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# Rapid microwave synthesis of CdS quantum dots stabilized with 4,4′-bipyridine and dioctyl sodium sulfosuccinate

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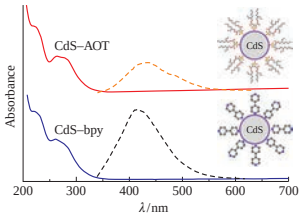
**A new rapid (5 min) microwave hydrothermal synthesis of CdS quantum dots stabilized with 4,4′-bipyridine and dioctyl sodium sulfosuccinate is proposed, and the influence of different capping agents on particles shape, size distribution and properties is discussed.**




Quantum dots (QDs) based on Group II–VI semiconductor materials are of interest due to their unique size-derived optical and electrical properties, which are readily exploited in photonics, photovoltaics and biomedicine.[1–3] These size-dependent properties remain in a focus of scientific studies on high-performance nanoclusters.[4] The properties of QDs can be tuned by surface modification, the reshaping of nanoparticles (NPs) and doping with admixtures.[5–7] Cadmium sulfide is a direct-band (2.42 eV) compound widely employed in solar cells and light sensors, photochemical catalysis, fluorescent labeling and drug delivery.[8,9] Methods for the synthesis of QDs[10,11] include the microwave (MW) heating of a reaction mixture to result in monodisperse nanostructures.[12]

A colloidal method for producing QDs is based on the mixing of water-in-oil microemulsions containing appropriate reactants within reversed micelles. A surfactant or capping agent is routinely added to the mixture preventing the coagulation of NPs. An oil-free reaction medium is favorable for a green chemistry approach. In this work, we used two capping agents for the mediation of particle growth in water solution. Dioctyl sodium sulfosuccinate (AOT) has two bulky alkyl tails and a negatively charged sulfonate group with the sodium counterion capable of forming micelles in water.[13] 4,4′-Bipyridine (bpy) is often used for constructing coordination compounds,[14] and it can serve as a bridging ligand to link metal ions (or clusters) or as a hydrogen bond acceptor. Both have been already employed for the synthesis of $Cd^{II}$ complexes.[13,14]

The MW-assisted solvothermal synthesis of CdS QDs as rod-like or spherical NPs (30–100 nm) from cadmium sulfate and thiourea in different solvents at 423 K in a time interval from 30 min to 6 h was studied.[15] Here, we present a new fast MW-assisted hydrothermal synthesis of CdS QDs from cadmium nitrate and sodium thiosulfate using AOT or 4,4′-bpy as a capping agent.[†] The samples of ~5 nm round NPs will be marked as CdS–AOT and CdS–bpy, respectively. In this work, the time of the synthesis of CdS QDs was only 5 min. In addition, we avoided the direct deposition of CdS using thiosulfate ions as a source of sulfur ions.

Figure 1 shows the TEM images of CdS–bpy and CdS–AOT samples. Dried CdS–bpy sample consists of slightly aggregated isometric polymorphs of 4.5–6.5 nm. They look more separated in comparison with oblate particles of about 4.7–6.2 nm immersed into thick shell in the CdS–AOT sample. The particle size distribution [Figure 1(*c*)] was plotted from the whole series of images. The XRD pattern [Figure 1(*d*)] exhibits three major reflexes at

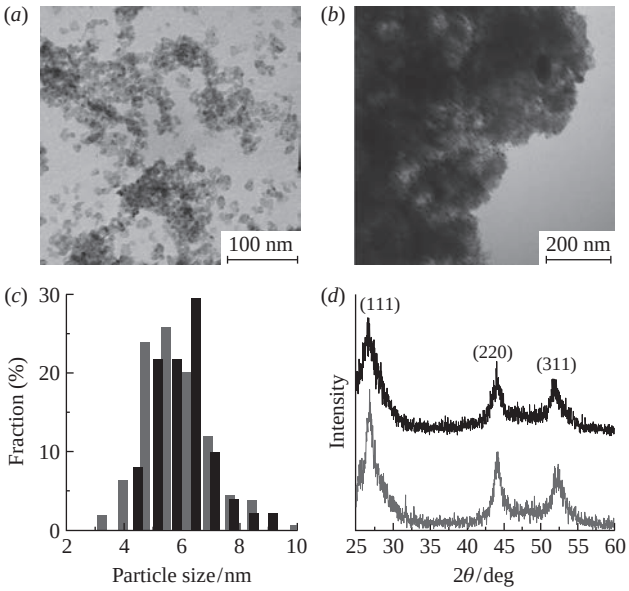



**Figure 1** TEM images for CdS QDs obtained with (*a*) bpy and (*b*) AOT; (*c*) particle size distribution histograms and (*d*) XRD patterns for CdS QDs with (black) bpy and (gray) AOT.

[†] All commercial reagents were of analytical grade, and ultra-pure water (18 MΩ cm) was obtained from a Simplicity UV system. Aqueous solutions of $Cd(NO_3)_2$, $Na_2S_2O_3$ and AOT ($C_{20}H_{37}NaO_7S$) or 4,4′-bpy ($C_{10}H_8N_2$) were taken in the molar ratio $Cd^{2+}:S_2O_3^{2-}$:AOT/bpy of 1:4:0.33. For each sample 5 ml of a 1 M solution of $Cd(NO_3)_2$ was mixed with 15 ml of a 1 M solution of $Na_2S_2O_3$. Then, 10 ml of an AOT or 4,4′-bpy solution was added. The mixture was homogenized with ultrasound upon heating. The reaction was performed in a MW oven (Discover SP, CEM, 2.45 GHz, 300 W) at 423 K for 5 min. After cooling the mixture to room temperature, the precipitate was collected by centrifugation and washed with water. Finally, the sample was dried at 333 K in air.

**Table 1** Particle size and lattice parameter for obtained samples.

| Sample | Particle size (TEM)/nm | Particle size (XRD)/nm | Lattice parameter $a$/Å | Cell volume $V$/Å$^3$ |
|---|---|---|---|---|
| CdS–AOT | 4.7–6.2 | 6.5 | 5.843(10) | 199.5(6) |
| CdS–bpy | 4.5–6.5 | 5.2 | 5.922(12) | 207.7(7) |

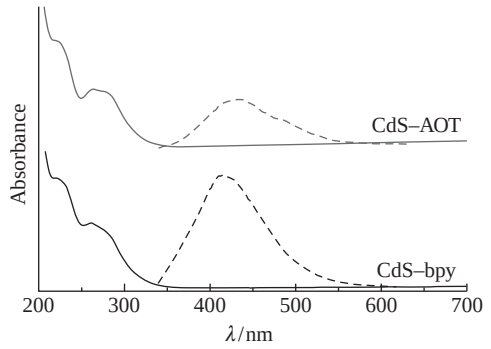



**Figure 2** UV-VIS spectra of CdS QDs obtained with (black) bpy and (gray) AOT. Dashed lines show luminescence with 340 nm excitation line.

2$\theta$ of 26.8, 44.1 and 52.2°. A further profile analysis‡ confirmed the presence of a single cubic phase (*F*-43*m*). The average diameter of crystallites was determined from the Scherrer equation[16] (Table 1). Synthesis without capping agents did not result in a single-phase sample.

Figure 2 shows the optical absorption and luminescence spectra of the colloidal solution of CdS QDs (excitation at $\lambda$ = 340 nm). The spectra have similar absorption band profiles at 220 and 260–280 nm. They are significantly blue shifted from the edge position for the bulk CdS (512 nm), evidencing strong confinement in NPs. The blue-shifted luminescence band at 420 nm (Figure 2) was stronger in the CdS–bpy sample.

To obtain information on the composition of shells surrounding CdS QDs, we measured FTIR spectra‡ (Figure 3). They inevitably contain the vibrations of water (bands at 3600–3000 and 1625 cm$^{-1}$) and $CO_2$ molecules (2350 cm$^{-1}$), which are present in air. The spectrum of CdS–bpy contains a sequence of clearly distinguishable bands at 3055, 1602, 1417 and 803 cm$^{-1}$ due to 4,4′-bpy molecules. In the spectrum of CdS–AOT, strong bands at 2923 and 2852 cm$^{-1}$ together with some other (1722, 1619, 1386 cm$^{-1}$) suggest the presence of AOT molecules in the sample. Both samples also exhibited bands at 1170 and 630 cm$^{-1}$ typical

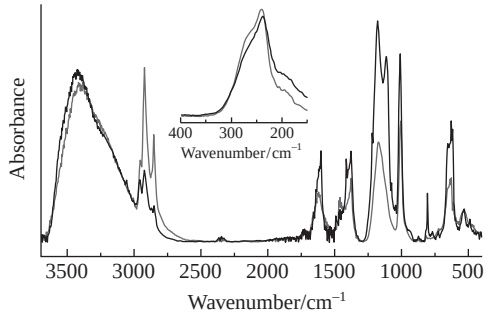



**Figure 3** FTIR spectra of CdS QDs obtained with (black) bpy and (gray) AOT. Inset: ATR Far-IR spectra of these samples.

‡ XRD patterns were collected on ARL X'TRA Powder Diffractometer (Thermo Scientific) using CuK$\alpha$ radiation. The Jana2006 package was used for profile analysis. TEM images were acquired on a JEM-2100 microscope (JEOL) operated at 200 kV. FTIR spectra were recorded on a Vertex 70 spectrometer (Bruker) equipped with a Platinum attenuated total reflectance (ATR) accessory. Diffuse reflectance (DR) UV-VIS spectra were obtained on a UV-2600 spectrophotometer (Shimadzu) in a sample diluted with $BaSO_4$.

of sulfate ions. The ATR-FTIR spectra (Figure 2) allowed us to appreciate Cd–S vibrations at 250 cm$^{-1}$ in a better way.

We assume the following reaction of particle formation:[17]

$$Cd^{2+} + S_2O_3^{2-} + H_2O \rightarrow CdS + SO_4^{2-} + 2H^+.$$

It is well known that cadmium ions can form complexes with 4,4′-bpy.[18] The formation of these complexes may be an intermediate step in the growth of CdS NPs. The free 5*s* orbital of the $Cd^{2+}$ ion and an unshared electron pair of nitrogen in 4,4′-bpy form a coordination bond, allowing 4,4′-bpy molecules to cover the surface of QDs. The hypothesis is supported by FTIR data (Figure 3), where the band at 464 cm$^{-1}$ can be attributed to Cd–N bond vibrations. The XRD analysis revealed that 4,4′-bpy molecules led to smaller particles as compared to those with AOT molecules. We believe that it is caused by a lighter weight and, therefore, a greater mobility of 4,4′-bpy molecules. After nucleation, these lightweight molecules can migrate faster to the surface of CdS particles and prevent their further growth and aggregation.

Moving to the case of AOT, one can expect that CdS QDs will be surrounded by surfactant molecules due to attraction between $Cd^{2+}$ surface ions and the head group of AOT. This is the only point for the strong bonding in the whole molecule, which has also long hydrocarbon tails covering the surface of NPs. The tails are unable to form strong bonds with either another CdS particle or another AOT molecule. Such a situation clearly favors the formation of separate particles without significant aggregation, and it is consistent with the experimental results.

Thus, the proposed rapid MW-assisted synthesis affords the single-phase crystalline CdS QDs of 4–6 nm capped with organic molecules. The use of 4,4′-bpy gives smaller NPs with stronger luminescence in comparison to those with AOT.

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