A novel hybrid nanostructure based on SiO_2@carbon nanotube coaxial nanocable

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We present a simple, generally applicable procedure for obtaining diameter-controlled SiO_2@ carbon nanotubes (CNTs) coaxial nanocables. These coaxial nanocables with high solubility in polar solvents, have been used as functional templates for assembling CNTs/Au nanorods heterogeneous nanostructures to form multifunctional assembly system. These hybrid nanostructures may find applications in nanoelectronics, photonics, and nanodevices.

1. Introduction

One of the most intriguing challenges in modern chemistry and materials science is the manipulation and assembly at the nanoscale. Recently, the controlled assembly nanostructure of hybrid materials has been attracted a great deal of attention due to their potential applications in fields such as electronics,[1] photonics,[2] and catalysis.[3] Once we are capable of control such structure, the creation of components and nanodevices which can exploit the fascinating, size-dependent properties will be possible. Over the past ten years, quite a few different approaches[4] have been developed towards the creation of tailored composite nanostructures, which often exhibit superior or new functional properties compared to their individual constituent materials. Carbon–semiconductor (SC),[5] SC–metal,[6] carbon–metal,[7] and SC–SC[8] heterojunctions have been prepared and shown to exhibit Schottky diode behavior, Ohmic contact, thermoelectric properties, and photoluminescence enhancement.[6c,d]

CNTs, which were discovered in 1991 by Iijima,[9] have received wide intensity because of their particular structure-dependent electrical, optical, and mechanical properties. Extensive potential applications have been proposed in various fields such as organic light-emitting diodes (OLEDs),[10] nanocatalyst,[11] scanning probe microscopy tips,[12] and electrochemical sensors,[13] among others. Due to the formation of big bundles held strongly together, CNTs are difficult to disperse homogeneously in different solvents, which will greatly impact their performance. So it is a central topic for scientists to functionalize CNTs using different methods. Noncovalent functionalization of CNTs is particularly attractive because it not only provides possibility of attaching chemical species without affecting the electronic structure of CNTs, but endows some functional performance for biomolecule immobilization. One of the approaches that has been widely used to prepare individual CNT is the noncovalent wrapping of CNTs by various species of polymers,[14] polynuclear aromatic compounds,[15] surfactants[16] and biomolecules.[17] It is known that SiO_2-glass is particularly attractive due to its optical properties and inherent stability, which would probably incorporate into CNTs.[18] Liu *et al.*[19] reported a new method of coating single-walled carbon nanotubes (SWNTs) with a thin layer of SiO_2 using 3-aminopropyltriethoxysilane as coupling layers. In this paper, noncovalent functionalization of CNTs with SiO_2 *via* sol–gel processing to form diameter-controlled SiO_2@CNTs nanocable was obtained. We can easily control SiO_2 homogeneous coating with the thickness of 75–250 nm, which relies on the well-known Stöber method.[20] High solubilization in polar solvents of CNTs with thin SiO_2 layer ($\sim$50 nm) was also obtained. Functionalizing CNTs with SiO_2 will not only solve challenges for poor solubilization of CNTs, but also probably achieve the applications in cell imaging, drug, vaccine and gene delivery.

Recently, several methods have been reported for the attachment of different types of nanostructures to CNTs.[21] Wong *et al.*[21b] have prepared carbon nanotube–quantum dot junctions using CdSe nanocrystal with the aid of intermediary linking agents, such as ethylenediamine. Zamborini *et al.*[21c] described the formation of heterojunctions between metallic one-dimensional (1D) gold nanorods and single-walled carbon nanotubes (SWNTs) assembled directly on solid surface. In addition, Liz-Marzán *et al.*[21d,e,f] presented the formation of Au linear 1D assemblies of nanorod, and SiO_2 coated Au nanoparticles by using CNTs as templates through polymer wrapping combined with layer-by-layer (LBL) assembly. In this paper, these diameter-controlled SiO_2@CNTs coaxial nanocables have been used as functional templates for assembling CNTs/Au nanorods heterogeneous nanostructure to form multifunctional assembly architecture. Gold nanorods are arranged on the surface of coaxial nanocables. It is expected that these multifunctional systems will have potential application in electronics, photonics, and nanodevices, *etc.*

2. Experimental

Materials

MWNTs (Shenzhen Nanotech Port Co, Ltd, China) with a diameter of 20–30 nm were obtained through the CVD

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method. Poly (*N*-vinyl-2-pyrrolidone) (PVP-K30), tetraethoxysilane (TEOS), sodium chloride (NaCl), ascorbic acid (AA), $HAuCl_4 \cdot 4H_2O$, $AgNO_3$, ammonium hydroxide ($NH_4 \cdot OH$), hydrochloric acid (HCl), and ethanol were purchased from the Shanghai Chemical Factory (Shanghai, China) and used as received without further purification. 3-mercaptopropyltrimethoxysilane (MPTMS) was obtained from Alfa Aesar Company. Water used throughout all expetiments was purified with the Millipore system.

Apparatus

Scanning electron microscopy images were determined with a Philips XL-30 ESEM. The accelerating voltage was 15 kV. The samples for SEM characterization were prepared by placing 100 μL of the suspension on the Al foil, and allowing the solvent to slowly evaporate at room temperature. TEM measurements were made on a JEOL 2000 transmission electron microscope operated at an accelerating voltage of 200 kV. The sample for TEM characterization was prepared by placing a drop of prepared solution on carbon-coated copper grid and dried at room temperature. UV-Vis-near-infrared spectra were collected on a CARY 500 Scan UV-vis-near-infrared (UV-vis-NIR) spectrophotometer. Thermogravimetric analyses (TGA) of samples were performed on a Pyris Diamond TG/DTA Thermogravimetric Analyzer (Perkin Elmer Thermal Analysis). Samples were heated under an air atmosphere from room temperature to 900 °C at 10 °C min^{-1}.

CNTs noncovalent functionalization

The MWNTs were wrapped with polymer (PVP). The PVP modified CNTs can be easily dispersed in polar solvents such as water, DMF, and ethanol. In a typical experiment, CNTs (50 mg) were dispersed in a 0.5 wt% PVP (30 000–40 000) salt solution (0.5 M NaCl, 250 ml), sonicated for 2 h. Then a homogeneous CNT solution was obtained. Excess polymer was removed through a 450 nm polycarbonate filtration membrane. Then a stable, homogeneous CNTs aqueous suspension (250 ml) was obtained.

Synthesis and functionalization of diameter controlled SiO_2@CNTs coaxial nanocables

A CNT–PVP water solution (50 ml) was added to a 7 ml mixture of TEOS, H_2O, and ethanol (volume ratio 2 : 1 : 4). The mixture solution was sonicated for 1 h and stirred overnight at room temperature. Then the mixture was centrifuged to wash CNTs with ethanol for 3 times. The sediment was redispersed in 50 ml of ethanol. After this, 2.1 ml ammonia (28 wt% in water) was added to the above solution under stirring. Immediately after this, 0.5 ml TEOS solution was added and stirred for 2 min. Then the mixture was stirred for 12 h and sonicated from time to time. Finally, the CNTs solution was centrifuged and washed with ethanol. A stable, homogeneous SiO_2 coated CNTs with the diameter of about 75 nm was obtained. In order to prepare thick SiO_2 coated CNTs, the above obtained thin SiO_2 coated CNTs ethanol solution was repeated according to the second step.

These coaxial nanocables were then functionalized with MPTMS. Briefly, 100 μl of MPTMS was added to 1.25 ml of thick SiO_2@CNTs coaxial nanocable ethanol solution under stirring, followed by adding 40 μl of 0.1 M HCl. The solution was stirred for 24 h, then the mixture was centrifuged and washed with ethanol and water for three times, respectively.

Synthesis of gold nanorods

Gold nanorods were prepared according to the seed-mediated growth method optimized by El-Sayed and co-workers.[22] Briefly, a seed solution was prepared by mixing 5 ml of CTAB (0.2 M) and 5 ml of $HAuCl_4$ (0.5 mM) with 0.6 ml of a freshly prepared 10 mM ice-cold $NaBH_4$ solution. The color of the solution changed from dark yellow to brownish yellow under vigorous stirring, indicating the formation of the seed solution. For the synthesis of gold nanorods, 1.5 ml of 4 mM silver nitrate aqueous solution was mixed with 50 ml of 1 mM $HAuCl_4$ and added to 50 ml of 0.2 M CTAB. After gentle mixing of the solution, 0.70 ml of 0.1 M AA was added. While continuously stirring this mixture, 120 μl of the seed solution was added finally to initiate the growth of the gold nanorod. Our experiments yielded gold nanorods with an aspect ratio of 3 ± 0.4. These gold nanorods were aged for 20 h to ensure full growth.

Coaxial nanocable assembly with gold nanorods for hybrid nano-heterogeneous structure

In a typical experiment, 4 ml of mecapto-functionalization coaxial nanocable aqueous solution was mixed with 400 μl of nanorod aqueous solution for 12 h. Then the solution was centrifuged for three times and redispersed in water.

3. Results and discussion

As is known, the sidewall of a carbon nanotube is chemically stable, making the functionalization of the nanotubes with sensing molecules a great challenge. So it is important for scientists to endow some functions on CNTs. Here, an advanced method for functionalizing CNTs with a diameter-controlled SiO_2 layer is reported, which can offer flexible approaches for further modification by utilizing the rich chemistry available for silica surfaces. SEM image (Fig. 1) shows the change on CNTs before and after silica coating. Before coating, the average diameter of CNTs is about 20–30 nm (Fig. 1A). After coating with thin SiO_2, the diameter of the SiO_2@CNTs increases to about 75–85 nm (Fig. 1B), corresponding to a 55 nm thick SiO_2 layer covered on CNTs. Alternatively, TEM image of SiO_2@CNTs coaxial nanotubes treated using the same procedure (inset of Fig. 1B) further indicates that the silica is homogeneously coated on the surface of CNTs with about 50 nm thick. These images clearly prove that silica is homogeneously deposited on CNTs to form coaxial nanocables. A modified Stöber method was employed to adjust the layer thickness of SiO_2. The SiO_2 surface obtained could be further functionalized with a large variety of functional groups by utilizing the chemistry of SiO_2 surface. Fig. 2A shows the SEM image of thick SiO_2@CNTs coaxial nanocables at lower magnification. It is evident that the silica is homogeneously coated on CNTs surface, although the coaxial nanocables obtained are bent. This is because the CNTs provided are not straight. Suppose the CNTs are perfectly straight, it is expected that we can obtain well-defined

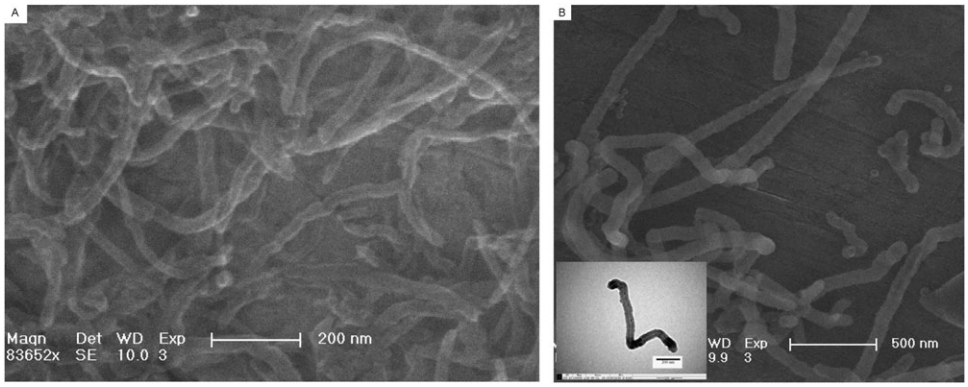

Fig. 1 SEM images of uncoated CNTs (A) and thin SiO_2@CNTs coaxial nanocables (B). The inset of Fig. 1B shows corresponding TEM image of SiO_2@CNTs coaxial nanocables. The scale bar of the inset is 200 nm.

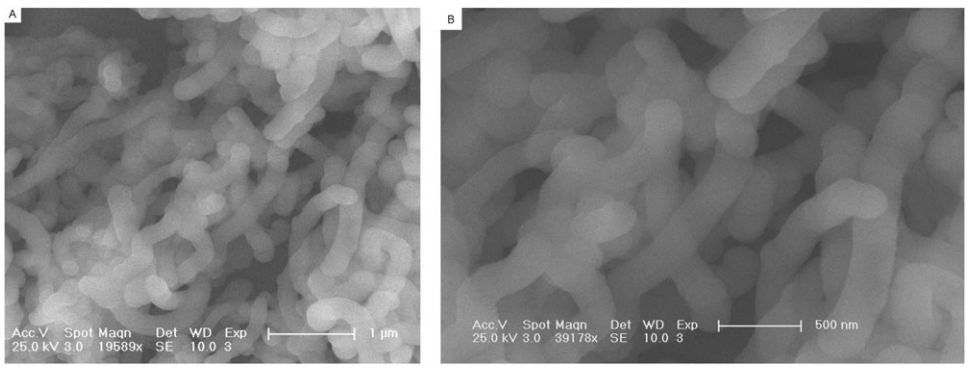

Fig. 2 SEM images of thick SiO_2@CNTs coaxial nanocables at low-magnification (A) and at high-magnification (B).

SiO_2@CNTs coaxial nanocables. A high-magnification SEM image (Fig. 2B) further illuminates that CNTs are homogeneously wrapped with SiO_2 with the diameter of about 250 nm. A corresponding TEM image at higher magnification (Fig. 3) shows that the surface of coaxial nanocables is smooth and homogeneously coated. In addition, The CNTs are obviously observed at the end of the coaxial nanocables (the inset of Fig. 3), which further confirms the formation of SiO_2@CNTs coaxial nanocable structure.

The chemical composition of SiO_2@CNTs was determined by energy-dispersive X-ray spectroscopy (EDX). EDX image (Fig. 4A, B) shows that SiO_2@CNT coaxial nanocables are made of the elements C, O, Si (the Al signal is from the Al substrate). It is obviously indicated that the SiO_2@CNTs nanocomposite structure is obtained. In order to further confirm the atomic number ratio of SiO_2 coated on CNTs surface, quantitative analysis of the obtained two samples was carried out. Table 1 summarizes the quantitative analysis results for coaxial nanocables. Obviously, the ratio of O to Si is about 2. These results further indicate that SiO_2@CNTs coaxial nanocables are indeed obtained based on our method.

CNTs and coaxial nanocables were also analyzed using TGA. TGA plot of pristine CNTs is shown in Fig. 5a, with one 100% weight loss observed. This indicates that pristine CNTs own high purity without any impurities. But this is not the case for coaxial nanocables, three weight losses were obtained (Fig. 5b). The first event, indicative of water loss, occurs at low temperatures. The second weight loss, which starts around 320 °C, coincides with the decomposition of the polymer PVP within the coaxial nanocables. The third case, which occurs at about 530 °C, corresponds to the oxidation of

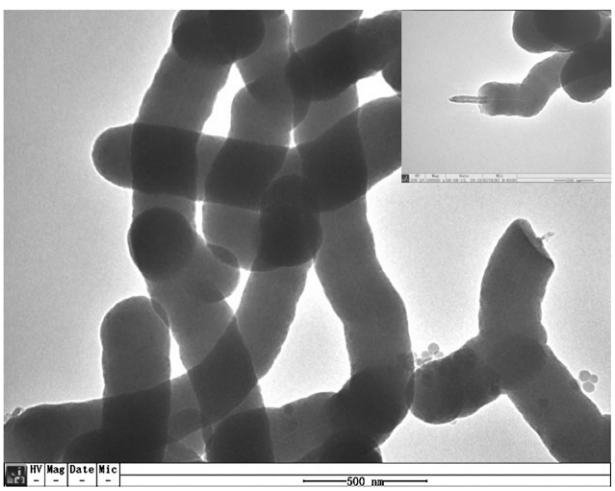

Fig. 3 TEM images of thick SiO_2@CNTs coaxial nanocables. The inset of Fig. 3 shows corresponding magnification image of coaxial nanocables. The scale bar of the inset is 200 nm.

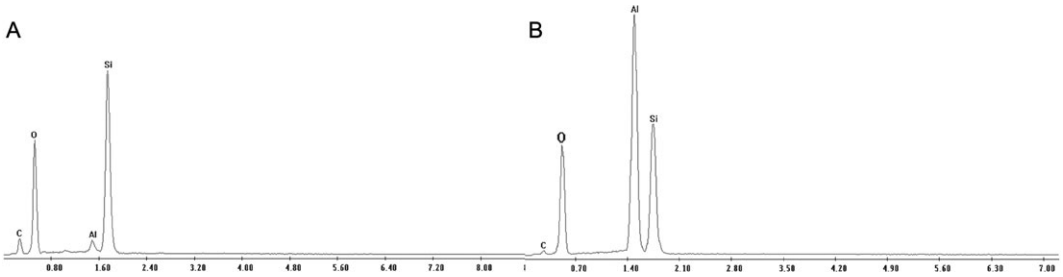

Fig. 4 EDX images of thin (A) and thick (B) SiO_2@CNTs coaxial nanocables.

Table 1 Quantitative analysis of thin and thick SiO_2@CNTs coaxial nanocables

Thin SiO_2@CNTs coaxial nanotube			Thick SiO_2@CNTs coaxial nanotube		
Element	Wt%	At%	Element	Wt%	At%
C	23.55	33.94	C	9.67	14.94
O	40.63	43.97	O	50.79	58.93
Si	35.82	22.08	Si	39.53	26.13
Total	100	100	Total	100	100

CNTs embedded in coaxial nanocables. The remaining mass after heating is the pure silica without any other materials remaining. Thus, from the TGA studies, we can conclude that coaxial nanocables were indeed obtained *via* this method.

In addition, modification by SiO_2 layer greatly changes the solubility of the CNTs in different solvents. The inset of Fig. 5 shows photographs of CNTs and thin SiO_2@CNTs coaxial nanocables dispersed in water and ethanol. From the photographs, we know that CNTs are difficult to dissolve in water (C) and ethanol (D) if CNTs is uncoated by SiO_2. However, SiO_2 coated CNTs exhibit good solubility in polar solvents, such as water (A) and ethanol (B). The concentration of CNTs within thin coaxial nanocables in water (A) and ethanol (B) reaches to 2 mg ml^{-1}. These coaxial nanocables do not precipitate for two weeks. This is because the obtained coaxial nanocable owns many OH-groups on its surface, which will make it well soluble in polar solvent. High solubility of the nanocable in water may lead to many applications in bioelectrochemistry.

In the above parts, we have obtained well-defined homogeneous SiO_2@CNTs coaxial nanocables. In order to achieve multi-functional properties, we first functionalize the obtained coaxial nanocables with 3-mercaptopropyltrimethoxysilane (MPTMS). A mercapto-functionlized surface will be generated as expected. As is known, gold is easily reacted with mercapto-functionlized surface. We mixed mercapto-functionlized coaxial nanocables with gold nanorods in aqueous solution, a multi-functional nanohydrid material was obtained. Fig. 6 shows TEM images of well-defined gold nanorods assembled on the surface of coaxial nanocables. The gold nanorods with the aspect ratio of about 3 uniformly cover the SiO_2 layer surface. The reason for not achieving a full coverage of the SiO_2 is probably related to the anisotropic surface potential of the nanorods.[21e] Also, we investigated the optical properties of nanohydrid materials and gold nanorods, as shown in Fig. 7, where the UV-vis spectra of the precursor nanorods and the final nanorod-coaxial nanocables assemblies are displayed. Typical transverse and longitudinal modes for gold nanorods

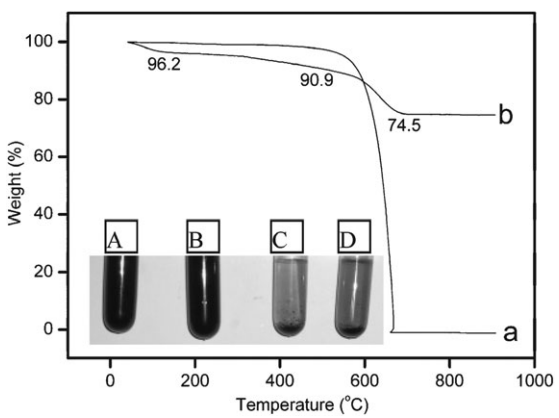

Fig. 5 TGA plots of CNTs (a) and coaxial nanocables (b) measured in air flow with a heating rate of 10 °C min^{-1}. The inset shows the photographs of CNTs (C, D) and thin SiO_2@CNTs coaxial nanocables (A, B) dispersed in water (A, C) and ethanol (B, D).

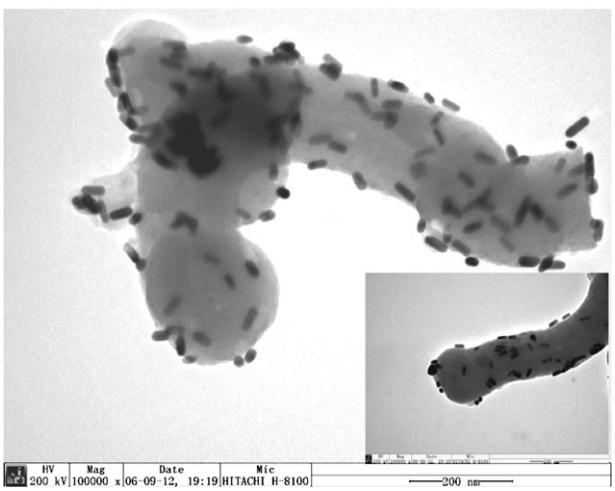

Fig. 6 TEM image of gold nanorods@SiO_2@CNTs hybrid nanostructures. The inset shows corresponding high magnification of hybrid nanostructure. The scale bar of the inset is 200 nm.

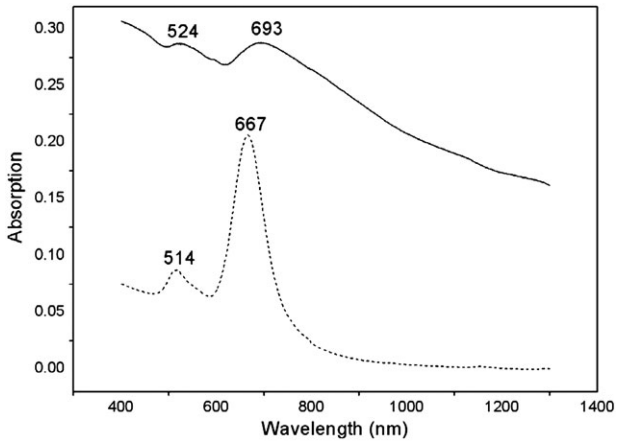

Fig. 7 UV-Vis-NIR spectra of aqueous dispersion of individual Au nanorods (dashed line) and nanorods attached on SiO_2@CNTs coaxial nanocables (solid line).

are obtained. After the formation of the nanohydrid system, the transverse surface-plasmon band of the gold nanorods is red-shifted with respect to the initial gold nanorods because of the local refractive-index increase due to the surrounding silica shell.[23] Meanwhile, the longitudinal modes are also red-shifted compared to the gold nanorods themselves due to inter-nanorod interaction and partial interconnection for nanorods, as was previously demonstrated for assemblies on flat surface[24] and on spherical latex particles.[25]

4. Conclusions

In conclusion, we have reported an advanced strategy for the size control synthesis of SiO_2@CNTs coaxial nanocables with smooth surface. A novel multi-functional nanohydrid system is obtained using well-defined coaxial nanocables as template. The results obtained are significant for the following reasons: firstly, these coaxial nanocables will exhibit superior multi-functional properties because of good electrical and mechanical properties of CNTs combined with the excellent biocompatible properties of SiO_2. These composite nanostructures will have potential application in bioelectrochemical sensors. Secondly, these coaxial nanocables own excellent surface chemistry, which enable CNTs dissolvable in polar solvents. More importantly, coaxial nanocables have been used as functional templates for assembling CNTs/Au nanorods heterogeneous nanostructures to form a multifunctional assembly system, which will have potential applications in electronics, photonics, nanodevices, as well.

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References

1 S. J. Park, T. A. Taton and C. A. Mirkin, *Science*, 2002, **295**, 1503.
2 F. García-Santamaría, V. Salgueiriño-Maceira, C. López and L. M. Liz-Marzán, *Langmuir*, 2002, **18**, 4519.
3 W. T. Muller, D. L. Klein, T. Lee, J. Clarke, P. L. McEuen and P. G. Schultz, *Science*, 1995, **268**, 272.
4 (*a*) Y. G. Sun and Y. N. Xia, *Adv. Mater.*, 2004, **16**, 3; (*b*) A. J. Mieszawska, R. Jalilian, G. U. Sumanasekera and F. P. Zamborini, *J. Am. Chem. Soc.*, 2005, **127**, 10822.
5 J. Hu, M. Ouyang, P. Yang and C. M. Lieber, *Nature*, 1999, **399**, 48.
6 (*a*) N. I. Kovtyukhova, B. K. Kelley and T. E. Mallouk, *J. Am. Chem. Soc.*, 2004, **126**, 12738; (*b*) J. Luo, L. Zhang, Y. Zhang and J. Zhu, *Adv. Mater.*, 2002, **14**, 1413; (*c*) J. Lee, T. Javed, T. Skeini, A. O. Govorov, G. W. Bryant and N. A. Kotov, *Angew. Chem., Int. Ed.*, 2006, **45**, 1; (*d*) J. Lee, A. O. Govorov and N. A. Kotov, *Angew. Chem.*, 2005, **117**, 7605 (*Angew. Chem., Int. Ed.*, 2005, **44**, 7439).
7 J. Luo, Z. Huang, Y. Zhao, L. Zhang and J. Zhu, *Adv. Mater.*, 2004, **16**, 1512.
8 (*a*) Y. Wu, R. Fan and P. Yang, *Nano Lett.*, 2002, **2**, 83; (*b*) M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith and C. M. Lieber, *Nature*, 2002, **415**, 617.
9 S. Iijima, *Nature*, 1991, **354**, 56.
10 D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M. E. Tompson and C. Zhou, *Nano Lett.*, 2006, **6**, 1880.
11 Lin Cao, Frieder Scheiba, Christina Roth, Franz Schweiger, Carsten Cremers, Ulrich Stimming, Hartmut Fuess, Liquan Chen, Wentao Zhu and Xinping Qiu, *Angew. Chem., Int. Ed.*, 2006, **45**, 5315.
12 S. S. Wong, A. T. Woolley, E. Joselevich, C. L. Cheung and C. M. Lieber, *J. Am. Chem. Soc.*, 1998, **120**, 8557.
13 (*a*) E. S. Jeng, A. E. Moll, A. C. Roy, J. B. Gastala and M. S. Strano, *Nano Lett.*, 2006, **6**, 371; (*b*) X. Tang, S. Bansaruntip, N. Nakayama, E. Yenilmez, Y.-l. Chang and Q. Wang, *Nano Lett.*, 2006, **6**, 1632.
14 R. Andrews, D. Jacques, D. Qian and T. Rantell, *Acc. Chem. Res.*, 2002, **35**, 1008.
15 (*a*) N. Nakashima, Y. Tomonari and H. Murakami, *Chem. Lett.*, 2002, **31**, 638; (*b*) K. A. S. Fernando, Y. Lin, W. Wang, S. Kumar, B. Zhou, S.-Y. Xie, L. T. Cureton and Y.-P. Sun, *J. Am. Chem. Soc.*, 2004, **126**, 10234; (*c*) H. Paloniemi, T. Aaritalo, T. Laiho, H. Liuke, N. Kocharova, K. Haapakka, F. Terzi, R. Seeber and J. Lukkari, *J. Phys. Chem. B*, 2005, **109**, 8634.
16 (*a*) V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge and R. H. Smalley, *Nano Lett.*, 2003, **3**, 1379; (*b*) O. Matarredona, H. Rhoads, Z. Li, J. H. Harwell, L. Balzano and D. E. Resasco, *J. Phys. Chem. B*, 2003, **107**, 13357.
17 E. Katz and I. Wilner, *ChemPhysChem*, 2004, **5**, 1084.
18 (*a*) T. Seeger, Th. Köhler, Th. Frauenheim, N. Grobert, M. Rühle, M. Terrones and G. Seifert, *Chem. Commun.*, 2002, 34; (*b*) M. Olek, K. Kempa, S. Jurga and M. Giersig, *Langmuir*, 2005, **21**, 3146.
19 Qiang Fu, Chenguang Lu and Jie Liu, *Nano Lett.*, 2002, **2**, 329.
20 W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
21 (*a*) A. V. Ellis, K. Vijayamohanan, R. Goswami, N. Chakrapani, L. S. Ramanathan, P. M. Ajayan and G. Ramanath, *Nano Lett.*, 2003, **3**, 279–282; (*b*) Sarbajit Banerjee and Stanislaus S. Wong, *Nano Lett.*, 2002, **2**, 195; (*c*) Aneta J. Mieszawska, Romaneh Jalilian, Gamini U. Sumanasekera and Francis P. Zamborini, *J. Am. Chem. Soc.*, 2005, **127**, 10822; (*d*) Miguel A. Correa-Duarte and Luis M. Liz-Marzán, *J. Mater. Chem.*, 2006, **16**, 22; (*e*) Miguel A. Correa-Duarte, Neli Sobal, Luis M. Liz-Marzán and Michael Giersig, *Adv. Mater.*, 2004, **16**, 23; (*f*) Miguel A. Correa-Duarte, Jorge Pérez-Juste, Ana Sánchez-Iglesias, Michael Giersig and Luis M. Liz-Marzán, *Angew. Chem., Int. Ed.*, 2005, **44**, 4375.
22 Babak Nikoobakht and Mostafa A. El-Sayed, *Chem. Mater.*, 2003, **15**, 1957–1962.
23 L. M. Liz-Marzán, M. Giersig and P. Mulvaney, *Langmuir*, 1996, **12**, 4329.
24 T. Ung, L. M. Liz-Marzán and P. Mulvaney, *J. Phys. Chem. B*, 2001, **105**, 3441.
25 V. Salgueiriño-Maceira, F. Caruso and L. M. Liz-Marzán, *J. Phys. Chem. B*, 2003, **107**, 10990.