CdS Nanowire-encapsulated, CdS Nanocrystals-enrobed Carbon Nanotubes Composites, and Their UV–vis Properties

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The fabrication of CdS nanowire-encapsulated and CdS nanocrystal-enrobed multiwalled carbon nanotube (MWNTs) heterostructures is reported; the enrobed hybrid nanocomposites exhibit blue-shift absorption in UV–vis spectrum and provide various routes to nanotube composites.

The atomically well-defined 1-D structure of MWNTs provides a new model system for basic scientific studies and pathways to nanoscale devices.[1] In recent years, novel strategies have been devoted to the fabrication of MWNT-based composites by surface modification or interior impregnation with inorganic species.[2–4] CdS is an important II–VI semiconductor with size-tunable photophysical, photochemical, and electronic properties.[5] The implications for the photophysics of CdS nanocrystallites with quantum size effect have generated considerable interests.[5,6] In this letter, we first report CdS nanowire encapsulated by MWNT using a simple capillary-filling method. Morever, by noncovalent interaction, CdS nanoparticle-coated MWNTs nanocomposites were also successfully fabricated employing two different dispersants, anionic sodium dodecyl sulfate (SDS) and cationic polyethyleneimine (PEI). Here the CdS-enrobed MWNT heterostructures with blue-shift absorption were reported. The noncovalent preparation of the composites would preserve the electronic properties of MWNTs.[3] It can be foreseen that these heterostructures would have potential use for various photophysical or nanoscale electronic applications with larger band gap, while preserving the electronic properties of MWNTs.[2,3]

The microstructure of MWNTs was observed in previous work.[7] To fabricate CdS nanowire-impregnated MWNTs composites, a simple capillary-filling method was used. Pristine MWNTs were heat-treated with NH_3 to achieve open-ended carbon nanotubes.[7] 0.2 g of treated-MWNTs was immersed into the solution of CdS precursor for 5 days. This solution was composed of $Cd(CH_3COO)_2$ (1.0 mmol) dissolved in acetic acid (20 mL), and equivalent molar $CS(NH_2)_2$ dissolved in 2-methoxyethanol (20 mL). Then the mixture with MWNTs was transferred into a Teflon-lined autoclave and maintained at 110 °C for 24 h. After further filtration and rinsing with ethanol, the product was pyrolyzed at 500 °C for 2 h under Ar atmosphere. To synthesize CdS nanocrystal-coated MWNTs composites, an in situ chemical reaction route was used. Pristine MWNTs were first dispersed in a 2 wt % dilute SDS or PEI aqueous solution by ultrasonication to modify the nanotube surface, respectively. After further rinsing and drying, 0.2 g of SDS-adsorbed MWNTs was mixed with 20 mL of 0.1 M $Cd(CH_3COO)_2$ aqueous solution. Then 20 mL of 0.1 M Na_2S was added slowly into the above mixture with vigorous stirring. For PEI-modified MWNTs, the same $Cd(CH_3COO)_2$ aqueous solution was added dropwise into the mixture of Na_2S and modified MWNTs. Subsequently, two different solutions in the presence of SDS-adsorbed or PEI-adsorbed MWNTs were placed into autoclave and maintained at 110 °C for 5 h, respectively. The final products were achieved by further filtering and drying. The composites were characterized by XRD (D/Max 2550V, Rigaku, Japan), TEM, HRTEM, EDS (JEM 2010, JEOL, Japan). The surface tension of CdS precursor was measured by the maximum bubble pressure method. The UV–vis absorption spectra of the samples were performed on a Perkin Elmer Lambda 20 spectrophotometer and compared with that of pure CdS nanoparticles obtained by the reaction of $Cd(CH_3COO)_2$ and Na_2S without MWNTs.

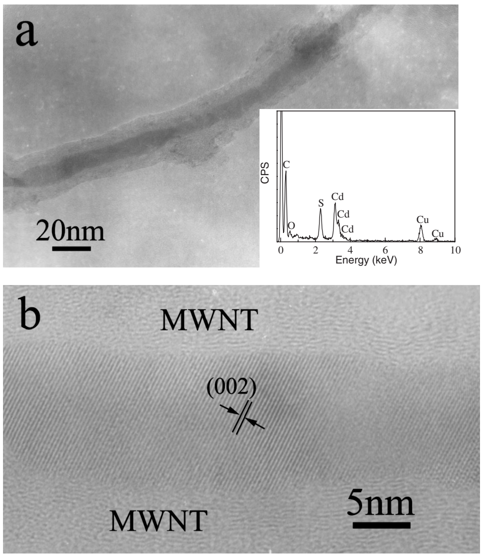

Figure 1. (a) Typical TEM image of CdS nanowire-impregnated MWNTs composite; (b) HRTEM image of the composite; Inset: EDS spectrum of the composite.

The pristine MWNTs were first heat-treated to make most of the nanotubes open and the opened-end pipes were then filled with CdS precursor solution. The upper threshold for the surface tension of the liquid-wetting MWNTs is 180 mN/m,[8] while the surface tension of CdS precursor is 37 mN/m. The threshold is wide enough for capillary filling and the precursor can be easily filled into MWNTs. CdS nanowire with ≈10 nm in diameter is formed in the cylindrical cavities (Figure 1a) owing to the capillary-induced filling and crystallization inside the nanotube.[9] The diameter of nanowire corresponds to the inner diameter of the MWNT. The nanowire can be straight or curved, depending upon the curvature of the CNT wrapping. EDS spectrum (inset

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in Figure 1a) clearly reveals that the nanowire is made purely of CdS. The peak of O is observed probably originating from oxidation of MWNT.[10] HRTEM image (Figure 1b) shows that the nanowire sheathed by a MWNT is composed of CdS nanocrystals. Measurements of lattice fringe spacing of nanowire show contributions mainly from (002) plane of CdS nanocrystal. The XRD pattern (Figure 2a) shows that the as-prepared CdS nanowire is in the hexagonal phase, wihich is close to JCPDS 41-1049. The average crystalline size is estimated to be about 10 nm from Debye–Scherrer formula, which corresponds well with the TEM result.

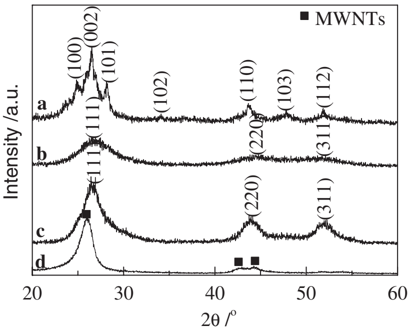

Figure 2. XRD patterns of (a) CdS-impregnated MWNTs composite, (b) CdS nanoparticle-coated PEI or SDS-modified MWNTs composite, (c) pure CdS bulk material, and (d) MWNTs.

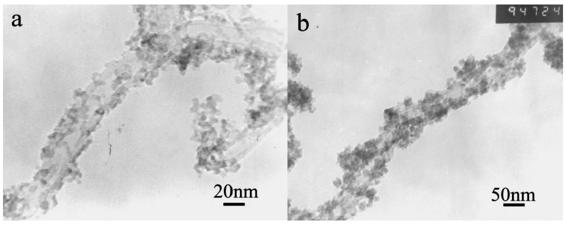

Figure 3. Typical TEM image of CdS nanoparticle-coated (a) SDS-modified MWNTs, (b) PEI-modified MWNTs.

Figure 2 also shows the XRD patterns of CdS-enrobed MWNTs composites (Figure 2b). It was found that the coated CdS nanoparticles are in the cubic phase, which is close to JCPDS 42-1411. The different phases of CdS existed in the CdS-encapsulated and CdS-enrobed composites are due to the different synthesis methods. According to the Scherrer formula, the average particle size in the composite is about 6 nm for both PEI- and SDS-treated MWNTs, which is smaller than that for pure CdS bulk material ($\approx$8 nm). Figure 3 shows the images of cubic CdS nanocrystal-enrobed MWNTs nanocomposites. The surface of MWNTs is uniformly covered with CdS nanocrystals with an average size of $\approx$5 nm both for SDS- and PEI-modified hybrids, which is consistent with the results of XRD analysis. The fabrication of CdS-coated MWNTs nanocomposites is realized by electrostatic interaction mechanism.[7] The anionic or cationic dispersant imparts negative or positive charge on MWNTs and then CdS nanocrystals are in situ produced. This route is easy and effective to fabricate nanoparticle-coated MWNTs composites.

The solid-state UV–vis absorption spectra of MWNTs, CdS nanowire-impregnated MWNTs, and CdS-coated MWNTs were shown in Figure 4. For clarity, several curves in Figure 4 have some significant offsets. MWNTs exhibit a very broad and featureless spectrum, while the absorption edge of CNTs either enrobed with CdS or impregnated with CdS nanowire is dominated by the characteristic absorption of CdS. No charge-transfer bands were observed for the composites,[4] which suggests that the fabrication methods here would preserve the electronic properties of MWNTs. For the hexagonal CdS nanowire-impregnated MWNTs, the absorption edge is at 515 nm (Figure 4e), which is similar to bulk hexagonal CdS (515 nm).[11] An interesting phenomenon is that a blue shift of band edge absorption is observed for the PEI-treated (528 nm) (Figure 4c) and SDS-treated composites (505 nm) (Figure 4d) compared with pure cubic CdS bulk material (550 nm) (Figure 4b). It can be suggested that the attached CdS nanoparticles (5–6 nm) cause the blue shift absorption due to the quantum size effect.[5]

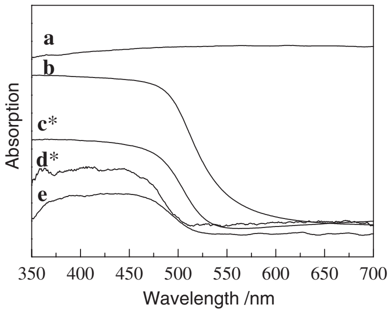

Figure 4. Solid-state UV–vis absorption spectra of (a) MWNTs, (b) pure CdS bulk material, (c) CdS-coated PEI-modified MWNTs composite, (d) CdS-coated SDS-treated MWNTs composite, and (e) CdS nanowire-impregnated MWNTs. * presents blue-shifted curve for CdS-coated composites.

In summary, various CdS nanowire-impregnated or CdS-enrobed MWNTs heterostructures were fabricated, which provides diverse routes to nanotube composites. The CdS-combined nanocomposites exhibit a slight blue-shift absorption due to the quantum size effect of the attached CdS nanoparticles on the outer wall of MWNTs. The composites would have potential use for photophysical applications.

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