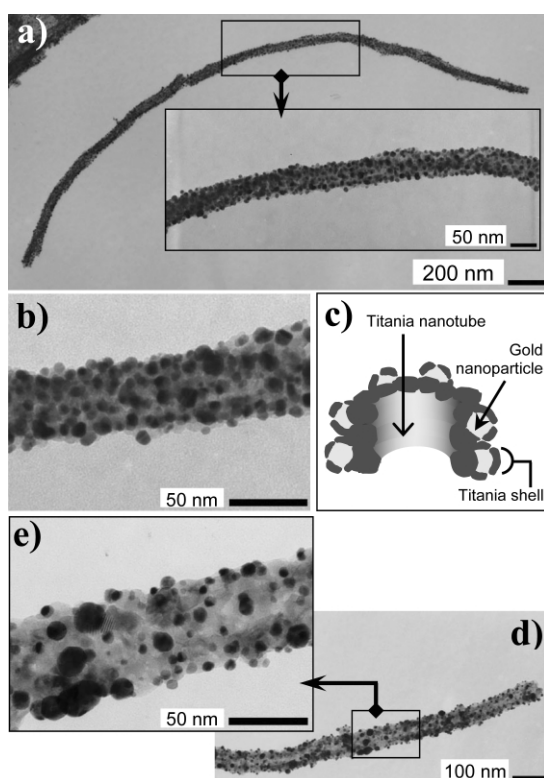


Fig. 2 (a) Transmission electron micrograph (TEM) of a hierarchical hybrid, $[(\text{TiO}_2)_{15}/\text{Au}$ -nanoparticle/ $(\text{TiO}_2)_5]$, derived from filter paper. The inset shows the details of the boxed area. (b) High magnification TEM image of an individual titania nanotube that is fully coated with gold nanoparticles. (c) Schematic illustration of the gold nanoparticle/titania nanotube hybrid (not to scale). (d) TEM image of unprotected gold nanoparticles on titania nanotube, $[(\text{TiO}_2)_{20}/\text{Au}$ -nanoparticle]. (e) An expanded image of the boxed area in (d), showing large gold nanoparticles formed by fusion of originally neighboring gold nanoparticles upon calcination. Specimens for TEM observation were prepared in a way similar to that for SEM. An ethanolic suspension of the gold/titania hybrid was dropped onto a silicon oxide-coated gold grid for observation. The TEM micrographs were acquired on a JEOL JEM-2000 instrument operating at 100 kV accelerating voltage.

nanoparticle/ $(\text{TiO}_2)_5]$; and their average size and the standard deviation are 4.9 and 1.4 nm, respectively, as estimated from Fig. 2b. In fact, the original size distribution (5 ± 1 nm) is not altered after a long period of calcination (6 h at 450 °C). In contrast, the particle fusion was observed when the nanoparticle was not protected by the titania layer. A specimen of gold nanoparticle-loaded titania nanotubes, $[(\text{TiO}_2)_{20}/\text{Au}$ -nanoparticle], was prepared without the final surface covering process under otherwise identical conditions, and it was subjected to calcination. As illustrated in Fig. 2d and 2e, gold nanoparticles with sizes as large as 20–30 nm are found on the outer surface of the titania nanotube. Such large nanoparticles are apparently formed by fusion of the originally smaller nanoparticles. The fusion caused low and non-uniform particle coverage (Fig. 2e), compared with that of the protected particle sample (Fig. 2b).

In conclusion, we could demonstrate herein an efficient and convenient chemical pathway to a gold nanoparticle/titania nanotube hybrid. Cellulosic substances are used as template for a hierarchical structure of titania nanotubes. The loading of gold nanoparticles is as high as 40 wt%, and their fusion at high temperatures is suppressed by surface coating with titania layers. It is clear that the “artificial fossil” approach provides highly effective sites for loading of nanoparticles, spanning from macroscopic to nanoscopic dimensions. We can ensure large surface areas, high and uniform metal loading, and enhanced particle stability in the hierarchical morphology. The one-pot fabrication of such complex loading matrices is rendered feasible by appropriate design of hierarchical templates, and should be extremely beneficial from the practical standpoint. Combining the rich varieties of nanoparticles and ceramic nanotubes, the present approach can produce versatile nano-precision systems with unique physical and chemical functions.

Notes and references

- (a) J. M. Planeix, N. Coustel, B. Coq, V. Brotons, P. S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier and P. M. Ajayan, *J. Am. Chem. Soc.*, 1994, **116**, 7935; (b) V. Lordi, N. Yao and J. Wei, *Chem. Mater.*, 2001, **13**, 733.
- J. Kong, M. G. Chapline and H. Dai, *Adv. Mater.*, 2001, **13**, 1384.
- (a) B. C. Satishkumar, E. M. Vogl, A. Govindaraj and C. N. R. Rao, *J. Phys. D: Appl. Phys.*, 1996, **29**, 3173; (b) S. Fullam, D. Cottell, H. Rensmo and D. Fitzmaurice, *Adv. Mater.*, 2000, **12**, 1430; (c) H. C. Choi, M. Shim, S. Bangsaruntip and 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 and M. Terrones, *Nano Lett.*, 2003, **3**, 275; (e) A. V. Ellis, K. Vijayamohan, R. Goswami, N. Chakrapani, L. S. Ramanathan, P. M. Ajayan and G. Ramanath, *Nano Lett.*, 2003, **3**, 279.
- (a) S. Banerjee and S. S. Wong, *Nano Lett.*, 2002, **2**, 195; (b) J. M. Haremsza, M. A. Hahn, T. D. Krauss, S. Chen and J. Calcines, *Nano Lett.*, 2002, **2**, 1253.
- (a) W.-Q. Han and A. Zettl, *Nano Lett.*, 2003, **3**, 681; (b) W.-Q. Han and A. Zettl, *J. Am. Chem. Soc.*, 2003, **125**, 2062. Boron nitride nanotube is used as host matrix in the latter literature.
- S. Lee and W. M. Sigmund, *Chem. Commun.*, 2003, 780.
- J. Huang and T. Kunitake, *J. Am. Chem. Soc.*, 2003, **125**, 11834.
- T. Yonezawa, S. Onoue and T. Kunitake, *Chem. Lett.*, 1999, 1061.
- T. Yonezawa, H. Matsune and T. Kunitake, *Chem. Mater.*, 1999, **11**, 33.
- F. Ercolessi, W. Andreoni and E. Tosatti, *Phys. Rev. Lett.*, 1991, **66**, 911.
- S. Onoue, J. He and T. Kunitake, Abstracts of Papers, 83rd CSJ (the Chemical Society of Japan) Spring Meeting, Waseda University, Tokyo, Japan, March 18–21, 2003.