

Versatile Formation of CdSe Nanoparticle-Single Walled Carbon Nanotube Hybrid Structures

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Nanotechnology has seen rapid progress in the development of nanoparticles^{1–4} and carbon nanotubes (CNTs),^{5–10} both of which have unique, structurally defined optical and electronic properties. Much effort has also been devoted to developing hybrid materials of nanoparticles and carbon nanotubes, with the hope of discovering new properties and applications.^{11–13} Efforts in making such hybrid materials have been focused mostly on two strategies. One is to attach certain bifunctional organic linkers to presynthesized nanoparticles and then to link the nanoparticles to the CNTs.^{12–14} The other is to grow nanoparticles directly on the CNTs by using established colloidal nanoparticle synthesis methods.^{11,15–17} The former strategy takes advantage of the maturity of many nanoparticle synthesis methods, for which the shape and monodispersity of nanoparticles can be controlled well. However, the complicated chemistry involved in treating the surfaces of nanoparticles and nanotubes to enable linkage limits the productivity and the nanoparticle loading efficiency in this strategy. The oxidation of carbon nanotubes, which is required in this approach, also greatly lowers the conductance of the hybrids and limits their use in electronic applications. The latter strategy, that of in situ growth, solves the problem of low loading of particles on the CNTs; however, the presence of CNTs in the nanoparticle synthesis solution severely changes the nanoparticle growth dynamics; the good control of particle shape and dispersity seen in CNT-free nanoparticle synthesis is not retained. In this manuscript, we report using single-walled carbon nanotubes (SWNTs) as ligands to stabilize and immobilize CdSe nanoparticles.¹⁸ Pyridine-protected nanoparticles are seen to have a native affinity for SWNT surfaces and to bind to SWNTs strongly without the aid of any linkers. The method can be easily adapted to produce various nanoparticle–nanotube hybrid materials, with well-controlled nanoparticle shape and quality.

The methods of synthesizing the CdSe nanoparticles,¹⁹ CdSe/ZnS core shell nanoparticles,²⁰ and CdSe nanorods²¹ are described in the cited references and the Supporting Information. For each type of particle, pyridine was added to the dried slurry of particles and the suspension was sonicated for 2 h during which it became a clear solution. Hexane was used to precipitate nanoparticles, and fresh pyridine was used to redissolve them. This sonication–precipitation–redissolution cycle was repeated two more times, yielding nanoparticles in the pyridine solution for use in further experiments. The HiPCO SWNTs were purified by heating raw tubes in air at 350 °C, followed by hydrochloric acid (5 M) soaking. The black powder was then repeatedly washed by DI water on filter paper and finally dried and redispersed in pyridine by sonication. The SWNTs grown by CVD on a SiO₂/Si substrate were immersed in pyridine for at least 30 min before use.

Nanoparticle–SWNT hybrid materials formed upon mixing the nanoparticle solution and SWNT samples, which were both in pyridine. The mixture was sonicated for 10 min to ensure

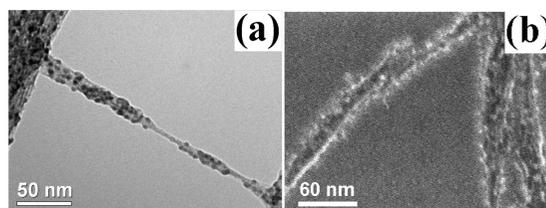


Figure 1. (a) TEM and (b) SEM images of HiPCO SWNTs decorated by 3.5 nm CdSe nanoparticles.

homogeneous mixing. The resulting suspension was then centrifuged, and the precipitates were washed with fresh pyridine, usually four times. Figure 1 shows TEM and SEM images of 3.5 nm diameter CdSe nanoparticles decorating what appears to be bundles of SWNTs. The loading of nanoparticles on SWNTs is comparable to that obtained by in situ growth of CdSe nanoparticles on SWNTs.¹⁶ Sidewall coverage is clear, but no particles at the ends of the tips are apparent. Energy dispersive X-ray spectroscopy shows the presence of C, Cd, and Se (Supporting Information). The UV–vis absorption spectra in Figure 2 of hybrid materials made from nanoparticles of different diameters (3.6 and 4.5 nm), after washing in pyridine four times, show peaks that appear to be the sum of the individual contributions of the nanoparticles (which are mostly bound to the SWNTs and are not free) and SWNTs. This suggests that there is still quantum confinement in the CdSe nanoparticle cores after attachment to the SWNTs. The first exciton absorption peaks of the two CdSe nanoparticles add to (the different) overlapping SWNT peaks to produce broadened peaks with maxima at wavelengths different than those of the components.

We believe the nanoparticles are immobilized on the surface of SWNTs by a strong interaction between nanoparticles and nanotubes, which prevents nanoparticles from migrating and aggregating. The origin of this interaction is assumed to be one of the following

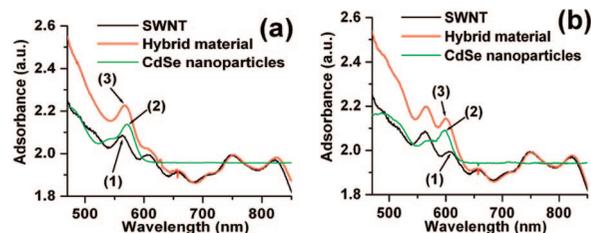


Figure 2. (a) UV–vis adsorption of HiPCO SWNTs, 3.6 nm CdSe nanoparticles, and the corresponding hybrid material. Peak (1) is the SWNT transition peak at 562 nm. Peak (2) is the first exciton peak of CdSe nanoparticles at 571 nm. These peaks contribute to the adsorption maximum at 568 nm [peak (3)] for the hybrid material. (b) UV–vis adsorption of HiPCO SWNTs, 4.5 nm CdSe nanoparticles, and the corresponding hybrid material, with the peaks at 598 nm, 607 nm, 600 nm, respectively. The vertical scales differ for each curve. All samples are measured in pyridine.

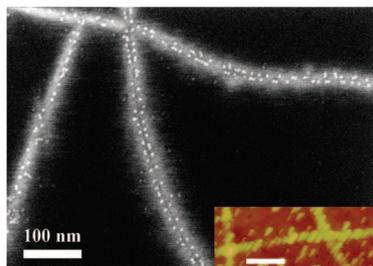


Figure 3. SEM image of SWNTs, grown on a SiO₂/Si substrate by CVD, decorated by 3.5 nm CdSe nanoparticles, with AFM inset. The scale bar in the inset is 100 nm.

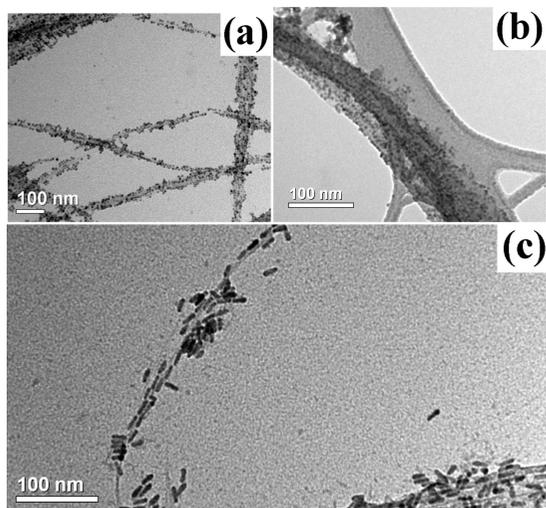


Figure 4. TEM images of HiPCO SWNTs decorated by different CdSe nanoparticles: (a) 6.6 nm diameter CdSe nanoparticles; (b) ZnS shell, 3.5 nm diameter CdSe core nanoparticles; (c) CdSe nanorods, 4.5 nm in diameter by 16 nm in length.

two mechanisms: (1) the binding of SWNT surface carboxylic groups on defect sites with the CdSe surface; (2) the π - π stacking interaction between SWNT sidewalls and the pyridine bound to the particle surface as a ligand. However, the nature of this interaction is still not understood, and a detailed investigation of the origin of this interaction is underway by our group. Nevertheless, pyridine-protected CdSe nanoparticles showed great affinity toward the SWNT surface and could not be washed off even after washing seven times with fresh pyridine. TEM showed no noticeable change after heating the structures in N₂ at 300 °C for 30 min, suggesting strong bonding and thermal stability even after pyridine evaporation (Supporting Information).

Figures 3 and 4 further show the versatility of this decoration strategy. Figure 3 shows SEM and AFM images of SWNTs, grown by CVD on a SiO₂/Si substrate, decorated by 3.5 nm CdSe nanoparticles. Particles of different sizes can be used, as is seen from Figures 1 and 2 and in Figure 4a, which shows that CdSe nanoparticles much larger than those used in Figures 1 and 2 (here 6.6 nm in diameter) can decorate HiPCO SWNTs. In Figure 4b, CdSe/ZnS core-shell quantum dots were used to decorate HiPCO SWNTs. The core-shell nanoparticle-SWNT hybrid materials may help in understanding energy transfer between quantum dots and SWNTs, because the ZnS shell eliminates the pathway that allows

an exciton to decay through surface traps of the nanoparticles. The loading of core-shell nanoparticles on SWNTs is similar to that of CdSe (only) nanoparticles, suggesting a similar interaction strength. CdSe nanorods can also be attached to HiPCO SWNTs as is shown in Figure 4c. Each type of prefabricated CdSe nanoparticle can be attached on SWNTs with high loading.

In conclusion, pyridine-protected CdSe nanoparticles were found to be able to decorate SWNTs spontaneously. The absorption of the hybrid has contributions attributable to the nanoparticles and the SWNTs; however, some electronic coupling between them is still possible. Several types of nanoparticles were shown to decorate SWNTs with a large loading factor by using this convenient method, which can be easily scaled up. More varieties of hybrid materials are being tested, as will be the luminescence characteristics of these hybrids. Such hybrids could find use in optoelectronic applications such as solar cells and optical sensors.

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Supporting Information Available: Details of nanoparticle synthesis and hybrid structure characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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