Electrochemistry of CdS Nanoparticles: A Correlation between Optical and Electrochemical Band Gaps

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This communication reports novel electrochemistry of cadmium sulfide quantum dots (Q-CdS) in *N,N*′-dimethylformamide (DMF). During the past two decades, semiconductor nanoparticles or quantum dots (QDs), in particular those of the cadmium chalcogenides, have attracted considerable attention due to their tunable electronic properties as a function of size—the so-called quantum size effect. Recently, TOPO (tri-*n*-octylphosphine oxide)-capped Q-CdSe has been used for stimulated light emission where the laser frequency was tuned through simple variation of particle size.[1] The photoelectrochemical[2] and photophysical[3] properties of these particles in their size-quantized states have been well-studied. However, there have been relatively few reports on the electrochemical properties of semiconductor QDs.[4,5] Using the "particle in a box" model, Brus[6] has predicted a dependence of redox potential on particle size for Q-CdS. However, to our knowledge, this model has not been tested by actual electrochemical measurements of QDs in solution, largely because of the limited solvent window of many solvent/electrolyte systems and the instability of the particles. Here this is considered, and we show a direct correlation between the electrochemical band gap and the electronic spectra of CdS nanoparticles in DMF.

Thioglycerol-capped, Q-CdS was chosen for study because stable monodisperse particles, which are readily soluble in DMF can be prepared relatively easily. We followed the method reported by Weller et al.[7] and as-prepared particles were size-selected[8] to obtain monodisperse (<10%) fractions. The final four fractions (six to ten, denoted **I**−**IV** hereafter) were chosen for further study, and these were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV−vis absorbance spectroscopy (Supporting Information). For the electrochemical measurements, CdS particle solutions were prepared in DMF with tetrahexylammonium perchlorate (THAP) as supporting electrolyte. All measurements were carried out in a helium-filled drybox, and the electrochemical properties of the dispersions were investigated by cyclic voltammetry (CV) at both Pt ($A = 0.062$ cm^2) and Au electrodes ($A = 0.3$ cm^2). A three-electrode configuration was used where a Pt coil and a silver wire
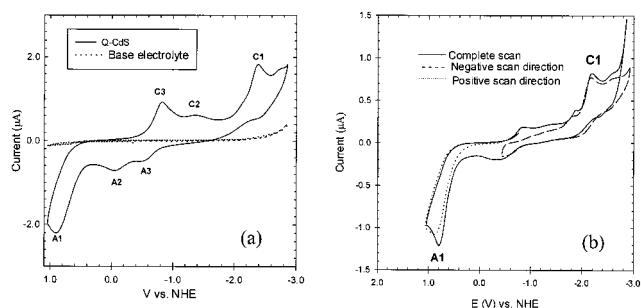

Figure 1. (a) CV response in the absence and presence of thioglycol-capped CdS Q-particles (1 mg/mL of fraction IV) at a Pt electrode. Sweep rate = 50 mV s^{-1} and [THAP] = 0.05 M. (b) Variation of the initial scan direction for IV illustrating that peaks A2, A3, and C3 are related to C1 and A1; sweep rate = 10 mV s^{-1}.
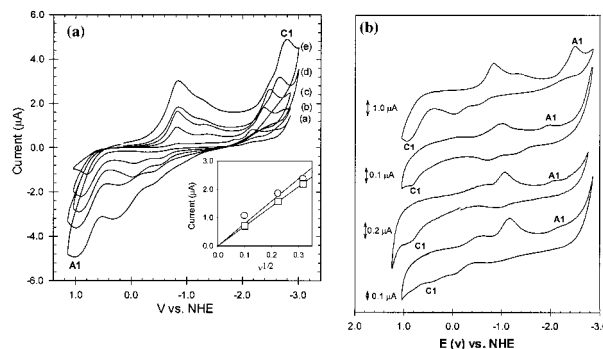

Figure 2. (a) Scan-rate dependence of the CV response for fraction **IV** Q-particles at a Pt electrode: ν = 10, 50, 100, 200, and 500 mVs^{-1}. Inset: linear dependence of peak currents for A1 ($\square$) and C1 ($\bigcirc$) on $\nu^{1/2}$ (to 100 mV s^{-1}). [THAP] = 0.05 M. (b) CVs illustrating the electrochemical band gap (A1−C1 peak separation) for fractions I−IV. Particles were added at 1 mg/mL for IV and to the saturation concentration (<1 mg/mL) for I−III. ν = 100 m Vs^{-1}

served as the counter and quasi-reference electrodes, respectively. The cell potential was normalized to NHE using the Fc/Fc$^+$ couple (with the potential of this couple taken as 0.47V vs NHE). The solubility of the particles in DMF was found to be inversely proportional to their size, and the final fraction (**IV**) (2.4 ± 0.3 nm diameter) was the most soluble. A typical CV for **IV** at the Pt electrode is given in Figure 1 where it is compared with the response for the supporting electrolyte alone (Figure 1a). Increasing the amount of Q-CdS added resulted in increases in all peak currents without significant shifts in peak potentials. An identical CV was obtained with a Au electrode. Clear oxidation and reduction peaks are apparent at -2.15 V (A1) and 0.80 V (C1), respectively. The additional peaks only appear on scan reversal after traversing either A1 or C1 (Figure 1b). To show that the CV response is due to redox reactions of a solution species rather than an adsorbed film, the dependence of peak current and potential on scan rate (ν) from 10 to 500 mVs^{-1} was also investigated (Figure 2a). The linear fit of peak current versus $\nu^{1/2}$ for peaks A1 and C1 up to 100 mV s^{-1} indicates diffusion of solution Q-CdS to the electrode surface. The peak position shifted with increasing ν, indicating kinetic effects. The current response for the other peaks was neither clearly proportional to ν nor $\nu^{1/2}$. The response was stable on repetitive scanning and for several days with no evidence of fouling on either electrode surface

The peak-to-peak separation between A1 and C1 is 2.96 V, a value comparable to the 3.23 eV (1s−1s transition) calculated from the electronic spectra (Supporting Information, Figure S1). Thus, these oxidation and reduction peaks can be correlated

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directly to electron transfer at HOMO and LUMO, respectively. Murray and co-workers have observed a similar correlation between the optical band-gap and the electrochemical potentials for quantized thiol-protected gold particles.[9] To the best of our knowledge, this is the first such correlation for semiconductor nanoparticles. For metallic particles, electron transfer to the core charges the sub-attofarad capacitance of the thiol cap produced current peaks at potential intervals, that is, charging of the metal core is quantized,[9] so-called quantized double-layer charging (QDL). The resulting single-electron-transfer reactions are reversible and limited by diffusion of the solution particles to the electrode surface. In contrast, here, the oxidation and reduction reactions are irreversible. In addition, taking into account the size of the particles and the concentration, the observed CV peak currents are about 2 orders of magnitude higher than expected for 1 e$^-$ transfer reactions for a diffusing solution species.[9] An approximate estimate based on size and diffusion coefficient of the particles suggests the passage of ca. 50 electrons/particle at the peak potentials. In light of this and the irreversibility for oxidation and reduction of Q-CdS, we propose an (EC)^n reaction, a multielectron transfer process where the electrons are consumed by fast coupled chemical reactions due to decomposition of the cluster. Essentially, the electron is scavenged immediately after injection into the particle, and unlike the case for thiol-capped metal particles, the Q-CdS can accept additional electrons at the same potential, giving rise to higher peak currents. The appearance of additional cathodic and anodic peaks in the middle of the potential window (A2, A3, C2, and C3) support this. As illustrated in Figure 1b, CVs recorded where the initial potential and direction of the scan were varied show that C1 reduction products are reoxidized at A2 and A3. Similarly, C2 and C3 are due to the reduction of oxidation products of CdS at A1. These can be tentatively be assigned to CdS/Cd^0 and CdS/S^0 couples.[10] The small shoulder apparent at ca. -1.8 V was insignificant at $\nu > 10$ mV s^{-1} (Figure 2a) and was thus neglected. This decomposition upon charge transfer to the particle can be viewed as the trapping of electrons (e.g., as Cd^0) and holes (e.g., as S) on the particle surface. Similar results were observed for PbS.[5] Thus, unlike quantized gold particles, Q-CdS is reactive and undergoes decomposition upon charging, acting as a source or sink of a large number of electrons at a single potential. In the recent report on the electrochemical properties of PbS nanoparticles,[5] the possibility of QDL was raised to interpret the observed voltammetric response, but as here, the authors propose that the peaks observed are instead due to redox reactions coupled with PbS decomposition. To observe QDL charging, semiconductor Q-particles need to be sufficiently stable to undergo electron transfer without associated following chemical reactions.

As the optical band gap is a function of particle size (Figure S1 Supporting Information), the electrochemical band gap should also decrease with increasing particle size. Thus, the electrochemical properties of the larger particle fractions, **I**−**III**, were investigated. As can be seen in Figure 2b, the voltammetric response obtained was similar to that found for fraction **IV**,

Table 1. Correlation of Optical and Electrochemical Band Gaps for Fractions I−IV Where ΔE Refers to the Peak Separation between A1 and C1

fraction	ΔE (V)[a]	ΔE (V)[b]	band gap (eV)[c]	size[d] (nm)
I	e	2.63	3.06	4.5
II	2.47	2.98	3.10	4.3
III	2.53	2.88	3.13	4.2
IV	2.96	3.39	3.23	3.9

[a] C1−A1 peak separation at 10 mV s^{-1}. [b] C1−A1 peak separation at 100 mV s^{-1}. [c] Estimated from UV−vis absorption peaks. [d] Estimated from electronic spectra.[6] [e] Peak not well defined.

although these studies were limited by the low solubility of the larger particles in DMF. There was clear evidence of kinetic effects, as for example, peak A1 for fraction **III** shifted to more positive potentials on repetitive scanning until it was no longer visible within the available potential window. On a qualitative level, the A1−C1 peak separations decreased with increasing particle size as predicted (Table 1). Some inconsistencies occurred with increasing scan rate (e.g., fractions II and III at 100 mV/s) and this is most likely due to the nature of charge transfer to Q-CdS particles (EC)^n. While the trend is consistent with the dependence of the optical band gap on particle size, as can be seen from Table 1, the electrochemical band gap obtained for these fractions is less than the optical band gap. Again the origin of this difference can probably be attributed to the fast following reactions which cause the peaks to shift to less extreme potentials. From the above studies,. we conclude Q-CdS can act as multi electron donors or acceptors at a given potential due to trapping of holes and electrons within the particle. Thus simple electrochemical methods clearly can provide useful information concerning the stability of Q-particles upon charge transfer, with the advantage of the QDs not being immobilized but rather freely diffusing in solution. For smaller Q-particles, there is an apparent correlation between optical and electrochemical band gaps despite decomposition,. Comparison of the responses for a variety of monodisperse Q-particles with a large difference in size with comparable solubility in the same organic solvent would enable more quantitative interpretation. This could be achieved by place exchange of thiol glycerol with a more hydrophobic alkane thiol,[11] improving solubility in nonaqueous solvents. Depending on the solvent/base electrolyte chosen, the upper limit for the available potential window for nonaqueous solvents is about 5 V; thus, the use of Q-particles with a smaller band gap would be more advantageous to study in terms of both stability and possible QDL phenomena. Work is continuing toward this goal.

Supporting Information Available: Absorption spectra, XRD, and TEM of Q-CdS, CVs and additional references (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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