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Preparation of CdS Microcrystals Covalently Bound with Viologen Groups and Their Photoelectrochemical Properties

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CdS microcrystals (Q-CdS) covalently bound with 1-decyl-1'-(3-mercapto)propyl-4,4'-bipyridinium were prepared. The surface viologen groups picked up photo-generated electrons in the conduction band of Q-CdS particles, causing a decrease of their emission. Irradiation of these particles resulted in new absorption peaks which are assigned to viologen radical cation monomers and their dimers. The photo-reduced viologen groups can mediate photo-generated electron transfer from Q-CdS to methylene blue in solution.

Semiconductor microcrystals (Q-particles) have attracted much attention because of unique photoelectrochemical properties that are indebted to the quantum size effects.1,2) In order to apply these Q-particles to the photocatalysts and the photosensitizers in solar cells, highly efficient charge separation of photo-generated electrons and holes are desired to avoid energy-loss due to the charge recombination. One of useful ways to achieve the efficient charge separation is to attach redox functionalities to Q-particles by preparing them in redox polymers. The redox polymer in that case works not only as an electron sink or an electron source but also as a stabilizer for Q-particles. It has been reported that pendant viologens on dimethylaminated nylon and polyethyleneimine worked as an efficient electron relay of photo-generated electrons from Q-CdS to Pt particles to evolve $H_2$3) and from Q-TiO_2 to enzyme to reduce NO_3^- to NO_2^-.4) These works have been done using Q-particles that were physically held in polymer matrices.

Recently, it has been demonstrated that surface modification of semiconductor particles with organic molecules is useful to prepare highly stable Q-particles, and effects of the modified molecules on photo-induced electron transfers from Q-particles to electron acceptors in solution have been investigated.5,6) However, to our best knowledge, no report has been published on the electron mediation of the organic molecules used for mediation of Q-particles. In this paper, we would like to report the first achievement of the photo-induced electron transfer from Q-CdS to covalently bound viologen groups which have abilities for the electron mediation to electron acceptors in solutions.

1-Decyl-1'-(3-mercapto)propyl-4,4'-bipyridinium dibromide ($C_{10}V^{2+}C_3SH$) was synthesized according to literature procedures.7,8) The synthesized compound was identified by ^1H NMR and IR spectra. Q-CdS was prepared using inverse micelles.9) 7.0 g of dioctyl sulfosuccinate (AOT) and 2.0 cm^3 of distilled water were dissolved in 100 cm^3 heptane to prepare an inverse micelle solution. 0.24 cm^3 of 1.0

mol dm^{-3} Cd(ClO$_4$)$_2$ aqueous solution and 0.16 cm^3 of 1.0 mol dm^{-3} Na$_2$S aqueous solution were added to 60 cm^3 and 40 cm^3 of the inverse micelle solution, respectively. After stirring individually for 1 h, these two kinds of solutions were mixed under vigorous stirring, and then 1.0 cm^3 of 0.10 mol dm^{-3} $C_{10}V^{2+}C_3SH$ dissolved in methanol was added and stirred for a day. With addition of pyridine to destruct the inverse micelles, Q-CdS particles modified with the viologen compound were obtained, which are denoted in this paper as $C_{10}V^{2+}C_3S$/Q-CdS. The powders were consecutively washed to remove impurities with heptane, petroleum ether and methanol, and then dried under vacuum. These procedures were carried out under N_2 atmosphere. As a reference to $C_{10}V^{2+}C_3S$/Q-CdS, Q-CdS particles modified with 1-decanethiol ($C_{10}SH$) were prepared using the same procedure, which are denoted as $C_{10}S$/Q-CdS.

To investigate the photo-induced charge transfer from Q-CdS to the modified viologen groups, the $C_{10}V^{2+}C_3S$/Q-CdS particles were dissolved in a mixed solution of DMSO and pyridine (2 : 1) containing 1.0 x 10^{-3} mol dm^{-3} triethanolamine as a hole scavenger. The amount of the particles dissolved was such that as to give the absorbance of 0.25 at 400 nm. 3.0 cm^3 of this solution was put in an optical quartz cell (1 cm x 1 cm x 4 cm height), evacuated to remove dissolved O_2, and finally filled with N_2. Then the solution was irradiated with a 500 W Xe lamp through a UV-cut off filter (λ > 400 nm). When electron mediation of the modified viologens of Q-CdS was investigated, 2.0 x 10^{-5} mol dm^{-3} methylene blue (MB$^+$) was added to the above solution. Irradiation in that case was made using lights of wavelengths covering from 400 to 450 nm.

Absorption spectra of $C_{10}V^{2+}C_3S$/Q-CdS and $C_{10}S$/Q-CdS solutions are shown in Fig. 1. A shoulder characteristic of exitonic transition appeared around 400 nm for both kinds of Q-CdS, suggesting that the size distribution of these two kinds of Q-CdS particles was almost the same. This was confirmed by transmission electron micrographs. The average diameter and its standard deviation of the $C_{10}V^{2+}C_3S$/Q-CdS particles were 2.1 nm and 0.39 nm, respectively, while those of $C_{10}S$/Q-CdS particles were 2.2 nm and 0.44 nm. Furthermore electron diffraction patterns showed that both kinds of Q-CdS particles had the same cubic crystal structures.

The achievement of the chemical modification with covalent bondings of $C_{10}V^{2+}C_3SH$ and $C_{10}SH$ to Q-CdS particles was evidenced by IR spectra of $C_{10}V^{2+}C_3S$/Q-CdS and $C_{10}S$/Q-CdS particles. Absorption due to -SH vibration at 2600 cm^{-1}, which was observed for $C_{10}V^{2+}C_3SH$ and $C_{10}SH$, was absent in the spectra of the modified Q-CdS particles, as already reported for Q-PbS particles covalently bound with 4-hydroxythiophenol.$^{10)}$ The thiol compounds were bound to CdS through their S atoms. The molar ratio of the modified thiol to CdS was 0.19 for the case of $C_{10}V^{2+}C_3S$/Q-CdS and 0.37 for $C_{10}S$/Q-CdS, as determined from elemental analyses and atomic absorption spectroscopy for these two kinds of Q-CdS particles. Though the molar ratios of the modified thiol to CdS were different

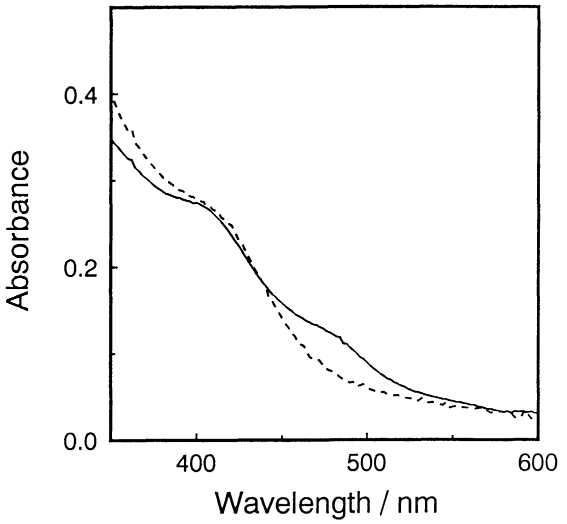

Fig. 1. Absorption spectra of CdS microcrystals modified with $C_{10}V^{2+}C_3SH$ (——) and $C_{10}SH$ (- - - -) in DMSO-pyridine (2 : 1).

between the two kinds of surface-modified Q-CdS particles, the following calculation suggest that the degree of surface occupation of the thiol molecules seems to be the same between the two. The areas occupied by a $C_{10}V^{2+}C_3SH$ and $C_{10}SH$ molecule on Q-CdS particle surfaces are thought to be 0.35 and 0.19 nm^2,11) respectively. If the product of the occupation area and the molar ratio of the modified thiol to CdS is obtained for the two kinds of Q-CdS particles, comparable values are obtained, suggesting that the surface occupation by modified thiols for unit mole of CdS was almost the same.

Both kinds of Q-CdS particles emitted the fluorescence around 560 nm, the wavelengths being longer than that expected from the band gap transition, indicating that surface trap sites were involved in the fluorescence emission. The emission at the $C_{10}V^{2+}C_3$/Q-CdS was weaker than that at the $C_{10}S$/Q-CdS as shown in Fig. 2. The result seems to reflect the situation that since the modified viologens can work as an electron acceptor, a fraction of photo-generated electrons in the conduction band of Q-CdS transferred to the viologen groups.

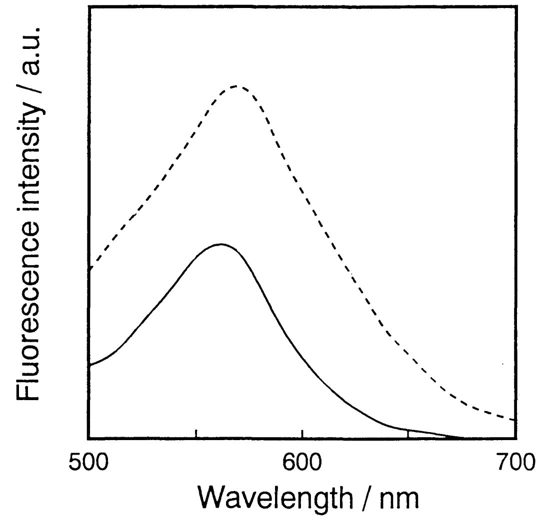

Fig. 2. Emission spectra of $C_{10}V^{2+}C_3S$/Q-CdS (——) and $C_{10}S$/Q-CdS (- - -) in pyridine. Excitation wavelength : 330 nm.

Irradiation of the $C_{10}V^{2+}C_3S$/Q-CdS solution caused changes of its absorption spectrum, as shown in Fig. 3. The absorption peaks at around 402 and 606 nm are indebted to monomeric cation radicals of the modified viologen compound, and those at around 372 and 538 nm are to the dimerized cation radicals.12) The finding that the absorbance of these peaks was increased with increase of the irradiation time evidences that the viologen compounds bound to Q-CdS particle surfaces were steadily reduced by photo-generated electrons. According to the absorption spectra given in Fig. 3, the absorption of the dimeric viologen cation radicals was a little greater than that of monomeric ones for the irradiation time of 20 s, but with irradiation for 320 s, the absorbance of the latter became greater than the former. Since the absorption coefficients of viologen cation radical dimer at 538 nm and monomer at 606 nm are 23300 and 12200 mol^{-1} dm^3 cm^{-1},12) respectively, the observed difference in the changes of absorbance with irradiation time between the dimeric and monomeric radicals mentioned above seems to suggest that dimeric radicals were more easily formed in a very early stage of irradiation, but with progress in the

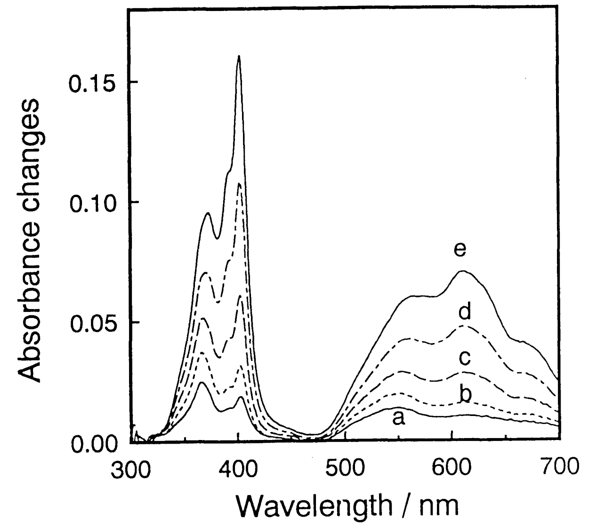

Fig. 3. Absorbance changes of $C_{10}V^{2+}C_3S$ /Q-CdS against irradiation time (λ > 400 nm). a: 20 s, b: 40 s, c: 80 s, d: 160 s, e: 320 s.

irradiation time, the monomeric radical formation became more pronounced. The detailed discussion on this subject will be published in a full article.

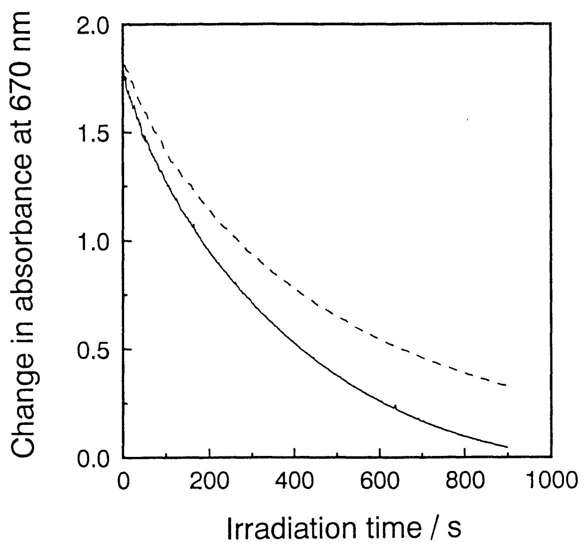

Fig. 4. Time course of changes in absorbance at 670 nm caused by photo-reduction of MB^+ in the presence of $C_{10}V^{2+}C_3S$/Q-CdS (——) and $C_{10}S$/Q-CdS (- - -).

Irradiation of both kinds of Q-CdS particles in the presence of MB^+ caused a decrease of absorbance of MB^+ at 670 nm as shown in Fig. 4, indicating that MB^+ was reduced by photo-generated electrons in Q-CdS. The reduction rate of MB^+ on $C_{10}V^{2+}C_3S$/Q-CdS particles was larger than on $C_{10}S$/Q-CdS. If the rate of reduction of MB^+ is evaluated from the time profile of the absorbance changes by assuming that the reduction follows the pseudo-first-order rate law,[13] the rate constant of 3.1×10^{-3} s^{-1} is obtained for $C_{10}V^{2+}C_3S$/Q-CdS, while 2.0×10^{-3} s^{-1} is obtained for $C_{10}S$/Q-CdS, the former being 1.6 times greater than the latter. Furthermore it was observed that when $C_{10}V^{2+}C_3S$/Q-CdS particles were used, absorption peaks of viologen radical cations were not definitely developed until MB^+ was completely reduced. These findings were rationalized by the mediation action of the modified viologen groups on Q-CdS particles. The redox potentials of $C_{10}V^{2+}C_3SH$ and MB^+ are -0.40 and -0.26 V vs. SCE, respectively, in a mixed solution of DMSO and pyridine (2 : 1), allowing the electron mediation of the modified viologen groups in the photo-induced electron transfer from Q-CdS to MB^+.

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