

# One-step construction of ZnS/C and CdS/C one-dimensional core-shell nanostructures

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ZnS/C and CdS/C coaxial core-shell nanowires, which consist of single-crystal semiconductor nanowires encapsulated by carbon nanotubes (CNTs), have been synthesized by simple one-step thermal processes. These coaxial core-shell nanowires have uniform outer diameters (80–180 nm for ZnS/C, 60–130 nm for CdS/C), and uniform shell thicknesses (*ca.* tens of nanometers) along their entire lengths up to tens of microns. The growth of the core-shell nanowires follows a novel metal reaction and self-catalysis vapor-liquid-solid (VLS) mechanism. The simple method could, in principle, be extended to synthesize other metal sulfide single-crystal nanowire-filled carbon nanotubes, which can find potential applications in various fields of nanotechnology.

## Introduction

In recent years, one-dimensional (1D) nanomaterials such as nanowires, nanotubes and nanobelts have attracted much research attention due to their unique electronic, optical, mechanical properties and potential applications in nanodevice fabrication.<sup>1</sup> Theoretical studies<sup>2</sup> suggested that introduction of foreign materials into hollow nanotube cavities may significantly modify their electronic and mechanical properties, as well as alter the properties of the filling materials. Moreover, nanoscale materials, like nanowires, often display high chemical reactivity because of their low dimensionality and high surface-to-volume ratio, which will lead to nanowire oxidation and contamination and thus degrade the performance of nanodevices. Therefore, it is important to have a protective sheath on a given nanowire to maintain its performance for a long time. Recently, core-shell nanowires, another type of 1D nanostructure with cores and sheaths from different materials, have aroused increasing interest and been pursued in a number of laboratories.<sup>3</sup> In general, complex *multi-step* processes involving filling nanotubes<sup>4</sup> or coating nanowires<sup>5</sup> with desired source materials were necessary to achieve such architectures. The development of simple and efficient *one-step* methods to fabricate core-shell nanowires still remains a key research challenge.

It is well known that ZnS and CdS are important II–VI semiconductors and have many commercial or potential applications in the fields of light-emitting diodes, solar cells, sensors, lasers and catalysis.<sup>6</sup> Recently, the synthesis of semiconductor/carbon nanotube (CNTs) heterostructures has emerged as an active field due to their eminent prospects and opportunities for new applications in a wide variety of areas.<sup>7</sup> For example, Banerjee and Wong synthesized TiO<sub>2</sub>/CNT and CdSe/CNT nanocrystal heterostructures by using an organic

molecule as a linker.<sup>7a</sup> Wang *et al.* prepared CNT/CdS core-shell nanostructures by a chemical reduction route.<sup>7d</sup> Willner *et al.* recently found out that a CNT/CdS hybrid system exhibited unprecedentedly high quantum yields for the generation of photocurrents.<sup>7e</sup> However, only a few single-crystal semiconductor nanowire/CNT core-shell nanostructures have been synthesized so far.<sup>8</sup> In this paper, we present a simple *one-step* method for the mass production of single-crystal ZnS or CdS nanowire-filled carbon nanotubes *via* a novel metal reaction and self-catalysis growth process.

## Results and discussion

The ZnS single-crystal nanowire-filled carbon nanotubes (ZnS/C core-shell nanowires) were fabricated in a horizontal tube furnace using copper bis(di(*n*-butyl)dithiocarbamate) [Cu(S<sub>2</sub>CNBu<sub>2</sub>)<sub>2</sub>] and zinc as starting materials. Cu(S<sub>2</sub>CNBu<sub>2</sub>)<sub>2</sub> and zinc were placed at the zones with temperatures of *ca.* 450 and 760 °C, respectively. High-purity N<sub>2</sub> was used as both carrier gas and protecting medium during the whole process. The dark product was grown at the temperature of 780–800 °C. The X-ray diffraction (XRD) pattern of ZnS/C core-shell nanowires is shown in Fig. 1. All

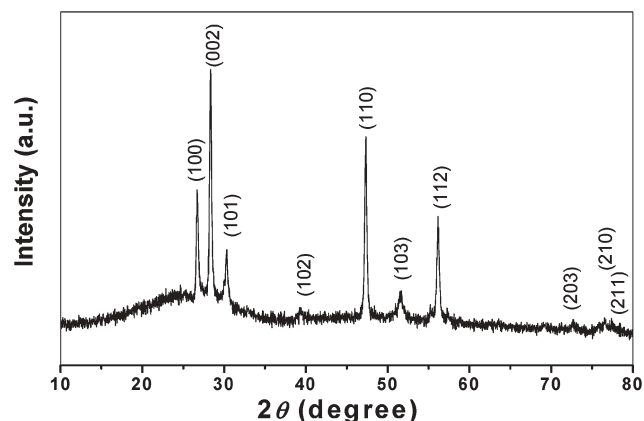
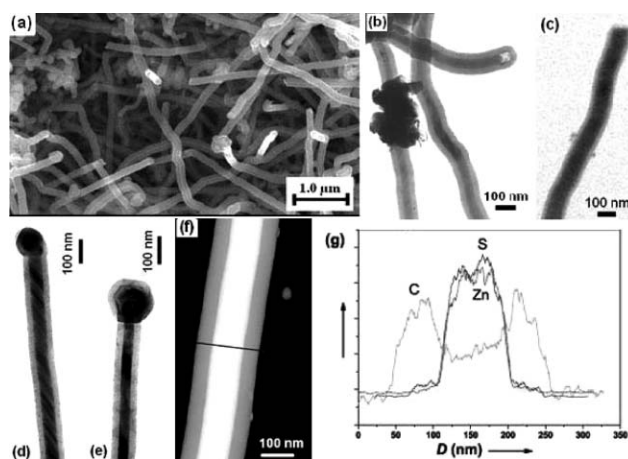


Fig. 1 XRD pattern of the ZnS/C core-shell nanowires.

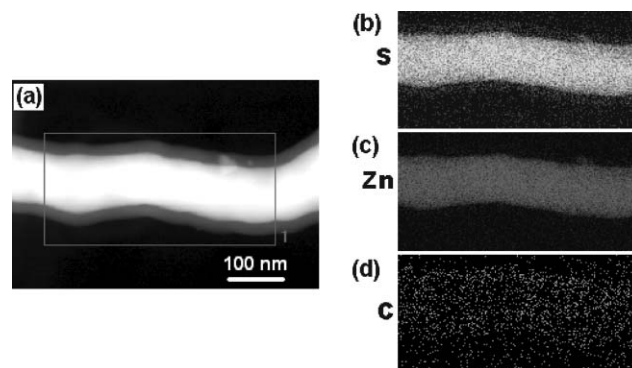
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the diffraction peaks can be indexed to hexagonal wurtzite (2H) ZnS with lattice constants of  $a = 3.821$  and  $c = 6.257$  Å (JCPDS 36-1450). The scanning electron microscopy (SEM) image (Fig. 2a) of the ZnS/C core-shell nanowires reveals that the products are of wire-like morphology with circular cross-sections. The wires have lengths ranging from several to tens of micrometers and diameters of 80–180 nm. Transmission electron microscopy (TEM) observation (Fig. 2b–e) showed that the nanowires have a light/dark/light contrast along their radial directions, suggesting the formation of coaxial core-shell nanowire heterostructures. The diameter of the core and the thickness of the sheath of an individual ZnS/C core-shell nanowire were uniform along its length, but those of different ZnS/C core-shell nanowires were not always the same and the thicknesses of the sheaths were in the range of 20–50 nm. In addition, several different kinds of ends of the core-shell nanowires, including a hollow hemispherical-like end (Fig. 2b), an open end (Fig. 2c) and an end with a small particle (Fig. 2d–e), were observed. The presence of the nanoparticles on the tips of the nanowires suggests a vapor-liquid-solid (VLS) growth mechanism.<sup>1a,9</sup> The EDS spectrum shows that the nanoparticles on the tips are composed of C, Zn and S elements with an atomic ratio of Zn : S  $\approx$  44 : 56. Fig. 2f–g show a high-angle-angular-dark-field (HAADF) image of a ZnS/C core-shell nanowire and the corresponding cross-sectional composition line profiles across the ZnS/C core-shell nanowire. The profile of elemental C shows two peaks on the right and left sides and a valley in the center, whereas the profiles of Zn and S both display a broad peak at the center, which indicate that the nanowire consists of a ZnS core and a C sheath. The elemental maps of C, S, and Zn concentrations of a ZnS/C core-shell nanowire are shown in Fig. 3. It is clearly seen from Fig. 3b and c that elements S and Zn were located in the core. Although the carbon signal (Fig. 3d) was weak owing to its low yield of characteristic X-rays, which was further weakened by deducting the background signal resulting from the carbon-coated copper grid, it can still be seen that the distribution of element C was wider than those of S and Zn,



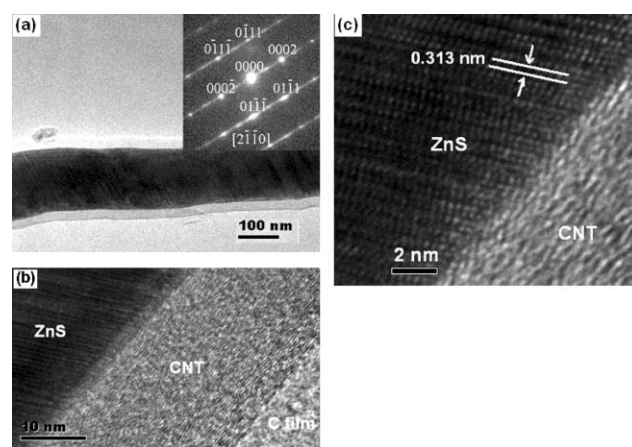
**Fig. 2** (a) SEM image, (b)–(e) TEM images, and (f) HAADF image of the ZnS/C core-shell nanowires. (g) Cross-sectional compositional line profiles of the ZnS/C core-shell nanowire [indicated by the line in (f)].



**Fig. 3** (a) HAADF image of a ZnS/C core-shell nanowire. (b)–(d) Elemental maps of S, Zn, and C concentrations in the nanowire indicated by the box in (a).

and consistent with the domain of the whole nanowire. The above results demonstrate unambiguously the successful preparation of the ZnS/C core-shell nanowires.

The microstructures of the ZnS/C core-shell nanowires were further investigated by high-resolution TEM and selective area electron diffraction (SAED). Fig. 4a is a low-magnification HRTEM image of an individual ZnS/C core-shell nanowire. The corresponding SAED pattern (inset in Fig. 4a) can be indexed as a hexagonal wurtzite (2H) ZnS single crystal recorded from the  $[2-1-10]$  zone axis and shows that the ZnS nanowire grows along the  $[01-13]$  direction. The streaking of diffraction spots along the  $[0001]$  direction originates from the stacking faults on the  $\{0001\}$  planes, as suggested by the streak-like contrasts on the corresponding planes in the TEM image. Fig. 4b depicts the HRTEM image of the interfacial domain between the CNT shell and the ZnS core of a ZnS/C core-shell nanowire, confirming that the core-shell nanowire is composed of a single-crystal ZnS nanowire core and a CNT shell. The C film in Fig. 4b comes from the carbon-coated copper grid. As shown in Fig. 4c, the clear lattice fringes with a  $d$ -spacing of 0.313 nm are consistent with the (0002) planes of hexagonal wurtzite (2H) ZnS. Some lattice defects, such as



**Fig. 4** (a) Low-magnification HRTEM image of a ZnS/C core-shell nanowire, the inset is the corresponding SAED pattern taken along the  $[2-1-10]$  zone axis. (b), (c) HRTEM image of the ZnS/C core-shell nanowires.

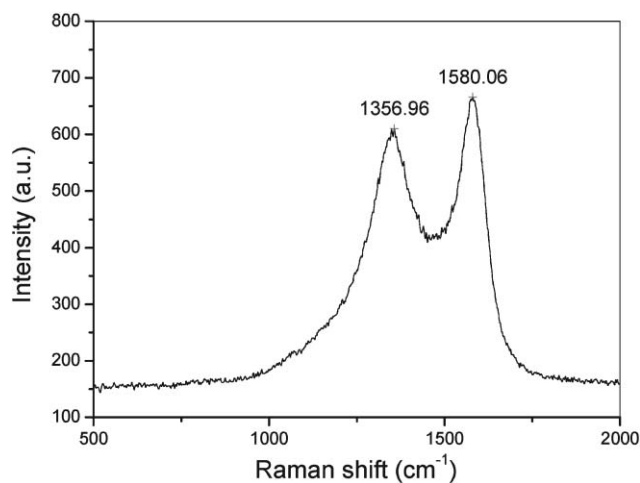


Fig. 5 Raman spectrum of the ZnS/C core-shell nanowires.

dislocations, stacking faults and microtwins, can be observed within the ZnS core, which is consistent with the above SAED observation and is the reason for ZnS nanowires bending. It can be seen that the CNT shell has a layered structure with some structure defects. The Raman spectrum (Fig. 5) of the ZnS/C core-shell nanowires shows two Raman bands at  $1580\text{ cm}^{-1}$  (G band) corresponding to an  $E_{2g}$  mode of graphite and relating to the vibration of  $sp^2$ -bonded carbon atoms in a two-dimensional graphite layer, and at  $1357\text{ cm}^{-1}$  (D-band) associated with the vibration of carbon atoms with dangling bonds at the plane termination of disordered graphite or glass carbon.<sup>10</sup> CNTs (Fig. 6) can be achieved by etching the ZnS/C core-shell nanowires with  $6\text{ mol L}^{-1}$  HCl.

In order to investigate the generality of this synthesis approach, we have prepared CdS/C core-shell nanowires in a way similar to that of the ZnS/C core-shell nanowires, except for the use of cadmium instead of zinc as a starting material. Cadmium was evaporated at *ca.*  $740\text{ }^\circ\text{C}$  and the products were grown at *ca.*  $830\text{--}850\text{ }^\circ\text{C}$ . The XRD pattern of the CdS/C core-shell nanowires is shown in Fig. 7. All the diffraction peaks can be indexed to the hexagonal CdS structure with lattice constants of  $a = 4.136$  and  $c = 6.713\text{ \AA}$  (JCPDS 6-0314). The SEM image (Fig. 8a) of the as-prepared CdS/C core-shell nanowires shows that the products have bent wire-like morphology with diameters in range of  $60\text{--}130\text{ nm}$  and lengths up to tens of micrometers. The EDS spectrum (Fig. 8b) reveals that the nanostructures are composed of Cd, S and C elements,

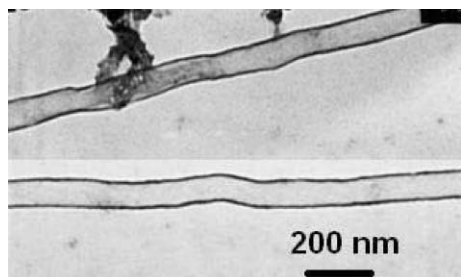


Fig. 6 TEM images of the carbon nanotubes (CNTs) obtained by etching the ZnS/C core-shell nanowires with  $6\text{ mol L}^{-1}$  HCl.

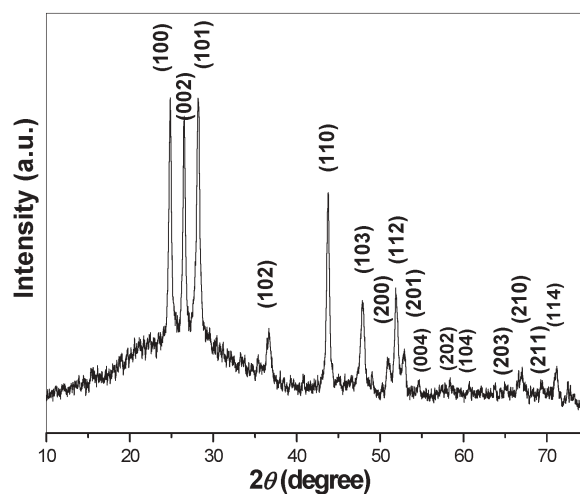


Fig. 7 XRD pattern of the CdS/C core-shell nanowires.

in which the gold originates from the gold-sputtered sample for SEM measurement. Fig. 8c–d show the TEM images and SAED pattern of the CdS/C nanostructures. It can be seen that the products have core-shell nanowire heterostructures with uniform diameters and shell thicknesses throughout their whole lengths. The diameters and shell thicknesses of the core-shell nanowires shown in Fig. 8c and d are  $60\text{ nm}$  and  $15\text{ nm}$ , and  $100\text{ nm}$  and  $25\text{ nm}$ , respectively. The SAED pattern (inset in Fig. 8d) can be indexed as a hexagonal CdS single crystal recorded from the  $[01\text{--}10]$  zone axis. These results show that CdS/C core-shell nanowires were also obtained.

In the synthesis of the core-shell nanowires, the complex  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$  underwent thermal decomposition to provide S and C. Metallic zinc and cadmium were used as zinc and cadmium sources, respectively. In view of the almost perfect filling and the filling lengths up to tens of micrometers in the core-shell nanowires, it can be inferred that the carbon

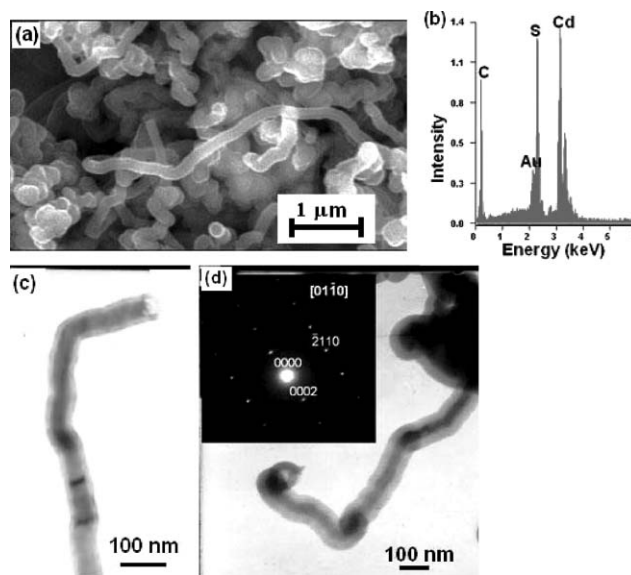


Fig. 8 (a) SEM image, (b) EDS spectrum, (c)–(d) TEM images of the CdS/C core-shell nanowires, the inset in (d) is the corresponding SAED pattern taken along the  $[01\text{--}10]$  zone axis.

nanotube and its filling form almost simultaneously: capillarity of empty nanotubes formed firstly does not adequately explain the formation of the filling with such a length. Therefore, carbon, metal and sulfur are intimately related in the growth process. Sulfur helps the precipitation of carbon and reacts with metal, also some sulfur is trapped by metal sulfide to form sulfur-enriched liquid drops. The growth will continue as long as the carbon, metal and sulfur species supply and temperature conditions are maintained. As mentioned above, the growth of the core-shell nanowires should follow a VLS mechanism due to the presence of a nanoparticle on the tips of the nanowires. In order to clarify further the formation processes of the core-shell nanowires, some contrast experiments were made. (1) Under the same conditions as the typical experiment, except using  $\text{Zn}(\text{S}_2\text{CNBu}_2)_2$  instead of  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$  as S and C sources, ZnS/C core-shell nanowires can be obtained, but the yield of the core-shell nanowires was much lower, which may be attributed to the lower volatility of  $\text{Zn}(\text{S}_2\text{CNBu}_2)_2$  than  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$ . (2) Using  $\text{Zn}(\text{S}_2\text{CNBu}_2)_2$  as all the Zn, S and C sources instead of metallic zinc and  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$ , ZnS/C core-shell nanowires were not formed and only naked ZnS blocks were obtained, which implies that the Zn metal plays a key role, not only as a zinc source, but also as a catalyst, in the formation of ZnS/C core-shell nanowires. From the experimental observations, we infer that the ZnS/C and CdS/C core-shell nanowires were grown *via* a VLS-like-catalytic growth mechanism, *viz.* the metal (Zn or Cd) served as both a reactant and a catalyst and sulfur helped the catalytic action of the metal. In the synthetic process, the metal was evaporated into metal vapor under heating, which was transported by the carrier gas ( $\text{N}_2$ ) to the middle-downstream region of the quartz tube, where it was condensed in the form of nanometer-sized liquid drops on the wall of the tube. C and S atoms from the decomposition of the organometallic precursor dissolved in the nanometer-size metal liquid drops. The carbon nanotube and metal sulfide nanowires grew from the metallic liquid drop surface at the same time. In contrast with the catalytic growth of usual carbon nanotubes,<sup>11</sup> there was a constant incoming flux of metal and S atoms. This is a necessary condition to allow for continuous filling. Owing to the spatial confinement effect of CNTs, the metal sulfide (ZnS or CdS) was grown within the CNTs forming one-dimensional nanowires. As a result, ZnS (or CdS)/C core-shell nanowires were formed. Sulfur played a crucial role for the formation of core-shell nanowires. Firstly, sulfur helped the precipitation and graphitization of carbon by acting as a cross-linker,<sup>12</sup> and then was released from the carbon tubes and was trapped in the metal sulfide fillings inside the nanotubes because of its strong affinity with the filling. Finally, the excess sulfur in the filling may favor the wetting between the nanotube and the filling material, in particular, through the sulfur atoms, which assisted the growth of the metal sulfide nanowires in the carbon nanotube. This is accordance with the experiment results that very high sulfur concentration was observed in the nanoparticle on the tips of core-shell nanowires. In addition, the absence of copper in the products may be attributed to the high melting point of the resulting copper sulfide,<sup>13</sup> which results in its deposition immediately after the decomposition of  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$ .

## Experimental

All chemicals and solvents used for the syntheses were reagent grade.  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$  was synthesized according to the literature method.<sup>13a</sup> The syntheses of the ZnS/C and CdS/C coaxial core-shell nanowires were carried out in a quartz tube mounted inside a horizontal tube furnace. In a typical synthesis,  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$  (~0.5 g) was placed at the upstream side of the furnace and *ca.* 0.5 g of a metal (Zn or Cd) was positioned downstream of the  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$ . The quartz tube was purged with high-purity  $\text{N}_2$  for 1 h prior to heating to remove any oxygen in the tube. The furnace was then heated to 800 °C for ZnS/CNT and 850 °C for CdS/CNT at a rate of 50 °C  $\text{min}^{-1}$ , and kept at this temperature for 1 h to synthesize the products. During the syntheses, the temperature of  $\text{Cu}(\text{S}_2\text{CNBu}_2)_2$  was *ca.* 450 °C and those of the Zn and Cd metals were *ca.* 760 °C and 740 °C, respectively. High-purity  $\text{N}_2$  with a flow rate of 50 mL  $\text{min}^{-1}$  was used as both carrier gas and protecting medium during the whole process. After the furnace was cooled to room temperature under a stream of  $\text{N}_2$ , a dark product (~0.25 g for ZnS/CNT and 0.12 g for CdS/CNT) was collected from the inner wall of the tube middle-downstream, where the temperature was *ca.* 780–800 °C for ZnS/CNT and 830–850 °C for CdS/CNT during heating.

The morphology and structure of the products were characterized by X-ray diffraction (XRD, D/Max-RA) with Cu K $\alpha$  radiation, scanning electron microscopy (SEM, JSM-840A) equipped with energy dispersion spectroscopy (EDS), transmission electron microscopy (TEM, JEM-200CX), and high-resolution TEM (HRTEM, TECNAI F-30) equipped with a high-angle-angular-dark-field (HAADF) detector. The elemental mapping was performed using a Gatan image filtering (GIF) system attached to the F-30 HRTEM. Raman spectra were recorded using a JY HR-800 Raman spectrometer with 487.97 nm excitation source from an Ar<sup>+</sup> laser.

## Conclusion

Large-scale ZnS/C and CdS/C core-shell nanowires have been synthesized by simple one-step methods *via* a novel metal reaction and self-catalysis growth mechanism. These core-shell nanowires have uniform outer diameters, uniform shell thicknesses and uniform core diameters along their entire lengths. The remarkable feature of our method is that the semiconductor nanowire encapsulated with CNT is a continuous single crystal, which is important for nanodevice fabrication. In these core-shell nanostructures, CNTs can protect the semiconductor nanowire against corrosion from air and moisture *etc.* Moreover, it can be expected that the introduction of semiconductors into CNTs may significantly alter their conducting, electronic, and mechanical properties, as well as even result in some unexpected phenomena. This unique method possesses potential for fabricating other semiconductor/carbon composite nanostructures. These new types of composite nanostructure can maybe find potential applications in optoelectronic nanodevices, catalysis, sensors and electrochemical energy storage, *etc.*

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## References

- (a) J. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435; (b) C. N. R. Rao, F. L. Deepak, G. Gundiah and A. Govindaraj, *Prog. Solid State Chem.*, 2003, **31**, 5; (c) G. R. Patzke, F. Krumeich and R. Nesper, *Angew. Chem., Int. Ed.*, 2002, **41**, 2447; (d) C. N. R. Rao and M. Nath, *Dalton Trans.*, 2003, 1; (e) J. H. Zhan, Y. Bando, J. Q. Hu, L. W. Yin, X. L. Yuan, T. Sekiguchi and D. Golberg, *Angew. Chem., Int. Ed.*, 2006, **45**, 228.
- (a) K. Laasonen, W. Andreoni and M. Parrinello, *Science*, 1992, **58**, 1916; (b) S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature*, 1994, **372**, 159.
- (a) Q. Li and C. Wang, *Appl. Phys. Lett.*, 2003, **82**, 1398; (b) Y. B. Li, Y. Bando, D. Golberg and Z. W. Liu, *Appl. Phys. Lett.*, 2003, **83**, 999; (c) S. Y. Bae, H. W. Seo, H. C. Choi, D. S. Han and J. Park, *J. Phys. Chem. B*, 2005, **109**, 8496; (d) Z. Zhou, J. J. Zhao, Z. F. Chen, X. P. Gao, J. P. Lu, P. V. Schleyer and C. K. Yang, *J. Phys. Chem. B*, 2006, **110**, 2529; (e) J. H. Zhan, Y. Bando, J. Q. Hu, T. Sekiguchi and D. Golberg, *Adv. Mater.*, 2005, **17**, 225.
- (a) B. K. Pradhan, T. Kyotani and A. Tomita, *Chem. Commun.*, 1999, 1317; (b) H. Cao, Z. Xu, H. Sang, D. Sheng and C. Tie, *Adv. Mater.*, 2001, **13**, 121; (c) J. Q. Hu, X. M. Meng, Y. Jiang, C. S. Lee and S. T. Lee, *Adv. Mater.*, 2003, **15**, 70.
- (a) Y. Yin, Y. Lu, Y. Sun and Y. Xia, *Nano Lett.*, 2002, **2**, 427; (b) X. H. Zhang, S. Y. Xie, Z. Y. Jiang, X. Zhang, Z. Q. Tian, Z. X. Xie, R. B. Huang and L. S. Zheng, *J. Phys. Chem. B*, 2003, **107**, 10114; (c) J. Q. Hu, Y. Bando, J. H. Zhan and D. Golberg, *Appl. Phys. Lett.*, 2004, **85**, 2932.
- (a) L. E. Brus, A. L. Efros and T. Itoh, *J. Lumin.*, 1996, **76**, 1; (b) T. V. Prevenslik, *J. Lumin.*, 2000, **87–89**, 1210; (c) X. F. Duan, Y. Huang, R. Agarwal and C. M. Lieber, *Nature*, 2003, **421**, 6920; (d) C. Falcony, M. Garcia, A. Ortiz and J. C. Alonso, *J. Appl. Phys.*, 1992, **72**, 1525.
- (a) S. Banerjee and S. S. Wong, *Nano Lett.*, 2002, **2**, 195; (b) S. Banerjee and S. S. Wong, *J. Am. Chem. Soc.*, 2003, **125**, 10342; (c) J. M. Du, L. Fu, Z. M. Liu, B. X. Han, Z. H. Li, Y. Q. Liu, Z. Y. Sun and D. B. Zhu, *J. Phys. Chem. B*, 2005, **109**, 12772; (d) J. Cao, J. Z. Sun, J. Hong, H. Y. Li, H. Z. Chen and M. Wang, *Adv. Mater.*, 2004, **16**, 84; (e) L. Sheeney-Haj-Ichia, B. Basnar and I. Willner, *Angew. Chem., Int. Ed.*, 2005, **44**, 78.
- (a) J. Q. Hu, Y. Bando, J. H. Zhan, C. Y. Zhi and D. Golberg, *Nano Lett.*, 2006, **6**, 1136; (b) J. H. Zhan, Y. Bando, J. Q. Hu, Y. B. Li and D. Golberg, *Chem. Mater.*, 2004, **16**, 5158.
- A. M. Morales and C. M. Lieber, *Science*, 1998, **279**, 208.
- X. G. Yang, C. Li, W. Wang, B. J. Yang, S. Y. Zhang and Y. T. Qian, *Chem. Commun.*, 2004, 342.
- (a) E. F. Kukovitsky, S. G. L'vov and N. A. Sainov, *Chem. Phys. Lett.*, 2000, **317**, 65; (b) Y. Homma, Y. Kobayashi, T. Ogino, D. Takagi, R. Ito, Y. J. Jung and P. M. Ajayan, *J. Phys. Chem. B*, 2003, **107**, 12161; (c) S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov and J. B. Nagy, *Science*, 1994, **265**, 635.
- (a) A. Oberlin, *Carbon*, 1984, **22**, 521; (b) X. Bourrat, A. Oberlin and J. C. Escalier, *Fuel*, 1987, **542**, 521.
- (a) M. Kemmler, M. Lazell, P. O'Brien, D. J. Otway, J. H. Park and J. R. Walsh, *J. Mater. Sci.: Mater. Electron.*, 2002, **13**, 531; (b) P. O'Brien, M. A. Malik, M. Chunggaze, T. Trindade, J. R. Walsh and A. C. Jones, *J. Cryst. Growth*, 1997, **170**, 23.