

Electrochemical Synthesis of CdSe Nanoparticles Using a Se-modified RVC Electrode and Mercaptoacetic Acid as a Stabilizer

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Semiconductor nanoparticles (NPs) are of fundamental and practical interest due to unique quantum size effects which result in strongly size dependent electronic, optical and electrochemical properties.¹⁻⁴ Among them, CdSe nanoparticles are of much interest because of applications in solar photo-voltaic cells, sensors and optoelectronic devices.⁵⁻¹¹ CdSe NPs have been extensively studied following the development of chemical preparation procedures using hot trioctyl-phosphine oxide (TOPO) as a capping agent.³ Unlike the original method which employed toxic dimethyl cadmium as a cadmium source, other researchers have developed a "green synthesis" route and they synthesized CdSe NPs using CdO as a precursor.¹²⁻¹⁴ While hot TOPO-based approaches require rather severe experimental conditions such as toxic chemicals and high temperatures, electrochemical methods can provide much more "green" environments.¹⁵⁻¹⁶ Recently, CdTe NPs have been electrochemically synthesized using a Te disc electrode.¹⁵ In this method, a Te disc electrode was cathodically polarized in the electrolyte containing Cd²⁺ and mercaptoacetic acid (MAA), which served as a stabilizer.¹⁵

We have developed a two-step method for the electrochemical synthesis of semiconductor films or particles.^{16,19} This approach is based on initial electrochemical modification of the substrate with the chalcogen. Subsequent electrochemical reduction of chalcogen in an aqueous electrolyte solution dosed with the desired metal generates compound semiconductor films on the substrate surface or particles in bulk solution with stirring. This approach has been successfully used for the synthesis of semiconductor NPs such as CdTe,^{16,22} and films such as FeS₂,²⁰ In₂S₃,²¹ CdS,¹⁸ CdSe,¹⁷ CdTe,¹⁹ and ZnTe.²³

Here we report the first example of electrochemical synthesis of CdSe NPs, in which particle size can be tuned by controlling heating time. In this study a RVC electrode was employed for the first time to synthesize CdSe NPs and this approach can be used for the synthesis of NPs in large quantities. Optical properties of NPs with different heating times were studied by absorption and photoluminescence spectroscopy.

Experimental

For voltammetry and film deposition, an EG&G Princeton

Applied Research (PAR) 273 instrument equipped with Model M250/270 electrochemistry software was used. The three-electrode cell was employed in the present work: a reticulated vitreous carbon (RVC, The ElectroSynthesis Co., Inc. 100 ppi) or a glassy carbon working electrode, a Pt wire counter electrode and a Ag/AgCl/3 M NaCl reference electrode. All potentials were quoted with respect to the Ag/AgCl/3 M NaCl reference electrode.

Cadmium sulfate hydrate (purity 98+%), selenium dioxide (purity 99.8%), mercaptoacetic acid (purity 98%), potassium chloride (purity 99+%), sodium hydroxide (purity 97+%) were obtained from Aldrich. All chemicals were used as received.

Absorption and photoluminescence spectra were recorded at room temperature with a Perkin Elmer Lambda 21 UV-Vis spectrometer and a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter, respectively. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100F field emission transmission electron microscope.

The Se-modified RVC electrode was prepared by holding a potential at -0.6 V in the electrolyte containing 50 mM SeO₂ and 0.1 M Na₂SO₄ for 1200 s (600 s for a glassy carbon electrode). Before electrodeposition, a RVC electrode was activated by cycling the potential 100 times between 1.44 V and 2.09 V in a concentrated H₂SO₄ solution with a scan rate 100 mV/s.²⁴ After rinsing the RVC electrode with a copious amount of H₂O, it was transferred into the 0.1 M KCl electrolyte containing 2 mM CdSO₄ and 4.8 mM MAA at pH 11 adjusted with 0.05 M NaOH solution. Pre-electrodeposited Se was reduced by scanning the potential from 0.0 V to -0.8 V with a 2 mV/s scan rate under the magnetic stirring. Electrolyte temperature was maintained at 50 °C. Thus synthesized NPs were kept in an oven at 70 °C for different time to change the size.

Results and Discussion

In a two-step approach for the synthesis of CdSe NPs, a pre-electrodeposited Se film on a reticulated vitreous carbon (RVC) electrode was electrochemically reduced in an electrolyte containing Cd²⁺ and MAA. The electrochemically generated Se²⁻ species reacted with Cd²⁺ in the electrolyte to produce

CdSe NPs in situ; these nanoparticles were stabilized by the MAA present in the electrolyte. The two-step method can be employed when pre-electrodeposited Se film is reduced before cadmium in the electrolyte is reduced.¹⁷ Therefore we first examined the electrochemical behavior of selenium and cadmium with linear sweep voltammetry (LSV). Figure 1A shows a linear sweep voltammogram for a glassy carbon electrode (GCE) in 0.1 M KCl electrolyte containing 2 mM CdSO₄ without (A1) and with (A2) 4.8 mM MAA. The pH of the solution was adjusted to 11 with 0.05 M NaOH solution. As shown in the figure, Cd deposition potential shifted more than ~400 mV with the addition of MAA. The chemistry of cadmium-MAA complexation and the potential shift in the electrolyte at pH 11 have been explained in detail by previous workers.¹⁵

Figure 1B shows a voltammogram for the Se-modified GCE in a 0.1 M KCl electrolyte containing 4.8 mM MAA. A Se film was pre-electrodeposited on the GCE at -0.6 V for 600 s using a 0.1 M Na₂SO₄ electrolyte containing 50 mM SeO₂. Selenium was reduced to selenide at ~-0.91 V, which is more negative than the potential corresponding to cadmium

deposition. As shown in the previous paper, CdSe films can be electrodeposited by a two-step method without a complexing agent like MAA.¹⁷ Note that MAA in this report acts as a complexing agent and a stabilizer at the same time. Figure 1 clearly shows that the two-step method can be utilized for the electrosynthesis of CdSe.

Recently, we reported that light illumination on the Te-modified electrode generated Te⁻ species, which reacted with Cd²⁺ ions to produce CdTe NPs with stirring.¹⁶ In this case, mechanical convection afforded formation of CdTe NPs in the bulk electrolyte, not on the electrode surface. Therefore, we employed magnetic stirring during the stripping of Se films in the 0.1 M KCl electrolyte containing Cd²⁺ and MAA. Note that a RVC electrode was employed for the electrodeposition of Se due to its higher surface area.

First, the RVC electrode was modified with selenium by holding a potential at -0.6 V for 1200 s in the electrolyte containing 50 mM SeO₂ and 0.1 M Na₂SO₄. Now, pre-electrodeposited Se was reduced in 0.1 M KCl electrolyte containing 2 mM CdSO₄ and 4.8 mM MAA at 50 °C by scanning potential from 0.0 V to -0.8 V with a 2 mV/s scan rate under the magnetic stirring. Electrochemically generated

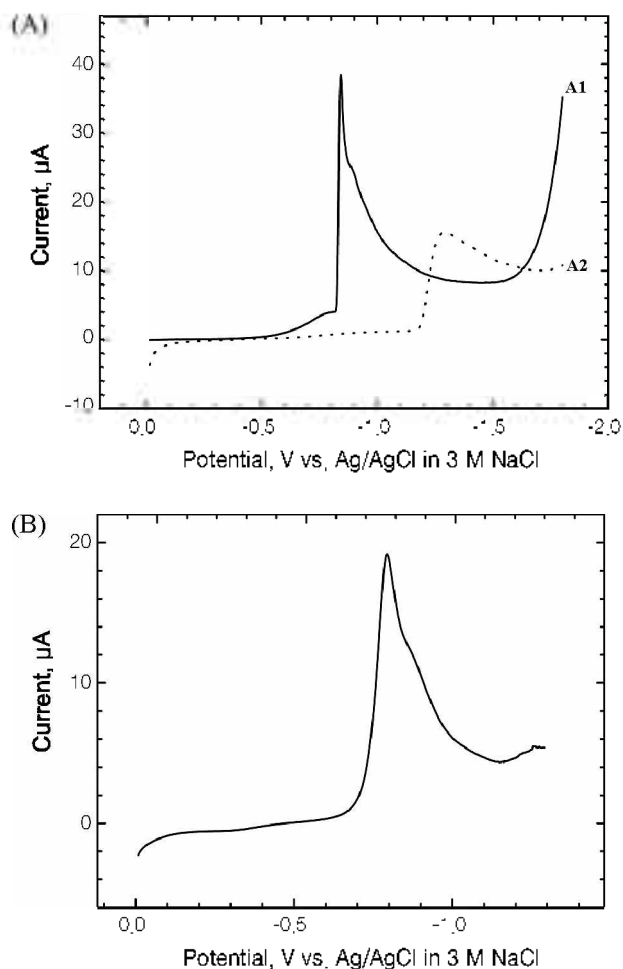


Figure 1. Linear sweep voltammograms for a glassy carbon electrode in a 0.1 M KCl solution (pH = 11) containing 2 mM CdSO₄ without (A1) and with (A2) 4.8 mM MAA. (B) A LSV trace for the reduction of pre-deposited Se layers in 4.8 mM MAA + 0.1 M KCl solution (pH = 11). The glassy carbon electrode was modified with Se at -0.6 V for 600 s using 50 mM SeO₂ in 0.1 M Na₂SO₄.

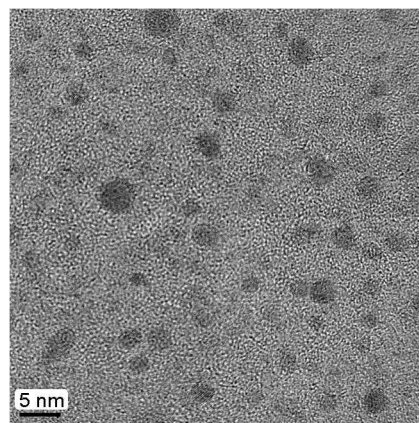


Figure 2. A TEM image of MAA-capped CdSe NPs after heating the synthesis solution at 70 °C for 1 h.

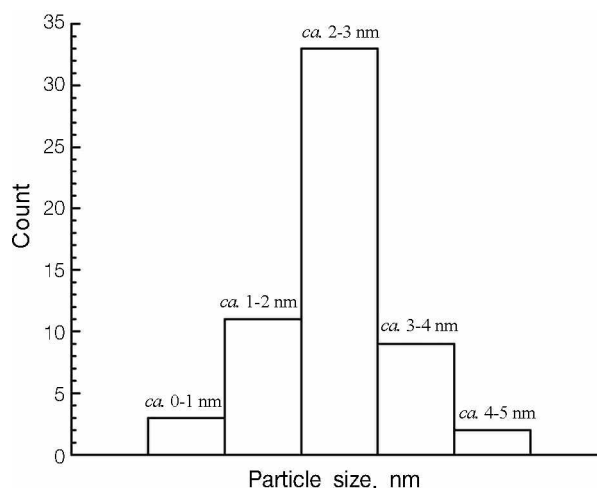


Figure 3. Histogram of particle size ranges from the TEM data in Fig. 2.

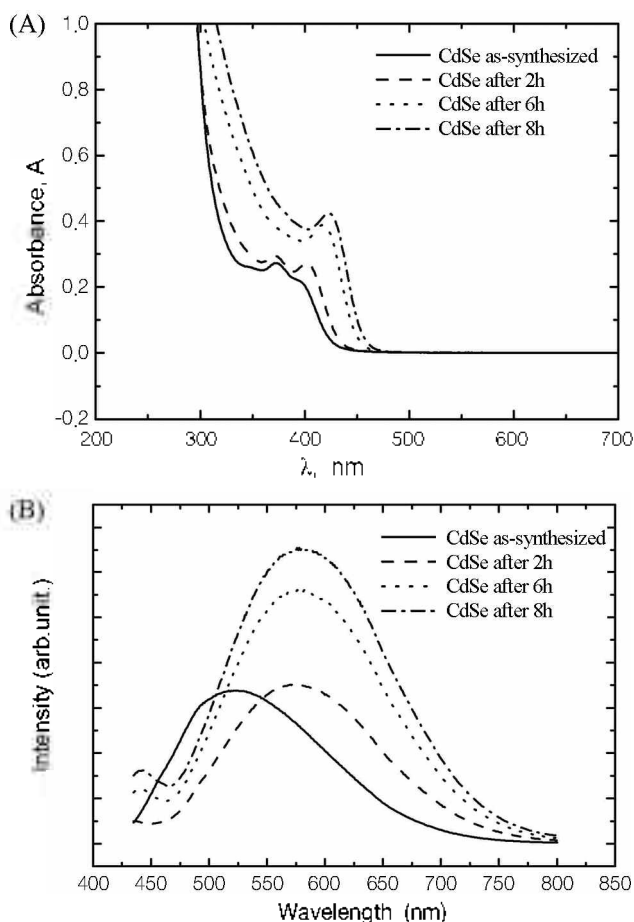


Figure 4. UV-Vis absorption (a) and PL spectra (excitation wavelength: 420 nm) (b) of MAA-capped CdSe QDs obtained at different heating times at 70 °C. Heating time is indicated in the figure.

Se²⁻ species reacted with Cd²⁺ ions to produce CdSe NPs in the bulk electrolyte in the presence of MAA. As synthesized CdSe NPs are polydisperse and irregular in shape (Figure 2). The TEM image shows that CdSe NPs are less than 5 nm in size and analysis of the particle size distribution yields the histogram in Fig. 3; 58 particles were measured and the highest population was in the 2–3 nm size range.

It is well known that semiconductor NPs with dimensions smaller than the bulk exciton Bohr radius exhibit unique quantum size effects and the absorption edges of CdSe NPs shift to higher energies from the bulk band gap (~1.7 eV, ~730 nm).^{3–4} Figure 4 shows typical absorption and photoluminescence spectra of CdSe NPs in H₂O. The size of NPs can be estimated from the absorption maximum.³ Also, this figure shows the development of the absorption and photoluminescence (PL) spectra of MAA-stabilized CdSe NPs as a function of time. As-synthesized NPs showed a main absorption peak at ~400 nm and a broad PL peak centered at 520 nm. The broad emission peaks confirm the polydispersity of the electrosynthesized NPs. With an increase of heating time at 70 °C, the absorption and PL spectral bands shifted to longer wavelength indicating an increase of particle size. Initially, the PL peak shifted more than 30 nm during the first 1 h and ~15 nm for another 1 h at 70 °C. After that, peaks shifted only ~15 nm for another 6 h. In addition, the full width at half

maximum (fwhm) increased from less than 150 nm to more than 160 nm with the heating time, which indicated that the NP dispersity had increased. However, absorption peaks shifted less than 30 nm for 8 h, which is less severe than the PL spectral case. Although it is difficult to elucidate the origin of the difference in spectral response, similar observations have been made in literatures.^{15,25} Data in Figure 4 clearly indicate that the band gap of CdSe NPs can be tuned by controlling the heating time.

In summary, we have been able to prepare CdSe NPs with a facile electrochemical method using a Se-modified RVC electrode in the electrolyte containing MAA and Cd²⁺ ions. The NP growth dynamics were monitored with UV-visible absorption and PL spectroscopy and we have shown that CdSe NPs with different sizes could be easily prepared by changing the heating time.

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