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Editor's Choice

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ABSTRACT

In this letter a new type of core-shell structure is presented. The core is made of tin-sulfide by colloidal route. The shell, made of indium-sulfide, by chemical bath deposition. These core-shell nanoparticles have been characterized by transmission electron microscope to study the size and the shape. High resolution TEM has allowed to determine the structure of the core and the shell. The chemical composition has been analyzed by energy-dispersive X-ray spectroscopy. In the end the optical absorption investigated by UV-vis changing the deposition time and temperature. Finally, the influence of these parameters on the band gap has been investigated.

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In the last 10 years semiconductor nanoparticles have received an enormous interest because their optical properties are strongly dependent on the size of the particles. By changing the size it is possible to tune the band gap; indeed, the band gap increases with decreasing of dimensions. This phenomenon is called quantum confinement. This property makes nanoparticles a unique material with characteristics between molecules and bulk semiconductors [1–4].

Nevertheless, incomplete passivation by ligands leads to trap states at the surface [5] which reduce the fluorescence quantum yield (QY), due to the increased electron-hole recombination. Thus, it is important to avoid this by maintaining the maximum sterically allowed surface coverage. A better approach is to replace the ligands with a shell made by another semiconductor material, creating a core-shell structure. It has been shown that core-shell structures exhibit good stability and less photodegradation [6]. Moreover, when the core is conformally coated by a shell, the number of dangling bonds at the surface that usually act as trap states is reduced.

The first work reported in the literature was on CdSe/ZnS nanoparticles by Hines and Guyot-Sionnest [7]. They covered CdSe cores with one to two monolayers of ZnS. Moreover, they showed that addition of the ZnS shell improves the fluorescent quantum

yield of the particles, achieving a quantum yield (QY) of even 50%. In the last half of the 1990s many papers have been published on core-shell nanoparticles [8,9].

Usually core-shell nanoparticles are synthesized in two steps: first, the core is synthesized chemically and then, after a purification step, the shell is grown.

So far, the most studied core-shell nanoparticles are structures such as CdSe/ZnS [10,11], CdSe/CdS [12–16], CdSe/ZnSe [17–20] and Cd/HgS [21].

Despite extensive investigations of these core-shell NPs due to which their properties are well known, their application is rather limited. Indeed, most of these structures contain toxic elements such as Cd and Pb, which are not environmentally friendly elements.

For this reason, in the last few years, there has been the necessity to develop non-toxic nanoparticles, for instance ZnO [22,23], ZnS [24] and SnS [25,26] nanoparticles.

In this letter the synthesis of a new type of core-shell nanoparticles is described. The nanoparticles reported in this work have a core made of tin(II) sulfide (SnS) and a shell of indium(III) sulfide (In₂S₃). In₂S₃ has been chosen as material for the shell because it has orthorhombic structure as SnS. Hence, damaging due to stress and strain is avoided.

SnS/In₂S₃ core/shell nanoparticles are synthesized by a chemical bath deposition (CBD) route whereby an ethanol dispersion of previously synthesized TOPO capped SnS NPs [27] are immersed

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Figure 1. TEM image of SnS/In₂S₃ core-shell NPs.

in the CBD bath for deposition of the In₂S₃ shell. Afterwards, the coated NPs are separated and washed in ethanol. The bath composition was InCl₃, thiocetamide, and acetic acid in water.

At first, the size and the shape of nanoparticles were checked using a TEM TECNAI20 with an electron beam of 120 kV. The samples have been prepared by depositing the nanoparticles on a lacey carbon grid by drop casting. [Figure 1](#) shows the TEM image of SnS/In₂S₃ core/shell NPs. It can be seen that the nanoparticles have a spherical shape. The size is in the range of 5–10 nm.

However, the resolution of this TEM image does not allow to distinguish the core-shell structure.

To determine the nature of the core-shell structure we used High-Resolution TEM (HRTEM). A Tecnai F20ST/STEM with an electron beam of 200 kV was used for imaging.

For these measurements the samples have been prepared with a different procedure than for TEM. The nanoparticles have been deposited on a glass substrate by spray pyrolysis and afterwards the samples have been cut to study their cross section. TEM samples were prepared by gluing a Si crystal from a wafer on the film side of the material, then cutting a slice with a thickness of 0.5–1 mm with a diamond saw, followed by mechanical grinding and polishing the slice down to a thickness of ~10 μm, then placing it on a Cu slot grid and thinning it to electron transparency using a Gatan PIPS 691 ion mill, using Ar.

In the HRTEM image, reported in [Figure 2](#), the core-shell structure of the nanoparticles is evident. It is possible to distinguish two different nanoparticle structures. On the left side of the picture a cluster of two nanoparticles is visible, a smaller and larger one. It is possible to distinguish two cores surrounded by a shared shell

Figure 3. EDX spectrum acquired on SnS/In₂S₃ core-shell NPs deposited on a lacey carbon grid.

(blue circle). On the right side of the image a single nanoparticle is observed (red circle). The core of this nanoparticle is darker and shows clear lattice fringes, while the shell, which covers the core completely, appears to have an amorphous structure. The size of this nanoparticle including the shell is slightly larger than 10 nm.

The chemical composition has been investigated by means of energy-dispersive X-ray spectroscopy (EDX). The EDX spectrum is reported in [Figure 3](#). This measurement confirmed the presence of the three expected elements: indium, sulfur and tin. Small quantities of other elements have been detected: chlorine from the InCl₃ used in the bath, copper and carbon due to the lacey copper grid used for TEM-EDX measurements.

The deposition time and temperature are two critical parameters for the deposition of the shell during the CBD synthesis. The process parameters play a crucial role in the thickness of the shell and thus the optical absorption of the core-shell structure. The effect of the deposition time and temperature has been studied ([Figure 4](#)). In the two graphs of [Figure 4](#) the red line corresponds to the absorption spectrum of ethanol used as a solvent to disperse the nanoparticles and acquired as background. This was necessary because, in this case, a single beam spectrometer was used and hence the background was not subtracted automatically.

In [Figure 4a](#) the influence of the deposition temperature is shown. [Figure 4b](#) shows the effect of CBD duration for the deposition at 70 °C and the difference between the absorption of SnS and SnS/In₂S₃ nanoparticles is reported. From [Figure 4b](#) the effect of the shell on the band gap is clearly visible. The band gap of core-shell structure is larger than for the bare SnS quantum dots, as expected. The band gap is monitored by the shift of absorption

Figure 2. HRTEM image of SnS/In₂S₃ core-shell nanoparticles. On the left side two cores surrounded by an unique shell are detected (blue circle); on the right side a single core-shell nanoparticle is visible (red circle). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Figure 4. Absorption spectra of SnS and SnS/In₂S₃ core-shell NPs (a) with two different deposition temperatures and (b) with different deposition times. The red line corresponds to the background spectrum, the absorption spectrum of ethanol.

edge in Figure 4. Even 5 min of CBD changes the band gap drastically. Figure 4 also clearly shows the possibility to tune the band gap by changing the thickness of the shell. The band gap increases monotonically with increasing deposition time.

In summary, a process has been described for coating SnS nanoparticles with an In₂S₃ shell. This provides better passivation of the SnS surface and improves the electrical properties of the nanoparticles. The shell has been deposited by the CBD technique. These nanoparticles have a size around 10 nm and they show a crystalline core surrounded by an amorphous shell. The optical absorption shows an increasing band gap due to the addition of the shell, which is in line with the shell thickness.

A CBD temperature of 60–70 °C was found to be appropriate to ensure the formation of a dense coating without damaging the crystalline particles. The shell thickness can appropriately be tuned by choosing the CBD duration.

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