

“Multipulse” Electrochemical/Chemical Synthesis of CdS/S Core/Shell Nanocrystals Exhibiting Ultranarrow Photoluminescence Emission Lines

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Ensembles of sulfur capped, cadmium sulfide nanocrystals (CdS/S NCs) which exhibit photoluminescence (PL) emission line widths of 15–35 meV at 20 K have been obtained. These CdS/S NCs were synthesized using a new variant of the electrochemical/chemical (E/C) method: Cadmium (Cd⁰) NCs were first electrodeposited from an aqueous Cd²⁺ plating solution using a train of 8–10 ms plating pulses separated by ≈ 1.0 s “mixing” segments at the open circuit potential. These Cd⁰ nanoparticles were then oxidized to Cd(OH)₂, and CdS/S NCs were obtained by exposure of Cd(OH)₂ nanoparticles to H₂S at 300 °C. Ensembles of 200 000–400 000 CdS/S NCs prepared using this “multipulse” technique exhibited PL emission lines narrower than 35 meV. CdS/S NCs were also synthesized using the same E/C method except that a single Cd⁰ plating pulse was employed, and these CdS/S NCs exhibited PL emission line widths of 125–180 meV. TEM analysis of Cd(OH)₂ precursor particles confirms that the narrower lines obtained using multipulse Cd⁰ electrodeposition result from improved size monodispersity of the CdS core, which is attributed to the diffusional decoupling of Cd⁰ nanoparticles during growth.

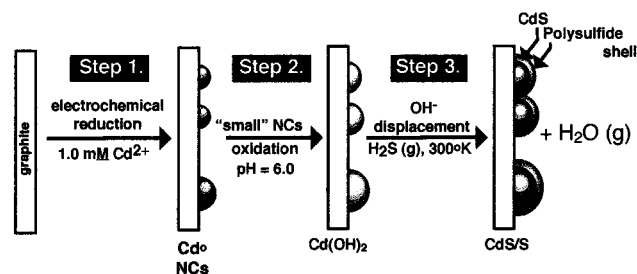
I. Introduction

Most of what is currently known regarding the size-dependent electronic properties of semiconductor nanocrystals has been learned by investigating suspensions of semiconductor nanocrystals which are narrowly dispersed in size (refs 1–5 are relevant review articles). These suspensions are usually obtained using variants of a technique pioneered in the 50s by Victor LaMer⁶ in which colloid particles are nucleated in a temporally discrete fashion, and then grown at diffusion control to the desired final mean diameter.⁷ This technique leads to very narrow particle size distributions because, as demonstrated by Reiss in 1954,⁸ small particles grow faster than larger particles.

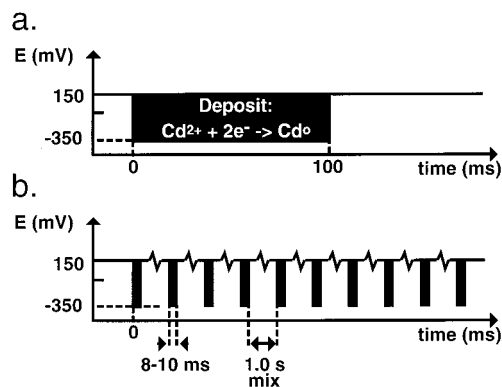
We have recently shown that this same strategy (i.e., instantaneous nucleation and diffusion controlled growth) does not lead to good size monodispersity for the growth of colloid particles on surfaces from solution-phase precursors.^{9,10} Brownian dynamics simulations¹¹ demonstrate that the growth of nearest neighbors on the surface are diffusively coupled, and the growth law for every particle is therefore based on the number and proximity of its neighbors, not simply on the diameter of the particle as in colloid suspensions. Ngo and Williams¹² have predicted that reduction or elimination of this diffusional coupling leads immediately to improved particle size monodispersity for particles which nucleate instantaneously.

In this letter, we describe a technique for dramatically improving the size monodispersity for cadmium sulfide/sulfur core/shell nanocrystals (henceforth CdS/S NCs) prepared on graphite surfaces using the electrochemical/chemical (E/C) method^{13–17} shown in Scheme 1. Improved size monodispersity was achieved by depositing cadmium precursor particles using

SCHEME 1. The Electrochemical/Chemical (E/C) Synthesis of CdS/S Core/Shell Nanocrystals



SCHEME 2. Two Voltage Pulse Programs Employed for the Electrodeposition of Cadmium Nanoparticles in This Work



a train of 8–12 ms deposition voltage pulses separated by 1–5 s “mixing” segments during which growth is suspended (Scheme 2b) instead of a single, longer deposition pulse (e.g., Scheme 2a). The effect of these shorter deposition pulses and mixing segments is to diffusively decouple the growth of densely nucleated regions on the graphite surface from sparsely nucle-

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ated regions.¹¹ Improvements in the size monodispersity of cadmium NCs translate into a narrowing of the PL emission lines for CdS/S NCs synthesized via the method of Scheme 1 using the multipulse approach, as well as increased spatial homogeneity of the mean size on the graphite surface. CdS/S NCs synthesized from cadmium NCs deposited using a single plating pulse exhibit photoluminescence (PL) emission line widths of 125–180 meV,^{13,14,16} whereas ensembles of $\approx 300\,000$ Cd/S NCs nanocrystals synthesized using the “multipulse” approach exhibit PL emission line widths of 15–35 meV.

II. Experimental Methods

CdS/S core/shell NCs were synthesized using the E/C procedure described previously.¹⁴ Briefly, the following three step procedure was employed: (1) Cd⁰ NCs which were narrowly dispersed in size were electrochemically deposited from an aqueous 1.0 mM CdF₂, 0.1 M NaF (pH \approx 6.2) plating solution onto a freshly cleaved graphite basal plane surface (the details of the Cd⁰ plating procedure are discussed in greater detail in the next paragraph); (2) Cd⁰ NCs spontaneously oxidized in the plating solution at open circuit (large Cd⁰ NCs having radii greater than 30 Å were incompletely oxidized); (3) the graphite surface was removed from the electrochemical cell, rinsed with Nanopure water, and transferred to a quartz tube furnace in which they were heated in flowing H₂S at 300 °C and atmospheric pressure for 10 min. As described in detail previously,¹⁴ this procedure yielded CdS/S core/shell NCs having a wurtzite core 17–50 Å in radius and a sulfur shell up to 30 Å in thickness. The size and monodispersity of the CdS core of these CdS/S NCs were determined by the corresponding properties of the Cd(OH)₂ (or Cd⁰) NCs which were deposited in step 1.

We make a comparison here between CdS/S NCs synthesized from Cd⁰ precursor particles deposited in a single 100 ms plating pulse (as shown schematically in Scheme 2a) and CdS/S NCs synthesized from Cd⁰ nanocrystals deposited using a train of 10 millisecond pulses separated by a second or more (Scheme 2b). In both cases, the deposition potential was –350 mV vs E^o_{Cd⁰/Cd²⁺}. When a train of 10 pulses was employed, the “mixing” potential (the potential applied between plating pulses) was near the rest potential for the surface and little or no current was detected. Photoluminescence spectra were acquired using the previously described spectrometer and procedures.¹⁴ Particles were sized using transmission electron microscopy (TEM), also as previously described.¹⁴

III. Results and Discussion

Cadmium nanoparticles were electrodeposited on graphite using either of two deposition waveforms: a single 100 ms plating pulse (i.e., Scheme 2a) or a train of 8 to 10 ms plating pulses separated by ≈ 1.0 s mixing intervals at the rest potential (Scheme 2b). Cd⁰ NCs were then permitted to oxidize at open circuit to Cd(OH)₂, and NCs of this intermediate were sized using TEM.¹⁸ Populations of Cd(OH)₂ nanoparticles synthesized using multiple plating pulses exhibited a relative standard deviation of the diameter, RSD_{diameter}, of 15 to 20%, whereas Cd(OH)₂ NCs synthesized using a single Cd⁰ deposition pulse have RSD_{diameter} values in the range from 30 to 50%. Cd(OH)₂ particle size histograms for two representative experiments are compared in Figure 1. The nucleation densities on these two surfaces were approximately equal: 2×10^9 cm⁻². The improvement in size monodispersity for the multipulse-grown Cd(OH)₂ can be attributed to decoupling of the growth between regions on the surface separated by a distance, r , which is

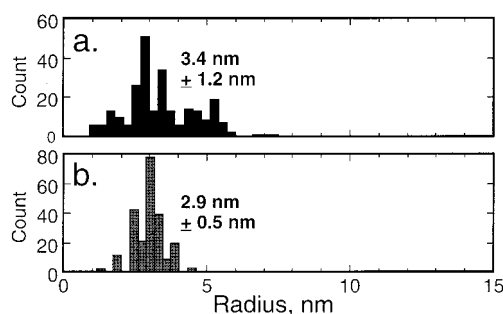


Figure 1. Histograms of Cd(OH)₂ NCs prepared by oxidizing metallic cadmium nanoparticles. The cadmium precursor particles were electrodeposited at –350 mV vs E^o_{Cd⁰/Cd²⁺} using either of two plating programs: (a) A single 100 ms deposition pulse or (b) A train of ten, 10 ms plating pulses separated by ~ 1 s.

brought about by growth pulses having a duration, $\tau = r^2/2D_{\text{Cd}^{2+}}$. For the plating pulse duration employed here of 10 ms, and the diffusion coefficient for Cd²⁺ of 2.4×10^{-6} cm² s⁻¹,¹⁴ $r \approx 2$ μ m.

We have recently shown¹⁴ that Cd(OH)₂ NCs prepared by electrodeposition can be converted on a particle-by-particle basis to CdS nanoparticles which are encapsulated in a sulfur or polysulfide shell (as shown in Scheme 1). Conversion to CdS/S core/shell NCs was effected by exposure of Cd(OH)₂ NCs to H₂S(g) at 300 °C for several minutes.¹⁴ Because every Cd(OH)₂ NC on the surface is converted into a CdS/S core/shell NC,¹⁴ improvements in the size monodispersity of the Cd(OH)₂ precursor particles should be immediately transferable to CdS/S NCs in step 3 of the E/C synthesis scheme. It has not so far been possible to resolve the CdS core of the CdS/S core/shell NCs by TEM so the size dispersion of the CdS core cannot be directly determined in this way.¹⁴

However, improvements to the size monodispersity of the CdS core should be immediately apparent from PL spectra of these CdS/S NCs since the emission line width is inhomogeneously broadened by particle size dispersion. Based on this fact, the expectation is that improved size monodispersity for the CdS core will translate into a reduced PL emission line width. This hypothesis is supported by the data shown in Figure 2. In Figure 2a, the PL spectrum for CdS/S NCs synthesized using a single, 100 ms Cd⁰ deposition pulse (spectrum “sp”) are compared with “multipulse” CdS/S NCs prepared using a train of 10×10 ms Cd⁰ deposition pulses (spectrum “x”). The PL emission lines in both spectra “x” and “sp” are blue-shifted from the CdS single crystal (spectrum “sp”) by ≈ 130 meV indicating that the mean diameter of the CdS cores are ≈ 42 Å.¹⁹ The line widths of these two spectra, however, are very different: The full width at half-maximum of the single pulse sample is 125 meV, whereas the line width for the sample prepared by multipulse deposition is 18 meV. A line width of 18 meV approaches the 15 meV line width which has been reported in two previous spectroscopic studies of *single* CdS nanocrystallites,^{20,21} but in Figure 2a, emission from a 200 μ m diameter area of the surface encompassing 200,000–400,000 CdS/S NCs was probed.

As shown in Figure 2b, the radius of the CdS core can be adjusted by increasing or decreasing the Cd⁰ plating pulse duration, while maintaining the decoupling time at 1 s. For example, the CdS/S NCs probed in spectrum “w” were synthesized using 10×8 ms Cd⁰ plating pulses. This spectrum exhibits a 150 meV blue shift (characteristic of a core radius of 39 Å) and a line width of just 15 meV. Increasing the pulse duration to 12 ms yields the CdS/S NC sample probed in

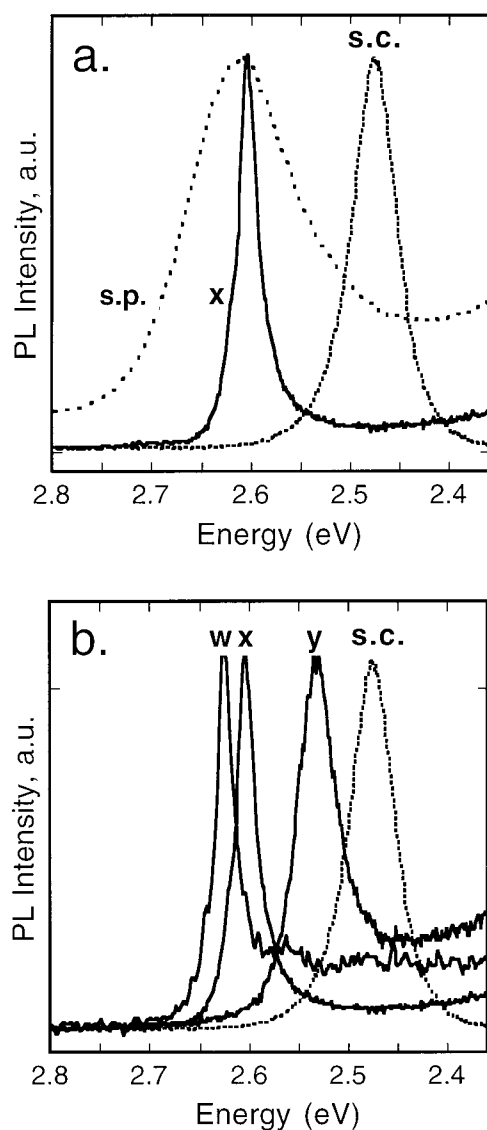


Figure 2. Photoluminescence spectra of CdS/S NCs on the graphite (0001) surface at 20 K using $h\nu_{\text{ex}} = 3.53$ eV. (a) Comparison of CdS/S NCs prepared from Cd⁰ NCs deposited using a single, 100 ms plating pulse (spectrum “sp”), multipulse CdS/S NCs deposited using a sequence of 10×10 ms Cd⁰ plating pulses (spectrum “x”), and a macroscopic (0001) oriented CdS single crystal (spectrum “sc”). (b) Comparison of three CdS/S samples prepared using the multipulse method with Cd⁰ plating programs of 10×8 ms (spectrum “w”), 10×10 ms (spectrum “x”), and 10×12 ms (spectrum “y”).

spectrum “y” having a blue shift of 58 meV (corresponding to a CdS core radius of 61 Å) and a line width of 35 meV.

It is readily possible to demonstrate that spectrum “sp” in Figure 2a is broadened as a consequence of particle size inhomogeneities. In Figure 3a, spectrum “sp” is again shown at the top together with three PL spectra which were acquired at three different 70 μm diameter areas located inside this larger 200 μm diameter region. Two effects caused by particle size inhomogeneity are observed in these three spectra: First, the emission line widths for the 70 μm diameter regions are narrowed from 125 to ≈70 meV, and, second, the energy of maximum emission varies for different 70 μm regions from 2.57 to 2.63 eV. On the basis of the predictions of the strong confinement model for CdS, we conclude that the mean radii of CdS/S NCs in these three 70 μm diameter regions differ by as much as 9–10 Å. These two “fingerprints” of size polydispersity are absent, or nearly so, at surfaces covered with CdS/S

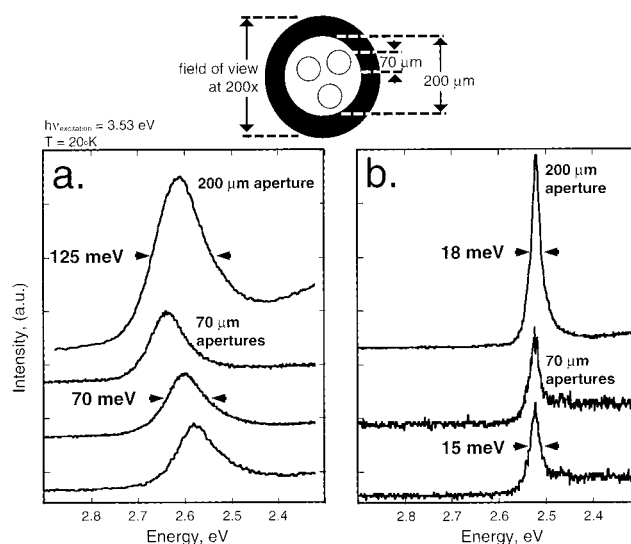


Figure 3. Photoluminescence spectra of CdS/S NCs on the graphite (0001) surface at 20 K using $h\nu_{\text{ex}} = 3.53$ eV involving the use of two different apertures (200 μm and 70 μm as indicated) for the acquisition of photoluminescence from the surface. (a) Spectra for the CdS/S NCs of spectrum “sp” in Figure 2a. (b) Spectra for the CdS/S NCs of spectrum “w” in Figure 2b.

NCs synthesized using the multipulse technique. In Figure 3b, for example, PL spectra from 70 μm regions of the graphite surface possess a line width of 15–18 meV which is comparable to the width seen for PL spectra of the “parent” 200 μm diameter region. The energy of maximum emission is identical to that of the parent spectrum.

As already noted, the PL emission line width seen for CdS/S nanocrystals synthesized using the multipulse technique approaches the line width observed for *single* CdS NCs in two previous studies: Guyot-Sionnest and co-workers²¹ observed PL line widths of 15 meV for CdS NCs having a diameter of 55 Å using two-photon excitation at 10 K, and Eychmüller and co-workers²⁰ measured PL line widths of 15 meV for 70 Å diameter CdS NCs at the same temperature (20 K) and excitation power densities (220 nW cm^{-2}) employed here. PL emission lines for multipulse CdS/S NCs (Figure 2b) did not exhibit phonon loss peaks which were also absent in the spectra of Guyot-Sionnest²¹ but which were observed in the spectra of Eychmüller²⁰ at moderate illumination intensities.

IV. Summary

We report a new E/C procedure for synthesizing CdS/S core/shell NCs involving the use of a train of 10 short 8–10 ms voltage pulses delineated by 1 s “mixing” periods to synthesize Cd⁰ precursor particles. Upon oxidation of these “multipulse” NCs to Cd(OH)₂, improved size monodispersity is evident in histograms of the Cd(OH)₂ precursor nanoparticles as compared with NCs synthesized using a single cadmium plating pulse of 100 ms. CdS/S core/shell NCs prepared from such Cd(OH)₂ precursors exhibit PL emission line widths of 15–35 meV. These PL emission line widths are much narrower than the PL emission lines observed for ensembles of CdS nanocrystals prepared using a single cadmium plating pulse, and are narrower than the PL emission lines seen in any previous study of this material to our knowledge. In fact, the line widths reported here approach the PL line width seen for a single CdS nanocrystallite in prior work.^{20,21}

The use of a train of short voltage pulses instead of a single longer pulse to synthesize cadmium NCs precursor particles is

effective because it minimizes the diffusional coupling between growing nanoparticles which leads to size dispersion for particles which are randomly nucleated on the surface.¹¹ Since neighboring Cd⁰ nanoparticles are separated by few hundreds of angstroms on average, a 10 ms pulse is much too long to diffusionally decouple these nanoparticles. The beneficial effect of these longer plating pulses may derive from the fact that the particle nucleation density fluctuations over distances of microns on the surface since in recent Brownian dynamics simulations of this nanoparticle growth process,¹¹ the mean particle diameter is inversely correlated with the local nucleation density. The PL microprobe data presented here indicate that these longer range fluctuations in the particle diameter are absent for samples of CdS/S core/shell NCs prepared using the multipulse technique.

On the basis of this analysis, further improvements in the particle size monodispersity should be obtainable using this approach simply by further reducing the pulse duration and increasing the number of pulses. Implementation of this multipulse strategy should permit similar improvements to be demonstrated for metal nanoparticles prepared by electrodeposition,^{9,10,22} and for nanocrystals of other semiconductors prepared using the E/C synthetic method.^{14,15}

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- (19) On the basis of the predictions of the Coulomb corrected strong confinement equation

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.786e^2}{\epsilon R} - 0.248E_{\text{Ry}}^*$$

the following materials parameters for CdS were employed for the strong confinement calculation: $e = 5.4$, $m_e/m_0 = 0.21$, $m_h/m_0 = 0.80$, where $m_0 = 9.11 \times 10^{-31}$ kg, E_g (20 K) = 2.56 eV, $E_{\text{Ryd}}^* = 29$ meV. Reference: Sze, S. M. *The Physics of Semiconductor Devices*, 2nd ed.; John Wiley & Sons: New York, 1969.

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