Engineering the surface chemical properties of semiconductor nanoparticles: surfactant-encapsulated CdTe-clusters

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Self-assembly of CdTe-nanoparticles and alkylammonium surfactants gives stable, hydrophobic surfactant-encapsulated CdTe-clusters that can be isolated as solid materials which dissolve in common organic solvents, spread at the air–water interface, and show enhanced photochemical stability.

Nanoparticles of semiconductors are at the focus of materials research owing to the novel electronic, catalytic and optical properties of these materials. The unusual properties can be attributed to two main factors: the high surface area to volume ratio and the spatial confinement of electronic states. The confinement results in discrete transitions with highly polarizable excited states that are tunable with particle size.[1]

The synthesis, purification and isolation of stable, discrete nanoparticles preferentially with a narrow size distribution and tailored surface chemical properties represents a considerable challenge because the large surface energy promotes aggregation to minimize the surface area. A successful synthesis should, therefore, result in monodisperse nanoparticles with robust surface passivation. Essentially, there are three methods to achieve these goals with varying success.[2] A common approach relies on decomposition of organometallic precursors, where surface passivation is achieved by coordination of solvent molecules, such as alkylphosphine oxides, to the cluster surface *in situ*.[3] In a second method, particle growth is restricted in confined media, such as polymer micelles.[4] Finally, nanoparticles can be synthesized *via* colloid chemistry where the particles are capped by suitable stabilizing molecules, such as thiocarboxylic acids.[5]

Following our recent work on encapsulated polyoxometalate clusters,[6] we present here, the synthesis and isolation of stable surfactant encapsulated CdTe-clusters (SECs). This self-assembly strategy relies on an ion exchange process of the cluster counter ions with surfactants. This approach has been applied to a variety of particles,[7] including gold colloids,[8] metal[9] and metal oxide clusters.[10] The advantage of our approach is that the preparation of the parent CdTe-clusters rests on well established experimental procedures.[11] The synthesis of CdTe-SECs is achieved in a second independent step by treating aqueous CdTe-solutions with the surfactant dimethyldioctadecylammonium bromide (DODABr). Encapsulation of the CdTe-clusters with surfactants results in hydrophobic SECs, which are readily isolated as solid powder. These semiconductor clusters possess many interesting properties and are, therefore, of considerable technological interest.[12]

The CdTe-clusters were synthesized by treating a demineralized aqueous solution containing thioglycolic acid and $Cd(ClO_4)_2 \cdot 6H_2O$ (0.013 M) at pH 11 with NaHTe in an inert gas atmosphere,[5,11] leading to particles of diameter *ca*. 4 nm.[13] A 4.5 ml aliquot of this solution was diluted to 100 ml with water and the pH was adjusted to 6 by addition of HCl. 50 mg of DODABr was then added and the resulting CdTe-SEC was extracted with chloroform. Quantitative transfer of the CdTe-clusters into the organic phase was observed by visual inspection after 20 min: the chloroform phase turned yellow–brown, while the aqueous phase became colourless. The organic phase was separated, dried and evaporated to yield the CdTe-SEC material as a brown–yellow solid, which readily dissolved
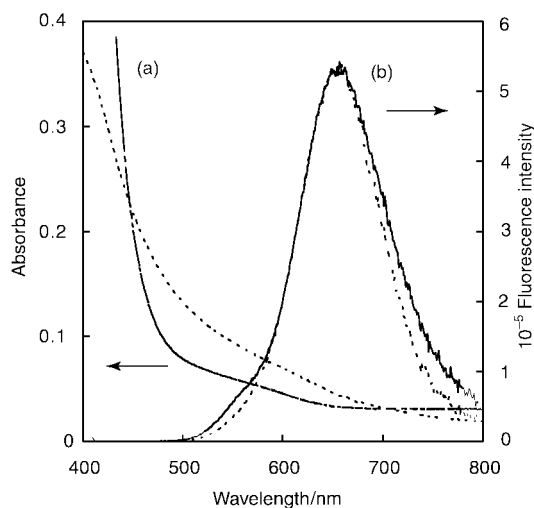

Fig. 1 UV–VIS spectra (a) and fluorescence spectra (b) of CdTe-clusters (——) and CdTe-SECs (- - - -). The fluorescence spectra are normalized for better comparison (excitation wavelength 400 nm). The spectra of the CdTe-clusters and the CdTe-SECs are nearly identical, indicating the structural integrity of the CdTe-clusters within the surfactant encapsulated clusters.

in common organic solvents. The solubility properties imply that the surfactant molecules form a closed, hydrophobic shell around the CdTe-core with the positive head groups of the surfactant molecules binding to the surface carboxylates.

UV–VIS and fluorescence spectroscopy demonstrate that the CdTe-clusters maintain their structural integrity upon encapsulation. The absorbance spectra of the parent CdTe-clusters and the CdTe-SECs are fairly similar (Fig. 1) with both samples showing characteristic shoulders at *ca*. 400 and 600 nm. The fluorescence spectra have similar band positions and widths, indicating that the particle size distributions of the two samples are similar. It is interesting that the apparent fluorescence intensity for the CdTe-SECs is larger by almost a factor of two. These observations demonstrate how sensitive the photophysical properties of the CdTe-nanoparticles are to surface derivatization and local field effects.[14]

A comparison of the long-term development of the fluorescence intensity is shown in Fig. 2. The parent CdTe-clusters show a decay of the fluorescence intensity by an order of magnitude within 4 h. Also shown is the UV–VIS absorbance as a function of time. A decrease in absorbance indicates a loss of material from within the probe beam volume. Although the use of thioglycolic acid for adjusting the pH of the aqueous solution extends the photochemical stability of the CdTe-clusters, the particles are completely decomposed after seven days with the fluorescence intensity and the absorbance falling close to zero. Because CdTe-solutions stored in the dark are stable over extended periods of time, we conclude that a light induced reaction occurs, which eventually results in precipitation of the CdTe-clusters. In contrast, the CdTe-SECs show a steady fluorescence intensity under the same experimental conditions (Fig. 2).† Even after seven days of illumination, the CdTe-SECs maintain most of their initial fluorescence. Clearly, the
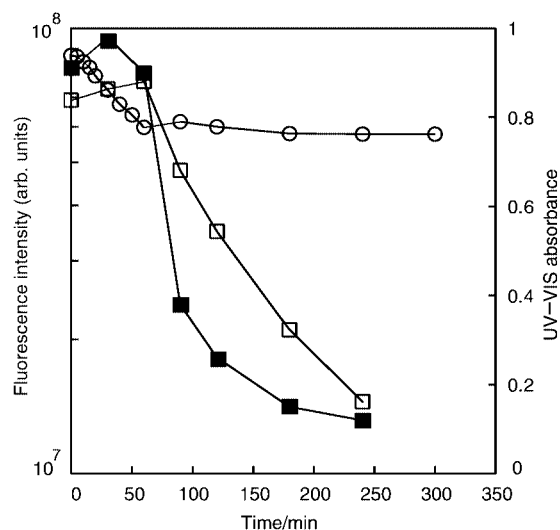
Fig. 2 Fluorescence intensity of CdTe-clusters (□) and CdTe-SECs (○) as a function of time. The CdTe-SECs show a nearly constant fluorescence intensity under irradiation at the excitation wavelength (400 nm). By contrast, the fluorescence intensity of parent CdTe-clusters decays under identical conditions. Also shown is the UV–VIS absorbance at 400 nm of the CdTe-clusters (■). The diminution with time corresponds to a loss of material within the probe beam volume (precipitation) which causes the decrease of fluorescence intensity.

surfactant shell effectively protects the CdTe-core from photo-induced decomposition and precipitation.

The hydrophobic nature of the CdTe-SECs is shown by the fact that they form stable Langmuir monolayers at the air–water interface‡ and Fig. 3 shows a representative compression isotherm which are very reproducible. The area per SEC cannot be obtained from the isotherm because the molecular mass of
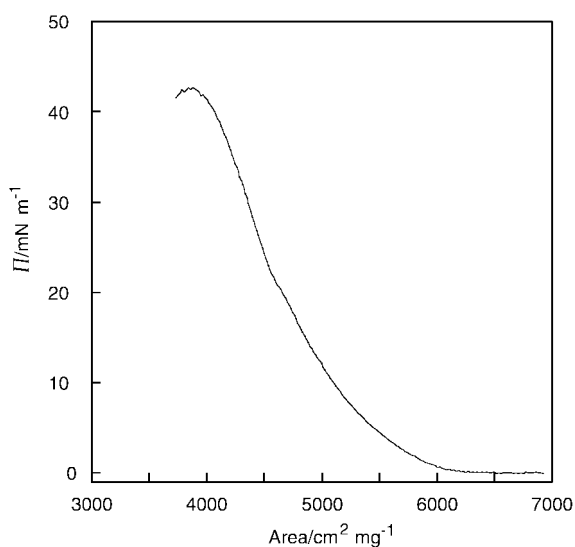

Fig. 3 Representative compression isotherm of a CdTe-SEC at the air–water interface. The Langmuir monolayers are quite stable as indicated by the high collapse pressure of *ca.* 42 mN m^{-1}.

the CdTe-SECs is, as yet, not known. The isotherm does not show well defined phase transitions, but only a slight shoulder at 20 mN m^{-1} while the collapse pressure is *ca.* 42 mN m^{-1}. Upon expansion a slight hysteresis is visible. The collapse pressure is relatively high, which indicates a good stability of the monolayer. This behavior is similar to that of structurally related surfactant encapsulated polyoxometalate clusters.[6]

In summary, we have presented a facile non-covalent strategy to tailor the surface chemical properties of semiconductor nanoparticles, including solubility and surface activity. The nanoparticles have been synthesized according to an established experimental procedure. Self-assembly of the charged clusters and dialkylammonium surfactants results in encapsulation and formation of discrete, hydrophobically encapsulated CdTe-clusters. Encapsulation enhances the fluorescence intensity and photochemical stability of the CdTe-nanoparticles.

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