

Carbon Supported CdSe Nanocrystals

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The extraordinary properties of nanosized materials have boosted intensive work in the development of several synthetic methodologies in the past decades. The so-called hot injection method¹ is a versatile and relatively cheap means that provides a high degree of perfection, reproducibility, and control of semiconductor^{2,3} and magnetic^{1,4} nanocrystals. This colloidal synthetic route is based on the reaction of highly reactive species in media where surfactants play an essential role in the final shape, size, and stability of the desired nanomaterial. However, small variations in monomer concentrations, temperatures, time, or presence of impurities may drive the reaction into different regimes. As a consequence, diverse sizes, shapes, and compositions of nanoparticles (NPs) can be obtained. A. J. Houtepen et al.⁵ describe the role of acetate in the synthesis of PbSe NPs. Traces of acetate can be responsible for a great variety of NP shapes. It is also known that traces of phosphonic acids can influence decisively the growth mechanism, the yield, and the shape of the NPs.^{6–8} As alternative to other synthetic approaches,^{9,10} the hot injection method was recently used to obtain CdSe-CNT composites.¹¹ It was observed that, in the presence of CNTs, CdSe nanorods evolved into pyramidal-like NPs that connected to CNTs by the wurtzite (001) facets.^{11,12} Furthermore, rods and pyramidal-like NPs showed a different interaction with CNTs, the latter showing a clear tendency to attach to the carbon lattice. Unlike heterogeneous growth on a seed surface, the reaction of CdSe nanorods in the presence of CNTs proceeds independently of the carbon lattice during their nucleation and growth. The proposed mechanism so far¹¹ suggested that the shape transformation of the NPs is a result of nanotube–nanoparticle interaction with a decisive role of octadecylphosphonic acid (ODPA). ODPA is used as complexing agent of the cadmium source and acts as capping ligand of the NPs at Cd sites.¹³

Here, we address the influence of the CNTs dispersant (solvent) and water on the shape of the NPs and the requirements for further attachment to the carbon lattice. The experiments reported here show that the final shape of the NPs (pyramidal-like) is related to the injection of DCE (1,2-dichloroethane), the carbon-material dispersant. We ascertain that the complex formed by Cd and ODPA is influenced by DCE, triggering a reaction where rod-like NPs change their shape and attach to sp² carbon lattices. The influence of water, the possible formation of HCl, and the requirements for the attachment of the NPs are also discussed. Their influence has also been studied in some other carbon allotropic systems like diamond powder, glassy carbon, and minimal-layer graphene exfoliated from highly oriented pyrolytic graphite (HOPG).

The synthesis of CdSe-CNT composites is based on the complexation of CdO by ODPA in trioctylphosphine oxide (TOPO) as solvent, followed by the injection of CNT in DCE and the subsequent removal of the solvent under vacuum (procedure A in the Supporting Information (SI)). After this step, the injection of

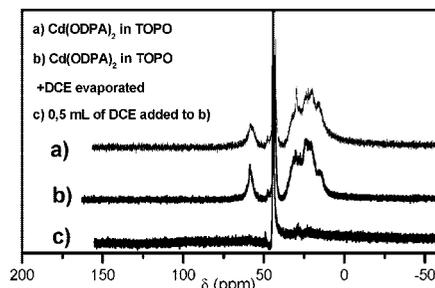


Figure 1. ³¹P {¹H} NMR chemical shifts of (a) Cd-ODPA mixture in TOPO (b) after addition and elimination under vacuum of 2 mL of DCE and (c) after the addition of 0.5 mL of DCE at RT.

Se dissolved in trioctylphosphine (TOP) promotes the formation of CdSe nuclei that grow along the *c*-axis of the wurtzite crystal. We observed that removing DCE appropriately is crucial, as the nonefficient removal of DCE (i.e., as a result of low vacuum power) may delay or even suppress the nucleation of CdSe NPs upon Se injection. Thus, small traces of DCE in solution or adsorbed on the CNTs may influence the formation of the NPs and/or further evolution of their shape. To address the effect of DCE on the Cd-ODPA complex, we carried out ³¹P-Nuclear Magnetic Resonance (NMR) analyses. Figure 1a shows the ³¹P NMR chemical shifts of a Cd-ODPA mixture in TOPO (see SI for further details). The spectrum contains three prominent features. A peak at 58 ppm, a set of multiplets around 25 ppm, and a sharp signal at 48 ppm.

A similar spectrum is observed (Figure 1b) when 2 mL of DCE are injected and removed under vacuum. No appreciable changes (at least, no detectable by NMR means) can be identified if the DCE is quickly removed (SI). For comparison, the spectrum of this mixture in the presence of 0.5 mL of DCE added at room temperature and not evaporated is shown in Figure 1c. The presence of DCE removes the signals centered around 25 ppm previously assigned to the complex Cd-ODPA.⁶ The same happens with the signal around 58 ppm, which may originate as a result of a Cd(ODPA)-TOPO hydrogen bonding interaction. The intensity of the peak related to TOPO (around 48 ppm) slightly increases and shifts, as a result of the new chemical environment upon the addition of DCE.

Concerning the synthesis, we found that the injection of exclusively DCE without CNTs and its subsequent removal under vacuum yields pyramidal-like NPs. Thus, DCE is able to change the shape of the particles during the reaction. We studied some other parameters such as the amount of CNTs. We observed that CNT concentrations 0.2–2 mg/run do not influence the shape of the particles or the CNT coverage. We also studied the effect of a second degassing process (SI) after Cd complexation to remove the released water according to the following reaction:^{13,14} CdO + 2(ODPA) → Cd(ODPA)₂ + H₂O.

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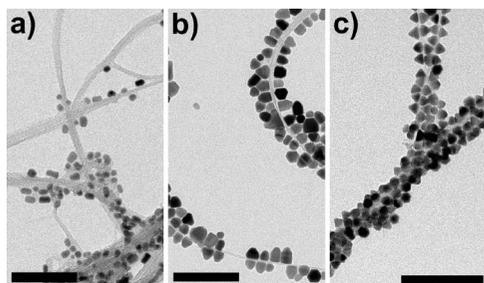


Figure 2. CdSe NPs and CNTs obtained upon injection of 20 μL of HCl (20 μmol of Cl) (a) after 3 h of reaction and (b) after 20 h. The injection of 10 μL of DCE (0.25 mmol Cl) instead yields the composites (c) after 20 h of reaction. Scale bars correspond to 100 nm.

Interestingly, the presence of water improves the coverage of the NPs around the tubes once the particles are pyramidal-like. Several works have addressed the formation of anhydrides of ODPA as products of this reaction.^{6,15} The presence of water would prevent the formation of such anhydrides, influencing the capping environment of the NPs. Taking into account that both water and DCE influence the reaction, HCl might be formed. Previous work reported on the change of the chemical configuration of molecules upon sonication in chlorinated solvents, in particular DCE.¹⁶ Traces of HCl in commercially available Cl-containing solvents or formation of HCl upon sonochemical degradation may change the photo-physical properties of different compounds. To prove the influence of HCl in the reaction, we performed the reaction by injecting CNTs in a Cl-free solvent like toluene. The addition of CNTs previously sonicated in a solvent is important to reduce the agglomeration of the CNTs or the CdSe-CNT composites. Injecting CNTs in toluene (followed by its removal under vacuum) does not yield the formation of pyramidal-like particles (see next section). However, the injection of HCl or DCE to this reaction mixture after the formation of rod-like NPs yields similar CdSe-CNT composites as the ones obtained when CNTs are injected in DCE, as can be seen in Figure 2. To a mixture of Cd(ODPA)₂ in TOPO, CNTs in toluene were included in the reaction mixture before the Se precursor. After the nucleation and growth of rods (30 min after the Se injection), 20 μL of 1 N HCl aqueous solution were added, without apparent formation of the CdSe-CNT composites after 3 h, as shown in Figure 2a. However, 17 h later, the samples obtained are similar to the ones obtained when CNTs are dispersed in DCE (Figure 2b). The amount of HCl added corresponds to 20 μmol of Cl. Due to the apparent degree of ripening, less polydisperse particles could be obtained by adding a higher concentration of HCl. The same experiment performed by injecting 10 μL of DCE (0.2 mmol Cl) after 30 min of reaction is shown in Figure 2c. In this case, the NPs are more monodisperse, what is related to the Cl concentration added. The sample was taken after 20 h of reaction, as in Figure 2a.

Since the presence of water is unavoidable even when degassing the Cd source after complexation, we propose that HCl may form when injecting CNTs dispersions in DCE in the reactant mixture containing Cd-ODPA, TOPO, and water. In a quick experiment it could be seen how the pH value of DCE/water mixtures slightly decreases at $\sim 80^\circ\text{C}$, suggesting the possible formation of HCl under these conditions.

But what is the role of DCE or HCl during the reaction? Its presence in the reaction modifies the Cd-ODPA complex and/or destabilizes the ligand environment of the rod-like NPs, boosting an intraparticle ripening that yields pyramidal-like ones. Together with an Ostwald ripening mechanism, the nonstable NPs attach to the carbon lattices that act as new ligands. If formation of new Cd

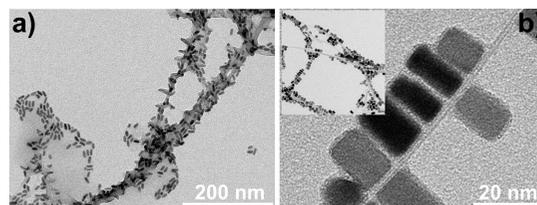


Figure 3. (a) Nanotubes covered by the products of the reaction and CdSe rods after 30 min. (b) Composites obtained after 48 h of reaction when the CNTs were injected in toluene 24 h after nucleation. Inset: lower magnification.

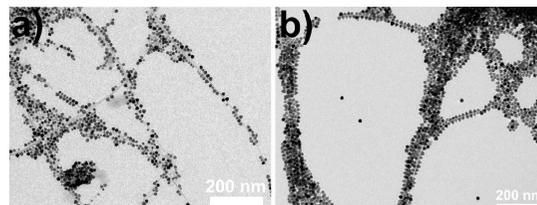


Figure 4. (a) CNT covered with CdSe NPs washed and incubated with CNT under stirring for 48 h. (b) Composite obtained after 48 h at 255 $^\circ\text{C}$ following the procedure described in ref 11.

species and/or removal of ODPA ligands by protonation or nucleophilic displacement are the mechanisms of such destabilization, this is definitely an issue to be addressed by further studies. Covalent functionalization of the CNTs by the presence of the acid is excluded, as previous Raman characterization confirmed.¹¹

The requirements for the attachment of the NPs to the tubes are (1) CNT surfaces free of ODPA and TOPO and (2) low passivated nanoparticle surfaces. Several examples clarify these two assessments:

(1) CNT Surfaces Free of ODPA and TOPO. We observed that, at early stages of the reaction (i.e., 30 min after nucleation), the rods are well capped (according to interparticle distances measured by TEM) and the CNTs are partially covered by the organic reactants (Figure 3a), both facts preventing a successful attachment. At this stage, washing these samples in toluene does not completely remove the organic products around the CNTs. A similar organic coverage has been observed by the precipitation of polymers on CNTs by means of the so-called “antisolvent-induced polymer epitaxy method”.¹⁷ However, the coverage of the CNTs by the organic products is removed as the reaction evolves (i.e., 24 h after nucleation). The fact that at this later stage the CNTs do not seem to be wrapped by organics is related to the evolution of the coproducts in the reaction. To understand the role of the wrapped CNT surface, we performed experiments adding CNTs in toluene 24 h after the rods are formed. Figure 3b shows the obtained samples 48 h after the CNT injection.

In this case, the CNT surface is free from the above-described wrapping products and the NPs also show a certain tendency to decorate the CNTs. The amount of NPs covering the CNTs is substantially lower than in the case reported for pyramidal-like NPs (Figure 4b). The particles do not show prominent facets from the {10–1} family of planes as pyramidal-like ones do, but rather mainly very flat (100) and (00–1) ones. Thus, the pyramidal-like shape of the NPs is clearly related to the effect of DCE or HCl and the attachment required, among other conditions, CNT surfaces free of organics. This result also points out that CNTs stabilize flat facets of the particles. NPs showing nondefined and more rounded facets (like the ones shown in Figure 2a) do not attach to the carbon lattice.

(2) Low Passivated Nanoparticle Surfaces. To understand the role of the passivating ligand environment, we performed experiments involving washing rod-like CdSe NPs and mixing them with

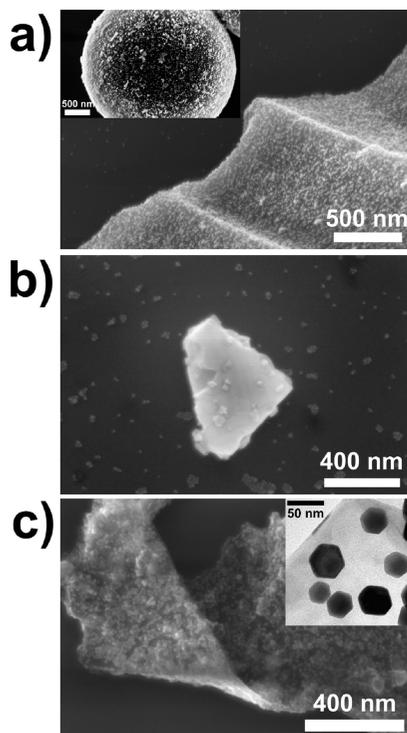


Figure 5. Glassy carbon surface covered with CdSe NPs (a) and diamond powder (b) where CdSe NPs can be distinguished on the SiO₂ substrate. The inset in (a) shows a glassy carbon microsphere covered by CdSe NPs. (c) Graphene layers covered by CdSe NPs on a SiO₂ surface.

CNTs under stirring at room temperature for 24 h (procedure B in the SI). The mixing was performed in toluene and in a destabilizing solvent like DCE. While in toluene the nanoparticle dispersion is stable, in DCE the particles preferentially decorate the CNTs, demonstrating again the ligating effect of CNTs. This result suggests the possibility of obtaining comparable CdSe-CNTs composites at room temperature. To address this issue we mixed pyramidal-like NPs obtained by the injection of DCE during the synthesis (without CNTs) with CNTs dispersed in toluene at room temperature (Figure 4a). For comparison, Figure 4b shows a sample obtained after 48 h, following the procedure described in the experimental section (A) at 255 °C. Although the amount of particles obtained is higher at higher temperature, a clear tendency of attachment is apparent for samples incubated at RT. Thus, low passivated (or eventually nonpassivated) NPs attach to the CNT surface.

Finally, to study the role of the hybridization state and thus the crystal structure of carbon on the attachment, we performed experiments where CNTs were substituted by other allotropes of carbon such as glassy carbon or diamond powder. The former is known to possess an sp² lattice, and the latter is sp³ hybridized. The experiments were carried out as in the case of CNTs by injecting the carbon media dispersed in DCE. Figure 5a shows an SEM picture of glassy carbon powder covered by CdSe NPs. The inset shows glassy carbon (in form of spheres) covered by CdSe NPs. TEM inspection of the NPs not attached to the glassy carbon showed a pyramidal shape. However, no apparent attachment is observed in the case of the diamond powder (Figure 5b) which

points to a clear role of the carbon crystalline sp² lattice, as has been already reported.¹² Our results support recent work reporting a fullerene-like structure for commercial glassy carbon.¹⁸ Due to the increasing interest in the use and understanding of the physics of graphene, a commercial piece of HOPG was sonicated in DCE before injection. The sonication results in the formation of small flakes that may eventually contain a single layer of graphite produced by exfoliation, the so-called graphene. Figure 5c shows an SEM picture of several graphene layers covered with CdSe NPs. The inset shows a TEM detail where the NPs show the (001) facet connected to the carbon substrate. Although a clear assessment to a single monolayer cannot be done without further characterization, the results show that it is possible to attach CdSe NPs to graphene by means of this approach, which we believe may bring fascinating physical and chemical properties to explore.

In conclusion, we give insights to the mechanism by which CdSe NPs attach to CNTs following the hot injection method. It was observed that the presence of water improves the nanotube coverage while DCE, HCl, or in general Cl is responsible for the shape transformation of the NPs and further attachment to the carbon lattice. The experiments also show that the mechanism taking place involves the right balance of several factors, namely, a low passivated nanoparticle surface, particles with well-defined crystallographic facets, and interaction with an organics-free sp² carbon lattice. Furthermore, this procedure can be extended to cover graphene by quantum dots.

Acknowledgment. B.H.J. thanks the European Commission for her Marie Curie Fellowship.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA805662H