PHYSICS, CHEMISTRY AND APPLICATION OF NANOSTRUCTURES, 2005

SIZE-DEPENDENT ELECTROCHEMICAL BEHAVIOR OF THIOL-CAPPED NANOCRYSTALS

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Electrochemical studies of thiol-capped semiconductor nanocrystals in an aqueous solution have demonstrated several distinct oxidation and reduction peaks in the voltammograms, with the peak positions being nanocrystal size dependent. It has been demonstrated that the method is very sensitive to the nanocrystal surface state, providing complementary information for better understanding of special optical properties of semiconductor nanocrystals.

1 Introduction

Strongly luminescing semiconductor nanocrystals (NCs) have found potential applications in bio-imaging [1], photovoltaics [2], LEDs [3], *etc.* Structural, photophysical and photochemical properties of the semiconductor NCs have been intensively studied [4,5], however, considerably less attention has been given to their electrochemical properties. Several reports have been devoted to the study of a correlation between the optical band gap of the NCs and the band gap estimated from the oxidation and reduction peak positions in cyclic voltammograms taken in non-aqueous media. A good agreement between electrochemical and optical E_g values for CdSe [6] and CdTe [7] NCs was found. At the same time, the electrochemical band gaps were found to be smaller than the optical gaps for CdS NCs [8]. The authors of the electrochemical studies noted that upon changing the particle size the reduction and oxidation peaks in the voltammograms were shifted in the direction predicted by theory [6-8].

Here we report results of electrochemical studies on CdTe NCs with different sizes and (or) different optical properties by use of cyclic voltammetry. The motivation for this research was to investigate the correlation between the electrochemical properties of CdTe NCs with different sizes and their optical properties and stability. The establishment of such a correlation in aqueous buffer solutions is of special interest for bio-applications of NCs and might also provide useful information on the surface of the NCs.

2 Methods

CdTe NCs stabilized by thioglycolic (TGA) or 3-mercaptopropionic (MPA) acids were synthesized and size-selected according to the procedure described previously [9]. Electrochemical measurements were done on Au electrodes with pre-adsorbed CdTe NCs in a buffer containing 0.1 M Na_2SO_4 and 0.02 M $Na_2B_4O_7$ (pH 9.2) in a three-electrode two-compartment cell with a Pt counter-electrode and an Ag|AgCl|KCl(sat.) electrode as the reference (+0.201 V vs. SHE).

The surface of the Au working electrodes was polished with diamond paste followed by a treatment in boiling concentrated HNO_3 and H_2SO_4. Then, the Au electrodes were washed with water and annealed at 700 °C. The cleaned electrodes were dipped into deaerated colloidal solutions of the NCs. This procedure results in the efficient adsorption of NCs on the electrode surface (Fig. 1). The NC-coated electrodes were then washed with buffer solution and transferred to the electrochemical cell under Ar atmosphere.

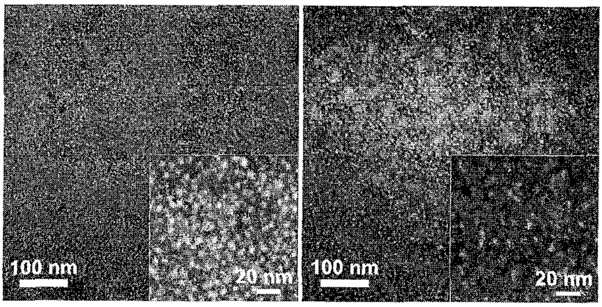

Figure 1. High-resolution SEM images of the surface of Au after adsorption of CdTe nanocrystals stabilized with TGA (left) and MPA (right). The mean particle sizes were 3.3 nm and 7 nm, respectively.

3 Results and discussion

Fig. 2(a) (dotted line) shows a cyclic voltammogram (CV) of the Au electrode in buffer solution. Oxidation of the gold electrode surface starts from 0.5 V with an anodic current peak at 0.67 V that gives a cathodic current peak at 0.36 V (C_3) during the reverse potential scan. When the potential of the Au electrode with pre-adsorbed NCs is swept from the open circuit potential (E_{OC}) in the positive direction (solid line), two distinct anodic peaks can be recorded in the potential regions from 0.3 to 0.4 V (peak A_1) and from 0.75 to 0.8 V (peak A_2). The peak positions depend on the CdTe NCs size. Fig. 2(a) also shows the first CV curve for the Au/CdTe electrode by scanning the potential in the negative direction from the open circuit potential (dashed line). A cathodic current peak C_1 is observed at about −1.2 V, which is associated with the reduction of the NCs. This peak is absent if the potential is initially scanned in the positive direction through the peaks A_1 and A_2.

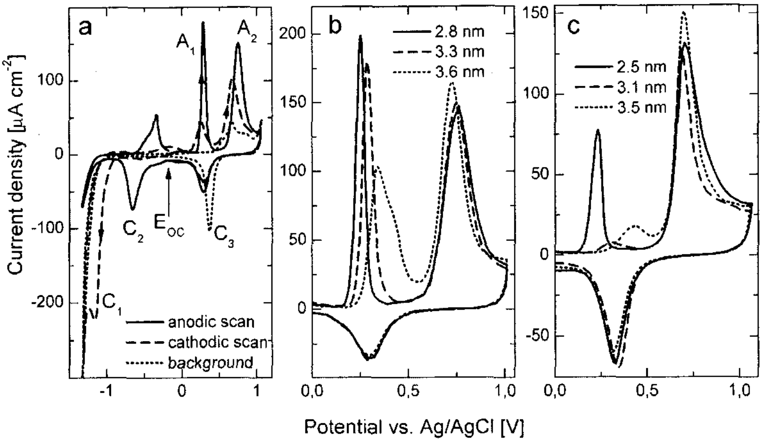

Figure 2. a) CVs of the Au electrodes with TGA-capped CdTe NCs in buffer solution. The potential sweep direction was -0.18 > 1.05 > -1.33 > -0.18 V (solid and dotted lines) and -0.18 > -1.33 > 1.05 > -0.18 V (dashed line). The CV of the bare Au electrode is shown as a dotted line; b,c) CVs of the Au electrodes with pre-adsorbed CdTe NCs of 3 different sizes capped with TGA (b) or MPA (c). The potential sweep rate was 20 mV s^{-1}.

Figs. 2(b and c) show the first CV curves of the anodic dissolution of TGA- and MPA-capped CdTe NCs of different sizes at the Au/CdTe electrode. The peak A_1 moves in the negative direction with decreasing the NCs size. At the same time, the position of the peak A_2 depends less on the NCs size than the position of the peak A_1. Since the positions of both the anodic and the cathodic (not shown) current peaks depend on the NC size, it was of interest to elucidate a relationship between electrochemical redox potentials and semiconductor band gap energies. The separation between the peaks A_1 and C_1 is 1.4-1.6 V, which is markedly smaller than the optical band gap of the CdTe NCs (2.0-2.3 eV) estimated from their spectra. At the same time, the A_2/C_1 peak separation correlates better with the optical gap, remaining slightly smaller than the latter value.

According to our expectation, the smaller CdTe NCs should be oxidized at more positive potentials and reduced at more negative ones than the larger NCs since the top of the valence band is shifted towards lower energies. The bottom of the conduction band is moved to higher energies with decreasing the particle size. Thus, the direction of the size dependent shift of the peaks A_2 and C_1 is in accord with this expectation. In contrast, the peak A_1 behaves abnormally, *i.e.* it shifts to the negative direction with decreasing the NC size. These observations allowed us to assume that the peak A_1 can be related to the oxidation of surface defects (most probably, surface Te atoms [9-11]) forming intra-band-gap surface states. The shift of this peak to more positive potentials with increasing the NC size indicates that the levels of Te-related traps move to lower energies when the NC size increases. The above-mentioned trend may explain the higher photostability of the larger NCs.

Whereas the detailed mechanism of the electrochemical oxidation of the CdTe NCs remains largely unknown at the moment, the anodic peak A_2 is most likely to be due to the oxidation of the rest of the CdTe core. Since the peak A_2 shifts only slightly in the positive direction with decreasing the NCs size, the electrochemical band gap calculated as a A_2/C_1 peak separation is less than the optical band gap especially for the smallest NCs. This can be attributed to a multielectron transfer process where the electrons (or holes) are consumed by fast coupled chemical reactions due to decomposition of the particles [7]. A total reaction involves several consecutive steps and the redox potential of the rate-limiting step may be different from that of the total reaction.

4 Conclusion

Electrochemical studies of thiol-capped CdTe NCs in an aqueous buffer solution have demonstrated several peaks in the CV, with the peak positions being NC size dependent. While the size-dependence of the reduction (C_1) and oxidation (A_2) potentials can be attributed to moving the energetic band positions owing to the quantum size effect, an extraordinary behavior was found for the oxidation peak A_1 observed at less positive potentials. This peak was assigned to the oxidation of Te-related surface traps. The results obtained indicate that the energy levels of these traps are shifted to lower energies as the NCs size increases, allowing thus to explain the higher photostability of the larger NCs.

Authors thank A. Eychmüller for fruitful discussion.

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