— Headline —

Electrochemistry of Size-quantized Semiconductor Nanoparticles

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The preparation and photoelectrochemical properties of various kinds of size-quantized semiconductor (Q-Sc) nanoparticles are described. The charge transfer across the Q-Sc particles is quantitatively discussed in terms of the size quantization and the effects of the surface modifiers on Q-Sc. Finally a novel technique of photoetching of Q-CdS particles is described as an effective means of the preparation of monodisperse Q-CdS particles.

Key Words : Semiconductor Nanoparticles, Electron Transfer, Size Quantization, Photoinduced Reactions

1 Introduction

Studies on chemistry and physics of size-quantized semiconductor (Q-Sc) nanoparticles emerged in the middle of 1980s from a purely scientific point of view.¹⁻³⁾ It is well-established that the bandgap of Q-Sc nanoparticles increases with decreasing their size, as shown in Fig. 1 for four kinds of semiconductors. Information that has been obtained so far for bulk semiconductor electrodes is useful for understanding photoelectrochemical properties of the corresponding Q-Sc, but we have several different research subjects in studies on Q-Sc. The most

important thing is how to prepare Q-Sc particles having a size distribution as small as possible. Since the Q-Sc particles have a high tendency for agglomeration, some techniques have to be applied for stabilizing these particles. Furthermore, since the bandgap of Q-Sc is different from the corresponding bulk materials, the energy level diagrams that have already been obtained for the bulk semiconductors are not directly useful, and the determination of the potential of the conduction and valence band gets important significance. It is an interesting subject in electrochemistry fields to study how electron transfers on Q-Sc is influenced by the size quantization and by the stabilizing agents used. In this paper, these research subjects are described based on our research results.

2 General Techniques Used in the Preparation of Q-Sc Particles

Chemical synthesis of Q-Sc particles is carried out using chemical reactions in solution. For example, Q-CdS is prepared by reacting Cd^{2+} ions with S^{2-} ions in the presence of an appropriate stabilizing agent such as hexametaphosphate. The stabilizing agent adsorbs on the resulting Q-CdS particles, thereby preventing the agglomeration of the particles. A lot of preparation techniques have been published so far. They may be classified into two categories.¹⁻³⁾ (1) Synthesis under rigid control in the preparation conditions such as the concentration of the constituting ions and temperature. The synthesis in the presence of surface modifying components for the resulting particles is included in this category. (2) Synthesis in a very small spaces such as inverse micelles, followed by surface modifications with organic sub-

Fig. 1 Bandgap vs. particle size relations obtained experimentally for four kinds of Q-Sc.

Table 1 Several examples of the preparation of Q-Sc particles.

Q-Sc	Reagents used	Stabilizer or Support	Average dia. (nm)	Std. devat. (nm)	Procedure
TiO ₂	Ti(isopropoxide) ₄	clay	1.5		hydrolysis
TiO ₂	Ti(isopropoxide) ₄	SiO ₂	3.5	0.5	hydrolysis
TiO ₂	Ti(isopropoxide) ₄	polyvinyl-pyrrolidinone	3.3	1.1	hydrolysis
Fe ₂ O ₃	FeCl ₃ + H ₂ O	Nafion			hydrolysis
CdS	Cd(ClO ₄) ₂ + H ₂ S	hexametaphosphate	4.4	1.3	mixing
CdS	Cd(ClO ₄) ₂ + Na ₂ S	CH ₃ (CH ₂) ₉ SH	2.2	0.44	inverse micelles
CdS	Cd(ClO ₄) ₂ + Na ₂ S	NH ₂ (CH ₂) ₂ SH	2.6	0.43	inverse micelles
CdS	Cd(ClO ₄) ₂ + Na ₂ S	NaO ₃ S(CH ₂) ₂ SH			
ZnS	Zn(ClO ₄) ₂ + Na ₂ S	SiO ₂	3.6	1	mixing
ZnS	Zn(ClO ₄) ₂ + Na ₂ S	CH ₃ (CH ₂) ₃ SH	3.9	0.4	inverse micelles
PbS	Pb(CH ₃ COO) ₂ + Na ₂ S + HOC ₆ H ₄ SH		2.8	0.47	mixing

Average dia. : Average diameter, Std. devat : Standard deviation

stances such as alkanethiols. Table 1 gives several techniques used in our laboratory for the preparation of several kinds of Q-Sc particles. As shown in the table, the prepared Q-Sc particles usually had size distributions of much greater than 10 %. In order to narrow further the size distribution, applications of post treatments which are described in the last section to Q-Sc particle colloids seem useful.

3 Determination of Energy Level Diagrams of Q-Sc

The potential of the conduction band edge and valence band edge of Q-Sc can be determined using several techniques that have been developed for bulk semiconductor particles and electrodes. However, the differential capacitance measurements which are very useful for bulk semiconductor electrodes are not useful for Q-Sc, because the particle size of Q-Sc is too small to build up any significant space charge layer in the particles. The energy level diagrams are obtained from photoelectrochemical measurements if Q-Sc particles are immobilized on conducting electrode substrates. For example, Q-PbS particles of various sizes were prepared by mixing soluble Nafion with lead nitrate of several different concentrations in methanol and then by casting the resulting solution on a Pt plate, followed by exposing the Pb²⁺-immobilized film to H₂S.⁴⁾ Photocurrent-potential curves of the prepared electrodes (Q-PbS / Nafion) were obtained in aqueous solutions containing tartarate as a hole scavenger, and by assuming that the onset potential of anodic photocurrents obtained gave the potential of the conduction band edge, it was determined as a function of the band gap, as shown in Fig. 2. It is clearly shown that the potential of the conduction band edge becomes negative with increasing the bandgap. The same experimental technique was

used to determine the energy level diagrams of Q-TiO₂ / Nafion,⁵⁾ and Q-Fe₂O₃ / Nafion.⁶⁾

The determination of the energy level diagram of Q-Sc can also be made using Q-Sc slurries.⁷⁾ The potential of the conduction band edge of Q-TiO₂ immobilized in the interlayer space of montmorillonite was determined as a function of solution pH by measuring oxidation currents of reduced methylviologen which was produced by reactions of methylviologen with photogenerated electrons in the irradiated Q-TiO₂.⁸⁾ The potential of the conduction band edge of Q-CdS was determined by using another

Fig. 2 Onset potential of anodic photocurrents of various Q-PbS / Nafion-coated electrodes as a function of their bandgaps.⁴⁾

method of using TiO_2 particles as a pH-dependent fluorescent quencher.⁹⁾ TiO_2 particles were suspended in Q-CdS colloid, and by measuring and analyzing the fluorescence intensity emitted from Q-CdS as a function of pH of the colloids, the Fermi level of Q-CdS particles which is approximated to the potential of the conduction band edge was determined. The potential of the conduction band edge determined in this way had a cathodic shift at -35 mV / pH for pHs between 9 and 15, being in accord with results obtained at hydroxylated CdS single crystal electrodes.¹⁰⁾ A lot of experimental works obtained so far confirmed that the potential of the conduction band edge of Q-Sc becomes negative and that of the valence band edge become positive with increasing the bandgap.

4 Electron Transfer at Q-Sc / Solution Interfaces

4.1 Colloidal systems

Reflecting the negative shifts in the potential of the conduction band edge due to the size-quantization effects, the rate of photogenerated electron transfer from the conduction band of Q-CdS to methylviologen (MV^{2+}) in solution in the presence of EDTA as a hole scavenger was enhanced with decreasing the particle size (*i.e.*, with increasing negative shifts of the conduction band) in such a way that the rate followed the electrode reaction kinetics formulated by Butler-Volmer equation.¹¹⁾ Figure 3 shows the initial photoreduction rate of MV^{2+} (r_{init}) as a function of the shifts of the conduction band potential (ΔE_c) at three different irradiation intensities. In all cases, the results are formulated by eq. 1,

$$\log(k_{\text{et}}/k_0) = -0.67\Delta E_c / 0.059 \quad \text{at } 25^\circ\text{C} \quad (1)$$

where k_{et} is the rate constant for the reduction reaction in an initial stage and k_0 the rate constant at the standard redox potential. Since negative shifts in the potential of the conduction band and positive shifts in the valence band, respectively, attach Q-Sc an enhanced reducing and oxidizing power, Q-Sc usually exhibits high activities for a variety of photoinduced reactions. For example, high activities in relative sense were observed at Q- TiO_2 / clay for photoinduced decomposition of carboxylic acid,⁸⁾ at Q-ZnS stabilized with fine silica¹²⁾ and at Q- TiO_2 immobilized in silica matrices^{13,14)} for photoinduced reduction of CO_2 , and at Q- TiO_2 immobilized in a polyvinylpyrrolidone film for photooxidation of 2-propanol.¹⁵⁾

The surface modification of Q-Sc particles with organic substances is a convenient way for preventing the agglomeration of the particles. So far a lot of studies have been carried out using Q-CdS and

Fig. 3 Size dependence of photoinduced reduction rates of $1 \text{ mmol dm}^{-3} \text{ MV}^{2+}$ in the presence of 1 mmol dm^{-3} EDTA as a hole scavenger.¹¹⁾ The absorbance of each particle colloid was adjusted to be 0.15 at 355 nm. ($\blacktriangledown$) 5 mW, ($\square$) 25 mW, and ($\blacklozenge$) 50 mW.

Q-PbS particles modified with thiol compounds. When the surface modification was made, it is important to evaluate the coverage of the surface modifier, because photoelectrochemical properties of the surface-modified Q-Sc particles will be influenced greatly by the availability of the naked surface. We proposed one determination method of the surface coverage of the modifier¹⁶⁾ in which experimentally determined molar ratios of individual elements constituting Q-PbS modified with 4-hydroxythiophenol [ArSH] were compared with those expected from fully-covered Q-PbS having the same size distribution profile. It was found that Q-PbS particles having incomplete coverage of ArSH deduced by this method decreased its reactivity for photoinduced reduction of methylviologen (MV^{2+}) with addition of Pb^{2+} ions to the solution, while the activity for the reduction reaction at Q-PbS with fully covered ArSH was not varied with addition of Pb^{2+} .

The surface modifier influences greatly charge transfer events across the particle / solution interfaces as already demonstrated for several electrochemical reduction reactions on insulating monolayers-covered electrodes.¹⁷⁾ The rate of photoinduced reduction of MV^{2+} in methanol on Q-ZnS particles covered fully with ethane-, butane-,

and octane-thiol¹⁸⁾ was decreased with an increase in the number of methylene group of the modifier. The electron tunneling probability seemed to determine the charge transfer rate in those cases. Besides controlling the electron tunneling, the surface modifier affects the apparent rate in photoinduced reactions by changing the surface concentration of either an electron acceptor or an electron donor on the Q-Sc surfaces. For example, Q-PbS modified with 4-aminothiophenol showed higher activities for photoinduced reduction of MV^{2+} when used in acidic medium in the presence of tartarate anion as a hole scavenger.¹⁹⁾ Positively charged surface modifier concentrated the hole scavenger around Q-PbS particles, resulting in the enhancement of photoinduced reduction of MV^{2+} .

Such effects of the surface modifier on the charge transfer events may be minimized if electrochemically active surface modifiers are used. It was confirmed that Q-CdS particles modified with 1-decyl-1'-(3-mercaptopropyl)-4,4'-bipyridinium bromide (VSH) showed high activities for photoinduced reduction of methylene blue in solution with an electron mediation action of the surface-modified VSH.²⁰⁾ The electron mediation can be achieved if such energy conditions are fulfilled that the potential of conduction band edge of Q-CdS is more negative than the electron acceptor in solution. If this finding is stressed, it may be said that the surface modification of Q-Sc particles with redox active species having different redox potentials will attach energy selectivities in electrochemical reactions to Q-Sc.

4. 2 Q-Sc particle-immobilized electrodes

If Q-Sc particles are immobilized on appropriate conducting substrates, the resulting electrodes will show similar high activities for photosensitized reactions to those of Q-Sc. One example is already given above for Q-PbS / Nafion. However, the ionic polymers like Nafion are electronically insulating and by this reason not always recommended as the matrices for immobilizing Q-Sc. We investigated alternative ways. One example of the preparation procedure of Q-CdS particles-immobilized electrodes is shown in Fig. 4.²¹⁾ A self-assembled monolayer of 3,3'-dithiobis(succinimidylpropionate) formed on a gold substrate reacts with 2-aminoethanethiol covered on Q-CdS particles, resulting in the immobilization of the particles. This procedure allowed the immobilization of Q-CdS particles in a relatively low surface density. By applying scanning tunneling spectroscopy to individual particle immobilized, its bandgap was successfully determined. With a similar idea of the immobilization, if a gold substrate covered with a self-assembled monolayer of 2-aminoethanethiol is

Fig. 4 One example of the preparation procedure of Q-CdS particles-immobilized electrodes.²¹⁾

immersed in 2-aminoethanethiol-modified Q-CdS colloids in the presence of glutaraldehyde, the particles are chemically bound to the gold substrate with glutaraldehyde as a cross-linking agent.²²⁾ If monodisperse Q-CdS particles of different sizes prepared by size selective photoetching, which is described below, were immobilized onto gold electrode substrate using this technique, the prepared electrodes exhibited size-dependent onset potentials of anodic photocurrents. By assuming that the onset potential of the anodic photocurrents gives the potential of the conduction band edge, the potential of the conduction band edge vs. particle size relations as shown in Fig. 5 were obtained.²²⁾ The potential of the valence band edge shown here was obtained by applying the bandgap value to the potential of the conduction band edge. The relations shown in this figure satisfy the theoretical prediction made by an infinite potential well model. However, since the amount of the immobilized particles in that case was

Fig. 5 The potential of the conduction band and valence band of Q-CdS particles as a function of the particle size, as derived from the onset potential of anodic photocurrents at Q-CdS particles-immobilized electrodes measured in aqueous solutions containing triethanolamine as a hole scavenger.²²⁾

also low and in the order of 10^{-8} moles cm^{-2} , anodic photocurrents obtained were less than $1 \mu\text{A cm}^{-2}$. To increase the amount of immobilized Q-CdS particles, another attempt of using the Langmuir-Blodgett technique was made to prepare the electrodes. A little greater anodic photocurrents were then obtained. The detailed preparation procedures of the electrodes will be published elsewhere.

5 Preparation of Monodisperse Q-Sc Particles

As already described above, it is important to use monodisperse Q-Sc particles in studies on various charge transfer reactions. So far a lot of techniques have been published concerning the preparation of Q-Sc particles, as already described in Section 2. Rigid control of the preparation conditions and the use of inverse micelles have been most frequently used. In order to further narrow the size distribution of Q-Sc particles, applications to Q-Sc colloids of post treatments such as gel chromatography,²³⁾ gel electrophoresis,²⁴⁾ and sedimentation and precipitation²⁵⁾ seem useful. However, as long as these post treatments are used, it is usually required to repeat the same procedures for getting monodisperse Q-Sc particles. We discovered that photoetching provides a

convenient and reliable means for the preparation of monodisperse Q-CdS particles.²⁶⁾

CdS is photocorroded in the presence of dissolved air, and with progress of the photocorrosion, the particle should become small. If CdS is in a size-quantization regime, a decrease in the particle size causes an enlargement in the bandgap. Let it be imagined that Q-CdS particles having a size distribution are irradiated with monochromatic light that allows photoexcitation of large particles contained in the colloid. The large particles will then be photocorroded until its size does not allow photon absorption due to the enlargement of the bandgap. By irradiation of monochromatic light of various wavelengths, therefore, Q-CdS particles will become such small size that its absorption threshold is equal to the wavelength of monochromatic light used, as shown in Fig. 6. Concrete examples on how the monodisperse Q-CdS particles were prepared are shown in Fig. 7.²⁷⁾ The results were obtained by irradiation of monochromatic light obtained from an Ar ion laser. An important thing to be noticed in this figure is that Q-CdS particles prepared by irradiation of 476 nm and 458 nm were not contained in the original colloid, and were prepared as a result of photoetching. Detailed studies of photoetching of Q-CdS revealed²⁶⁻²⁸⁾ that (1) the absorption threshold of Q-CdS colloids after photoetching was in good agreements with the wavelength of monochromatic lights used, as shown in Fig. 6, (2) the standard deviation of the average diameter of photoetched Q-CdS became small with decreasing the particle size,

Fig. 6 Steady state absorption spectra of Q-CdS particle colloids after irradiation with monochromatic lights of various wavelengths. The spectra are normalized so as to give almost the same absorbance at the exciton peak or shoulder in the spectra. The number given in the figure is the wavelength of monochromatic light used for irradiation.

Fig. 7 Size distribution profiles of Q-CdS particles after photoetching with use of monochromatic light of different wavelengths obtained from an Ar ion laser.²⁹⁾ D_{av} denotes the average diameter and σ its standard deviation.

(3) fine structured spectra appeared with promotion of photoetching, and (4) the total number of CdS nanoparticles decreased with promotion of photoetching. The principle of photoetching can be applied to the preparation of other kinds of monodisperse Q-Sc particles. However, to achieve this it is important to find out suitable conditions that allow wavelength-

dependent photoetching. Recently we found that even in the case of CdS, monodisperse Q-CdS particles will not easily be prepared if very large CdS particles having an order of μm in the diameter are used, though the reason for this is not straightforwardly understood presently.

6 Summary

Studies on the preparation and properties of Q-Sc have been conducted so far from view points of basic science, and photoinduced reactions on Q-Sc particles have been investigated in relation to applications to photocatalysts. Electrochemical studies provide useful information to understand photocatalysis of Q-Sc. Unfortunately, however, it is not known at present whether or not the use as the photocatalysts can find any practical applications. Recently several other applications are emerging including single electron transistors,²⁹⁾ electroluminescence devices,³⁰⁾ photoluminescence devices,³¹⁾ and quantum dot lasers.³²⁾ These applications utilize also charge transfer events at the Q-Sc particle interfaces, and electrochemical studies directed toward such applications will be of great importance.

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