The Solid-State Electrochemistry of CdS and Cu(I)-Doped CdS Nanocrystals

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Cadmium sulfide (CdS) is one of the typical inorganic semiconducting compounds employed in the investigation of the physical properties of the nanoparticles and the application in the optoelectronic devices.1,2 Nanosized CdS particles are very interesting because the band structure of CdS nanoparticles is tunable with the size/shape and chemical composition of the nanoparticles.3-6 It could be p-type semiconductor transited from n-type if it is doped with copper, which extends the application of CdS nanomaterials.7-10 CdS and doped CdS nanoparticles have been widely investigated and reported to be the light emitter in the quantum dot LEDs,11-14 the electron acceptor CdS nanoparticles have been widely investigated and reported to be the cells,19 and etc.20-25

The band structure of CdS nanoparticles, as well as other semiconducting inorganic nanoparticles, can be determined by electrochemical measurements, e.g. cyclic voltammetry, coupled with other techniques.26-30 Usually, the electrochemical measurements were conducted in the solution of the nanoparticles. The evaluation of the band structure is, however, limited by the electrochemical window/stability of the nanoparticles, as well as the band structure from the liquid might introduce deviation in understanding the mechanism of the operating devices. The band structure derived from the solid-state CdS particles is thereby plausible. The band structure from the solid-state electrochemistry of CdS particles, includes the deviation between the band structures from the liquid and solid, should be investigated.

In this paper, the solid-state electrochemistry of CdS and Cu(I)-doped CdS nanoparticles are presented. The redox behavior and the electrochemical stability of the nanoparticles, as well as the band structure derived from the electrochemical measurements, are discussed from the viewpoints of counterion diffusion, electrochemical reversibility of the redox couples, and coupled electrochemical/chemical(EC) mechanism of the following chemical reactions after the electrochemical redox reactions.

Results and Discussion

The CdS nanoparticles are not electrochemically active, as shown in Fig. 1a, while the mixture of CdS nanoparticles and TBAF, the solid supporting electrolyte, exhibits redox behavior as the potential scans. The oxidation of CdS begins at −0.50 V, and shows saturation at around 1.0 V. The reverse scan results the two reduction processes, one reduction peak at −0.31 V and another one at −0.51 V. The clear oxidation of CdS is nearly undistinguishable in the consequent potential scan, and the reduction peak current at 0.31 V decreases, which indicate the loss of the electrochemical activity of CdS nanoparticles. When the potential scan ranges from 0.0 V to 0.9 V, there is no conservation of electrochemical activity observed yet, as shown in Fig. 1b, the peak current of both the oxidation and reduction decreases with the potential scan. Fig. 2 shows the second reduction peak (at −0.51 V shown in Fig. 1a), shifts from −0.51 V to −0.15 V due to the change of the potential scan window, appears only when the CdS is oxidized, is not fully responsible for the loss of the electrochemical activity of CdS reasonably. As reported, CdS is not electrochemically active.26 S 2 tends to be oxidized to S 0, and Cd 2+ , reduced to Cd 0. Accordingly, this second reduction comes from the reduction of Cd 2+ and S 2 species. However, this reduction process is not reversible, which contributes to the continuous loss of the electrochemical activity. The EC mechanism in the electrochemistry of CdS is proposed to explain the origin of the derived peaks other than the redox peaks which related directly to the frontier orbitals (HOMO and LUMO) of CdS and 1:7.1 determined by the inductively-coupled plasma optical emission spectrometer (ICP-OES), which are denoted as CdS:Cu(I) (9:1) and CdS:Cu(I) (7:3), respectively. The average diameter of CdS and CdS:Cu(I) is less than 5 nm with a narrow size distribution.

Home-made integrated electrode of three electrodes sealed in epoxy was used in the solid-state electrochemical measurement. The electrode structure is the same as reported before.32 The working electrode was platinum disk with a diameter of 80 micrometer. The reference electrode and counter electrode were silver disk and platinum disk of 1 mm in diameter. Before the CdS nanoparticles solution with TBAF (tetraethylammonium hexafluorophosphate, used as the supporting electrolyte) was dropped on, CdS:Cu(I) mixtures were further dried with air blow to ensure the removing of residual water for measurements.

The electrochemical measurements were conducted on CHI 750D. In the AC impedance, the amplitude was 5 mV, the frequency ranged from 10 kHz to 1 Hz. In the square wave voltammetry, the potential step is 0.04 V with the amplitude of 25 mV and the frequency of 15 Hz.

Experimental

CdS and CdS:Cu(I) nanoparticles were prepared using a one-pot reaction according to previous report.31 These nanoparticles are soluble in most organic solvents, such as chloroform, hexane, tetrahydrofuran, etc. Herein, the original molar ratio of Cu(I) to Cd is 0.5:9.5 and 3:7, resulting in the actual molar ratio of Cu(I) to Cd of 1:35.2...
nanoparticles. The oxidation peak shifts positively, while the reduction peak shifts negatively, the peak potential separation enlarges during the continuous potential scan. This means that the electrochemical reversibility of CdS decreases, in addition to its electrochemical activity loss. In the solid-state electrochemistry, the diffusion of any species is highly restrained. The electrochemically generated and EC produced species remain at the surface of CdS nanoparticles. The electrochemical reversibility and activity of these species affect the redox process of CdS obviously. Thereby, the redox behavior and the loss of electrochemical activity of CdS can be attributed to the covering of the inactive species on the CdS nanoparticles.

Fig. 3 presents the square wave voltammogram of CdS nanoparticles. Both the oxidation and the reduction, from the HOMO of CdS, show plateau rather than peak, which might reflect the nature of multielectron transfer in the redox of CdS. However, this result shows clear the electrochemical quasi-reversibility of CdS.

In order to understand the movement of ions in the mixture of CdS and TBAF and the electrode kinetics, AC impedance measurements were conducted at different potentials. As shown in Fig. 4a, the impedance spectrum at 0.0 V gives a charge transfer resistance in high frequency range and Warburg impedance which demonstrates the diffusion of electrolyte counterions. The charge transfer resistance increases with the bias potential, but the diffusion of counterions will not affect the electrochemistry when the potential is high as 0.60 V, the electrochemistry is controlled by the charge transfer process. The observation of charge transfer semicircles at 0.0 V and 0.3 V in the Nyquist plot is confusing because CdS is not subjected to redox process. When the impedance spectra are inspected in the form of Bode, we can notice there are two possible charge transfer resistance in the high frequency range, e.g. at 0.0 V, as shown in Fig. 4b. By fitting, the equivalent circuit, also given in Fig. 4, is found to be composed of a Ru (uncompensated, bulk resistance), a Randle subcircuit, and another serial subcircuit containing a Warburg element. The phase 1 in the range over 15 kHz could be from the surface state of CdS nanoparticles, and it does not change with the bias potentials. Phase 2 is directly related to the distinguishable semicircle, charge transfer resistance, in the Nyquist plot. The charge transfer resistance increases when the bias potential was set from 0.0 V to 0.3 V, At 0.3 V, for example, the CdS is polarized (positively charged), the polarized CdS may have enhanced interaction with the capping molecules, n-dodecanethiol, because the –SH group of n-dodecanethiol is electron-rich. This interaction can be further enhanced or weakened under AC perturbation. The binding/unbinding of electron-rich –SH groups to the polarized nanoparticle surface under AC perturbation behaves like charge transfer process, which leads to charge transfer responses in the AC impedance spectra. In addition, there is no electrochemical reaction in such an electrochemical window. We here tend to propose that the phase 2 in the range from 100 Hz to 15 kHz may correspond to the binding of capping molecules to nanoparticles. The increase of the charge transfer resistance of phase 2 with the bias potentials probably indicates the binding/unbinding difficulty of the capping molecules to the nanoparticles. As the bias potential was set in the oxidation range of CdS, the contribution of the redox reaction to the charge transfer semi-circle is not distinguishable from the phase 2, but the semicircle enlarges at higher bias potentials than 0.3 V. However, the disappearance of clear Warburg impedance indicates the suppressed diffusion of counterions at 0.6 V, which means that the electrode kinetics of the oxidized CdS is mainly controlled by the charge transfer process, little counterion diffusion contribution to the kinetics is observed.
When CdS is doped with Cu\(^+\), the oxidation of CdS:Cu(I) (19:1) nanoparticles begins at \(\sim 0.55\) V in the cyclic voltammetry, as seen in Fig. 5. There are two oxidation processes peak at 0.80 V and 1.18 V. Further oxidation at higher potentials introduces a loop, a sign of new phase formation on the electrode,\(^{32,39}\) which is not so clear so far that what the cause is. These oxidation processes are not reversible electrochemically. The following reduction gives a broad peak at \(-0.2\) V and another irreversible reduction process starts at \(\sim -0.6\) V. It is noticed that, in the second scan, a new peak at 0.36 V appears. Apparently, this new electrochemical reaction relates to the reduction process of CdS and coupled chemical reactions only. The oxidation at 1.18 V is not observable anymore. When the potential scan was limited to 1.2 V, the oxidation of CdS:Cu(I) (19:1) at 1.18 V is observable for many cyclic scans. This indicates that the loop at high potential is relative to the overoxidation of this oxidized state. The decrease of the reduction current, as well as the oxidation current in the second scan and the 3rd scan indicates clearly the loss of the electrochemical activity of CdS:Cu(I) (19:1) nanoparticles.

Figure 4. (a) The Nyquist plot of CdS nanoparticles at different potentials, and the equivalent circuit obtained from the fitting; (b) Bode plot of CdS at 0.0 V, as an example (dot: the phase, square: the impedance). The solid line is the fitting results based on the equivalent circuit.

Figure 5. The electrochemical behavior of CdS:Cu(I) (19:1) nanoparticles in the cyclic voltammetry. The scan rate is 50 mV/s.

When the potential scan starts from 0.0 V to \(-0.6\) V, CdS:Cu(I) (19:1) nanoparticles show irreversible reduction, and then the reduced species can be oxidized at \(\sim 0.08\) V and \(\sim 0.36\) V (see Fig. 6). Along with the potential scans, the peak current of these two oxidation increases. Very small cathodic current at \(\sim 0.0\) V is observed, which means that the reduction at \(-0.2\) V in the cyclic voltammetry, see Fig. 5, comes from the oxidation rather than the reduction of CdS:Cu(I) (19:1) nanoparticles.

In order to reveal the Faraday current in the electrochemistry of CdS:Cu(I) (19:1), the square wave voltammetry was also conducted.\(^{40}\) The potential first scans from 0.0 V to 1.2 V, which results in two clear oxidation peaks at 0.73 V and 1.10 V, as shown in Fig. 7. The following scan was then conducted immediately from 1.2 V to \(-0.6\) V. This process gives two neglectable and tiny cathodic peaks around 0.0 V. Finally, the potential scans from \(-0.6\) V to 1.2 V. The clear four oxidation processes are consistent with the results from cyclic voltammetry. The square wave voltammetry on CdS:Cu(I) (7:3) shows similar voltammetric behavior as that of CdS:Cu(I) (19:1), which can be found in Fig. 8, though that origin of small oxidation peak at 0.33 V, probably from the impurity or surface state, remains unclear. Compared with Fig. 7, it is noted that the peak current ratio between the oxidation at 0.76 V and 1.12 V of CdS:Cu(I) increases from 1.26 to 1.75 as the copper content increases from 1:19 to 3:7. The reduction peak of CdS:Cu(I) (7:3) at \(-0.18\) V is more pronounced. These indicate that the oxidation occurs at 1.12 V, indicated in square wave voltammogram, origins mainly from the oxidation of Cu\(^+\) to...

Figure 6. The cyclic voltammetric curves of the potential scans from 0.0 V to negative confirms the appearance of the two peaks at \(+0.1\) V and \(+0.35\) V are from the reduction of CdS:Cu(I) (19:1). The scan rate is 50 mV/s.
Cu\(^{2+}\), the cathodic process at ~0.18 V is the reduction of these oxidized species. The anodic processes at ~0.0 V and ~0.4 V are attributed to CdS/S\(^0\) and CdS/Cd\(^0\).

We have shown here, by the solid-state electrochemistry, that the CdS and Cu(I)-doped CdS are actually unstable electrochemically. The disappearance of reduction peak current at 0.31 V in Fig. 1, compare with the voltammetric curves in Fig. 5, indicates CdS:Cu(I) is extremely sensitive to the oxidation. The daughter products of CdS decomposition are electrochemically active but not reversible, in contrast to that of CdS:Cu(I). The introduction of copper into the CdS matrix affects the electrochemical reversibility of the CdS. The redox processes of CdS and CdS:Cu(I) have to be subjected to the decomposition of the cluster, oxidation/reduction, coupled chemical reactions, and etc. The electrochemical inactive species generated on the electrode will not diffuse away as it happens in the liquid electrolyte, which impedes the electrochemical measurements. This brings great difficulty in determining the band structure of CdS and CdS:Cu(I) by electrochemistry in the solid state, especially for the evaluation of LUMO levels. However, the HOMO levels, or the valence bands, of CdS and CdS:Cu(I) can be obtained reliably through cyclic voltammetry. Though CdS and CdS:Cu(I) give different electrochemical behavior, the HOMO levels, which are derived from the onset potential of the oxidation in the cyclic voltammetric curves, are the same, 0.50 V. Here, we use onset oxidation potential of ferrocene (mixed with TBAF) in solid as the reference, rather than the redox potential of ferrocene in liquid electrolyte. Given the onset potential of solid ferrocene is 0.40 V, and the ionization potential of ferrocene is 4.80 eV, the HOMO level of CdS, as well as CdS:Cu, is 4.90 eV. This value is obtained in the solid state of CdS nanoparticles, and the experimental environment is very similar to that of CdS in the devices. It is suggested that this HOMO level value can be used in the construction of new devices with CdS nanoparticles reasonably.

Conclusions

The redox reactions of the CdS and CdS:Cu(I) nanoparticles are electrochemically quasi-reversible and irreversible respectively. The loss of electrochemical activity of the nanoparticles is due to the decomposition occurred in the electrochemical measurements. CdS:Cu(I) is more unstable than CdS electrochemically besides the coupled chemical reactions. The decomposition of nanoparticles during the electrochemical reduction leads to the infeasibility in determining LUMO level by solid-state electrochemistry. However, the HOMO levels of CdS and CdS:Cu(I) nanoparticles are 4.90 eV from the cyclic voltammetry reliably.

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References