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Assembly of modified CdS particles/cationic polymer based on electrostatic interactions

Mingyuan Gao, Xi Zhang, Bai Yang, Feng Li, Jiacong Shen *

Key Laboratory of Molecular Spectrum and Structure, Jilin University, Changchun 130023, People's Republic of China

Abstract

A stable CdS nanoparticle hydrosol was prepared upon addition of mercaptoacetic acid as a stabilizer agent. The carboxylic groups from the mercaptoacetic acid modified on the surface of the particles resulted in an anionic surface of the CdS particles. Using an ionene (I-6-Me-BF4) as the oppositely-charged species, the anionic CdS particles were intercalated based on electrostatic interactions. The UV–Vis and quartz crystal microbalance (QCM) results proved that the CdS nanoparticles were assembled successfully. The monolayer coverage was estimated to be about 39.8% by the QCM method.

Keywords: Modified CdS particles; Quartz crystal microbalance; Surface density; Surface coverage

1. Introduction

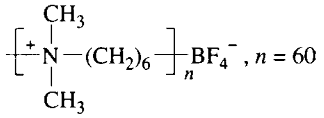
Considerable interest has been shown in recent years in the study of semiconductor nanoparticles because of their special properties caused by the quantum-size and surface effects [1,2]. Many methodologies have been developed in assembling the semiconductor nanoparticles in different matrices in order to form special functional materials [3–7]. The order structure of the semiconductor nanoparticles constructed by different molecular film methods has shown potential applications in molecular or supramolecular devices. It has been proved that the molecular deposition (MD) method via electrostatic attractions between oppositely-charged species is a successful method in organizing PbI_2 nanoparticles. The strong electrostatic attraction between the nanoparticles and the oppositely-charged parts not only stabilizes the PbI_2 nanoparticles but also guarantees a mono-molecular layer structure of the organic/inorganic alternating film during the deposition process [6,7].

In this paper, the results of assembly of CdS nanoparticles by the MD method are reported. The solubility product of CdS is greatly larger than that of the PbI_2, so it is very difficult to prepare CdS nanoparticles in water without the stabilizer agents at room temperature. In our experiment, a stable CdS nanoparticle hydrosol was prepared upon addition of mercaptoacetic acid as a stabilizer. Long-chain alkane thiols have been found to be useful in stabilizing quantum-size CdS particles in non-aqueous solvents [8]. While using the mercaptoacetic acid, the water-soluble CdS nanoparticles with carboxylic acid groups modified on the particle surface can be obtained [9], the ionized surface of the CdS nanoparticles is essential in organizing it using the MD method.

The CdS nanoparticles was observed with transmission electron microscopy (TEM). The multilayer structure of the organic/inorganic (CdS nanoparticles) was characterized by UV–Vis absorption together with the quartz crystal microbalance (QCM) method. All the results proved that an alternating multilayer was successfully constructed by the MD method.

2. Experimental details

The $CdCl_2$, Na_2S, 12-mercaptododecanemanine, 3-aminopropyltriethoxysilane and mercaptoacetic acid used were all analytical grade reagents. The ionene (I-6-Me-BF4) was kindly provided by Dr. Jianguo Wang, from MPI-Polymer Science, Germany, and its chemical formula is shown below.



$$\left[\overset{+}{N}(CH_3)_2-(CH_2)_6 \right]_n BF_4^-, \; n = 60$$

2.1. Preparation of the CdS nanoparticle hydrosol

A 50 ml solution of 1×10^{-3} M $CdCl_2$ was prepared, and to this solution a 50 ml solution of 2×10^{-3} M mercaptoacetic

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* Corresponding author.

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acid was added. Na_2S (6 ml, 1×10^{-3} M) was then injected with fast stir, resulting in a clear and yellow solution. Lastly, a stable yellow solution was obtained after being dialyzed for 24 h in a dialysis bag.

2.2. *Process of substrates with a cationic surface*

The quartz substrate covered with aminopropylsilane was prepared by treating with the vapor of 3-aminopropyltriethoxysilane as reported in the literature [10]. After reacting with HCl solution, a positive-charged quartz was obtained for further use. The silver electrode with an ionized surface for QCM detection was treated with 12-mercaptododecaneamine in alcohol solution for 24 h, then protonated by treating with dilute HCl solution.

2.3. *Preparation of an alternating multilayer structure*

The above-mentioned substrates with a cationic surface were immersed into the CdS solution for 0.5 h, after being washed with deionized water the substrate was covered with one layer of CdS nanoparticles. The substrate was then dipped into the I-6-Me-BF4 (1 mg ml^{-1}) solution for 0.5 h, then the second layer was added. The alternating multilayer structure was obtained by repeating the above procedure using the CdS solution and the I-6-Me-BF4 solution respectively.

2.4. *Preparation of the CdS sample for TEM detection*

The TEM sample of the CdS nanoparticles was prepared by dripping one droplet of the CdS solution onto a copper grid covered with a thin layer of Formvar and then blowing dry with N_2.

A photograph of the CdS nanoparticles from TEM and a photograph of the electron diffraction image were obtained with a HITACHI H 8100 transmission electron microscope. The UV–Vis absorption spectra were recorded on HITACHI 3100.

3. Results and discussion

It was proved by the IR method that the S–H vibration band located around 2 567 cm^{-1} in the spectrum of mercaptoacetic acid disappeared completely in the IR spectrum of CdS-modified nanoparticles, while the vibration band of C=O around 1 717 cm^{-1} in the spectrum of mercaptoacetic acid shifts to 1 572 cm^{-1}. This results implies that the mercaptoacetic acid was chemically modified on the surface of CdS nanoparticles and the COOH was in a state of COO^-, making it possible to use the surface-modified CdS nanoparticles as an analogous polyanionic compounds in the molecular deposition process.

By TEM method, the particle size of the surface-modified CdS nanoparticles was measured as 5.8 nm. The electron diffraction results indicated that the CdS particles are of cubic structure.

The UV–Vis absorption spectrum of the CdS hydrosol is shown as Fig. 1. That the absorption edge of the CdS nanoparticles is near 500 nm indicates that the size of the CdS nanoparticles is close to that of an exciton of bulk CdS semiconductor whose absorption edge is near 515 nm. The absorption spectrum with an absorption shoulder around 460 nm represents a typical UV–Vis spectrum of CdS nanoparticles reported elsewhere [1]. The absorption spectra of the alternating multilayer films with different numbers of layers are shown in Fig. 2. Because the I-6-Me-BF4 does not absorb visible light, the similarity of the absorption spectra of the alternating films to that of the CdS nanoparticles in the visible regime implies that the CdS nanoparticles were assembled in the alternating film successfully. The inset of Fig. 2 presents the plot of the absorbance at 340 nm, 400 nm and 461 nm as a function of the number of layers of the alternating multilayer films. As seen the absorbance increases linearly with the number of layers and the extrapolation of the linear lines passes through, or very close to, the zero point, which suggests that the opposite-charged species were deposited equivalently in different steps during the preparation process. Using Lambert's law $A = \epsilon l c$, where A is the absorbance and ϵ, l and c are the extinction coefficient, the thickness of absorption cell, and the concentration of the surface-modified CdS hydrosol respectively, one can calculate the surface

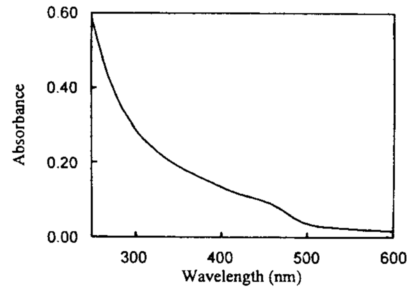

Fig. 1. The UV–Vis absorption spectrum of the CdS nanoparticle hydrosol, the concentration of CdS is 0.476×10^{-3} M.

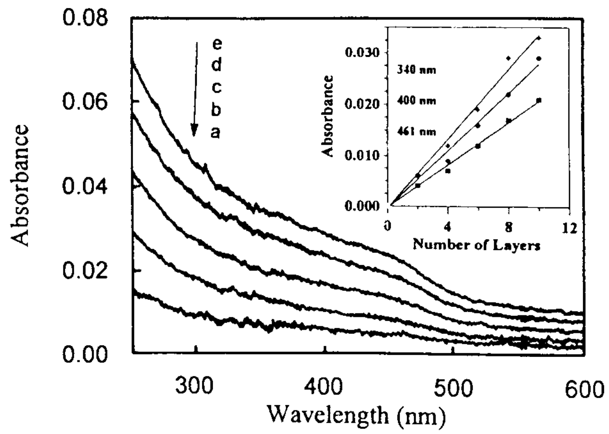

Fig. 2. The UV–Vis absorption spectrum of alternating MD films of CdS nanoparticles and I-6-Me-BF4 with (a) 2, (b) 4, (c) 6, (d) 8, (e) 10 layers. Inset: absorbance vs. number of layers at 340 nm, 400 nm, 461 nm.

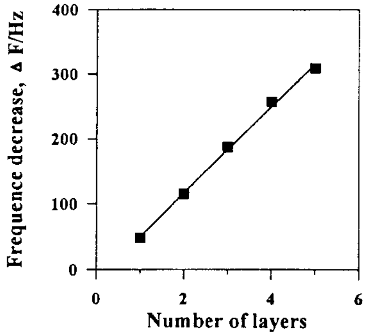

Fig. 3. The plot of the $\Delta F_{\mathrm{CdS\ nanoparticles}}$ caused by the deposition of one layer of CdS nanoparticles in different steps.

coverage $d_{\mathrm{surf}} = A\epsilon^{-1}$ [11]. The extinction coefficients calculated from Fig. 1 were 176 $\mathrm{M^{-1}\ cm^{-1}}$ ($\lambda(H_2O) = 461$ nm), 281 $\mathrm{M^{-1}\ cm^{-1}}$ ($\lambda(H_2O) = 400$ nm) and 424 $\mathrm{M^{-1}\ cm^{-1}}$ ($\lambda(H_2O) = 340$ nm) respectively. The surface densities obtained at different wavelengths from Fig. 2 were 1.153×10^{-8} mol $\mathrm{cm^{-2}}$ (461 nm), 0.9609×10^{-8} mol $\mathrm{cm^{-2}}$ (400 nm) and 0.7783×10^{-8} mol $\mathrm{cm^{-2}}$ (340 nm) respectively, resulting an average surface density of 0.9641×10^{-8} mol $\mathrm{cm^{-2}}$. Hence, the surface coverage was calculated as 38.7%.

The X-ray diffraction results provided other proof for the layer structure of the composite assembly: one diffraction peak around 1.3° (2θ) appeared for the multilayer structure, the d-spacing calculated as 6.8 nm and the thickness of one-layer ionene as about 1 nm.

The deposition process was also monitored by QCM which can detect the adsorption of the charged species on the silver electrodes with a precision of 1 ng. Fig. 3 shows the QCM frequency shift dependence of CdS nanoparticles layers. The linear relationship between $\Delta F_{\mathrm{CdS\ nanoparticles}}$ and the number of deposition layers also demonstrated the uniform depositing process. The mass change can be calculated by the following equation [12]:

$$\Delta F = \frac{-2F_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m$$

where ΔF (Hz) is the measured frequency shift per layer, F_0 is the parent frequency of QCM (6×10^6 Hz), Δm is the mass change (g), A is the electrode area (0.196 $\mathrm{cm^2}$ for one side), ρ_q is the density of quartz (2.65 g $\mathrm{cm^{-3}}$), and μ_q is the shear modulus (2.95×10^{11} dyn $\mathrm{cm^2}$). The average of $\Delta F_{\mathrm{CdS\ nanoparticles}}$ per layer was measured as 62 Hz. The average mass change on one side of the electrode was 140 ng, calculated by the above equation, which amounted to a surface coverage of about 39.9% using the density of bulk CdS for the nanoparticles. The surface coverage obtained by the UV–Vis method is 38.7% which is slightly smaller than that by the QCM method. This is comprehensible, because the mass change caused by the CdS surface binding mercaptoacetic acid cannot be detected by the UV–Vis method. Fig. 4 is the schematic drawing of the multilayer structure.

In conclusion, the modified CdS nanoparticles were synthesized and successfully organized into a multilayer structure. This may provide a new assembling methodology for CdS particle, which is of diversified properties, and for other nanoparticles with modified surfaces.

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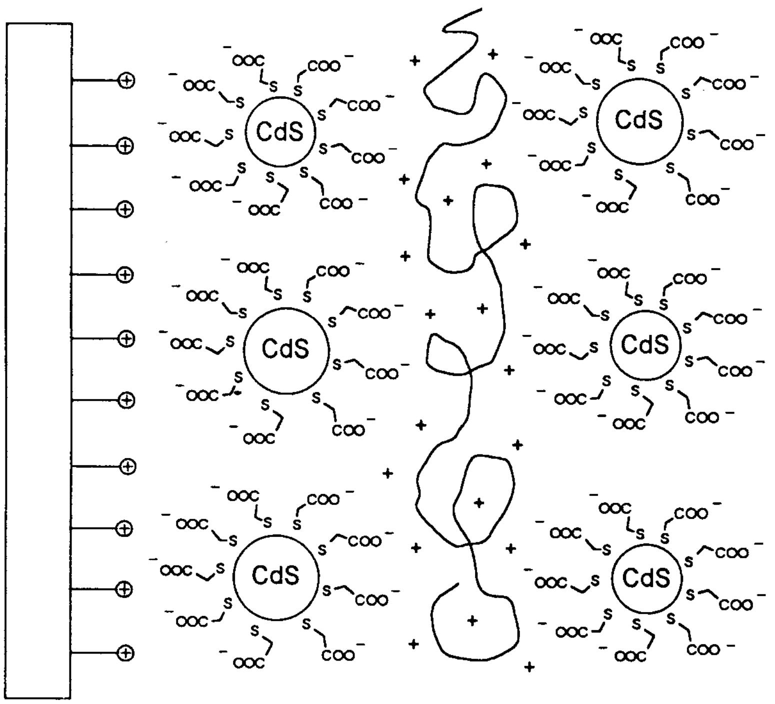

Fig. 4. Schematic illustrations of the alternating MD film of CdS nanoparticles and I-6-Me-BF4.

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