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Formation and Photoreaction of PbI_2, HgI_2, and BiI_3 Layered Ultrasmall Particles

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Abstract. Formation of ultrasmall particles of PbI_2 in methanol was observed by means of stroboscopic stopped-flow spectroscopy. Pulse-laser induced electron transfer from PbI_2, HgI_2, and BiI_3 to viologens was measured for various laser intensities and for various viologen concentrations. The electron transfer yields were 0.24, 0.08, and 0.03 for HgI_2, PbI_2, and BiI_3, respectively. The laser-intensity dependence differed from the previous observation for CdS and showed that the low yield is not attributable to the direct electron–hole recombination in the particle.

INTRODUCTION

Photoreaction of semiconductor particles has been a subject of growing interest since its possible utilization for the chemical conversion of light energy was suggested. The transparent characteristics of ultrasmall particles in solution have been employed to investigate the photoinduced reaction occurring at semiconductor–solution interfaces.[1] The quantum size effect on photocatalytic activity has been reported[2] for metal oxides such as TiO_2 and for metal carcogenides such as ZnS and CdS. Since the photoinduced charge separation in the semiconductor particles is one of the important functions of the photocatalyst, we have investigated the photoinduced electron transfer for CdS[3–5] and In_2S_3.[3] The small-size effect of photocatalytic reduction of viologens has been defined as the decrease in space for photoinduced charge separation.[3] Metal iodides such as PbI_2 are known to form layered ultrasmall particles.[6–10] Therefore, it is interesting to investigate the effect of photoinduced charge separation on the layered semiconductors whose shape is different from CdS. No reports about the photocatalytic reaction of metal iodides have been published so far. Since acetonitrile is widely used as the solvent for metal iodides, poor stability of the particle in solution may cause difficulty in the photocatalytic experiments. In the present study methanol was employed as a solvent. This solvent provides relatively stable metal iodide solutions and can dissolve viologens without aggregation of the semiconductor particles. Thus, the laser-induced electron transfer from metal iodides could be measured and the experimental results compared with those of the spherical ultrasmall semiconductors reported previously.[3,4]

EXPERIMENTAL SECTION

Metal iodide ultrasmall particles were typically prepared by adding 0.08 mL of a freshly prepared methanol solution of 20 mM KI (obtained from Nacalai Tesque Co.) to three 4.0 mL methanol solutions containing 0.2 mM of $Pb(NO_3)_2$, $HgCl_2$, and $BiCl_3$ (Nacalai Tesque), respectively, at room temperature. Since the solubility of these metal salts in methanol is very small, 2 vol% of H_2O was added for Pb^{2+} and for Hg^{2+}, and 4 vol% of acetonitrile for Bi^{3+}. The samples for the laser photolysis were prepared under red light and an argon atmosphere. Dibenzyl-4,4'-bipyridinium dichloride (benzylviologen, BV^{2+}), methylviologen (MV^{2+}) (Aldrich Chemicals) and 1,1'-bi(3-sulfonatopropyl)-4,4'-bipyridinium (sulfonatopropylviologen, SPV)[11] were used as electron acceptors.

Laser flash photolysis was performed with a homemade N_2 laser (337 nm, pulse width (FWHM) of 9 ns). Samples were placed in a 10-mm × 10-mm Pyrex glass cell and bubbled with Ar gas before and during the measurement. The photolysis apparatus has been described in detail elsewhere.[3] The response time used in the present experiments was about 0.1 μs. Incident laser intensity was measured with triplet–triplet absorption of anthracene in a cyclohexane solution, as described previously.[3] The laser intensity was occasionally attenuated with several sets of glass filters.

Absorption spectra of methanol solution of ultrasmall semiconductor particles were measured with a Hitachi U-3210 spectrophotometer.

A stroboscopic stopped-flow apparatus was arranged by using an RA-type mixing chamber (Ohtsuka Denshi Co. Ltd.). A flow control valve and the timing for microflash discharge were manipulated by a microcomputer (OKI, if–800). A linear image sensor PCD (Hamamatsu Photonics, S2301/C2325) was operated directly by the microcomputer with a homemade

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circuit. Signals from the PCD were averaged for 8 flow-stops and processed for obtaining transient UV-vis spectra by the microcomputer.

RESULTS AND DISCUSSION

Formation of Ultrasmall Metal Iodide Particles

Several reports[6–10] deal with the formation of PbI_2, HgI_2, and BiI_3 ultrasmall particles in acetonitrile or 2-propanol solution. When 2-propanol was used as a solvent, PbI_2 turned into PbI(OH), and HgI_2 was not formed at a low concentration.[8] In acetonitrile, the concentration dependence of the PbI_2 spectrum and the formation of I_3^- were reported.[7,8] We confirmed that the PbI_2 spectrum changed into that of I_3^- after 24 h in acetonitrile and observed that the spectrum of PbI_2 maintained its shape when an electron donor, mercaptoethanol, was added to the solution. On the other hand, methanol provided stable PbI_2 particles without the electron donor, where the spectrum of PbI_2 showed the same features as those obtained by dissolution of yellow PbI_2 powder,[8] and maintained the features with concentration change, as shown in Fig. 1.

The absorption bands of PbI_2 have been tentatively assigned, by using a particle-in-a-box model, to the transitions for PbI_2 particles containing 20–100 molecules.[6,8] Ab initio molecular orbital calculations for $(PbI_2)_7$ showed that the treatment with the particle-in-a-box model is ambiguous.[12] That model also assumes an infinite potential barrier, which yields an artifactually large size when it is estimated from the energy shift.[13] The absorption bands at 270 and 320 nm have recently been assigned to the clusters consisting of two and three PbI_2 molecules, respectively. Although this assignment is based on the change in the spectrum by consecutive incorporation of molecules into zeolite cavities,[14] it is not supported by the following experimental result.

Figure 2 shows the change in the spectra after the fast mixing of methanol solutions of $Pb(NO_3)_2$ and KI. A growth of a 270-nm band was observed at 1–280 ms after the mixing. The spectrum remained almost constant in the time range of minutes. The initial formation of 270-nm and 320-nm bands occurs too quickly to be observed by means of the stopped-flow technique. However, the growth of a 270-nm band is slower than that of a 320-nm band. This observation may contradict the band assignment by Tang et al.,[14] insofar as an increase of dimer is most likely followed by trimer formation. Micic et al.[8] reported a stopped-flow experiment for PbI_2, but they performed it using 2-propanol solution and the observed change involves the formation of I_3^-.

The spectrum of 0.2 mM HgI_2 prepared in methanol shows a peak at 268 nm which corresponds to the 275-nm band obtained on dissolution of the solid material in 2-propanol.[8] For BiI_3 in methanol, two peaks, at 322 and 380 nm, and a shoulder at 424 nm were observed, which may correspond to the peaks at 288, 358, and 430 nm observed in acetonitrile.[10]

Laser Flash Photolysis

There are few reports on the photolysis of the metal iodide ultrasmall layered semiconductors. Micic et al.[8] described the formation of I_3^- by the continuous irradiation of PbI_2. In the present study, laser-pulse-induced electron transfer was measured. Figure 3A shows the transient spectra obtained immediately and 15 µs after the pulse for a PbI_2 solution containing BV^{2+}. Absorption peaks at 400 and 610 nm are attributable to the reduced form of BV^{2+}. Figure 3B shows the transient spectra in the absence of BV^{2+}. For each spectrum, an absorption peak was observed

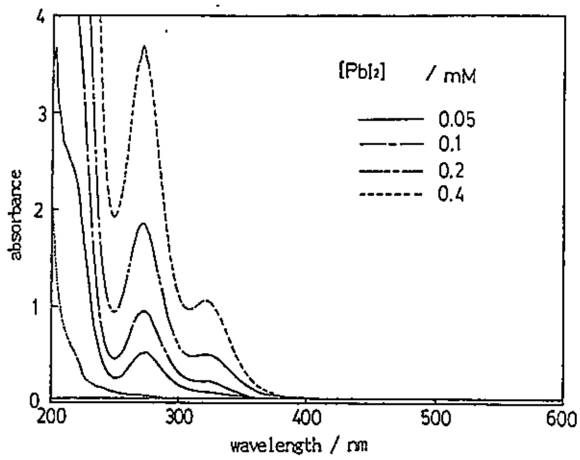

Fig. 1. Optical absorption spectra of PbI_2 in methanol solution at several concentrations. The dotted curve is the spectrum of the solvent.

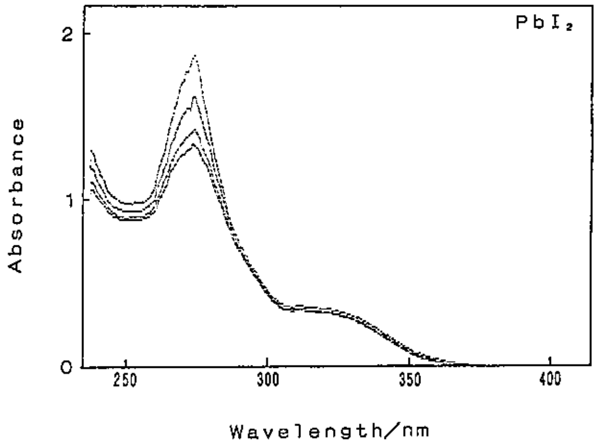

Fig. 2. Evolution of absorption spectra upon fast mixing of 0.4 mM $Pb(NO_3)_2$ methanol solution with freshly prepared 0.8 mM KI methanol solution. The periods of time after mixing are 1, 10, 64, and 280 ms.

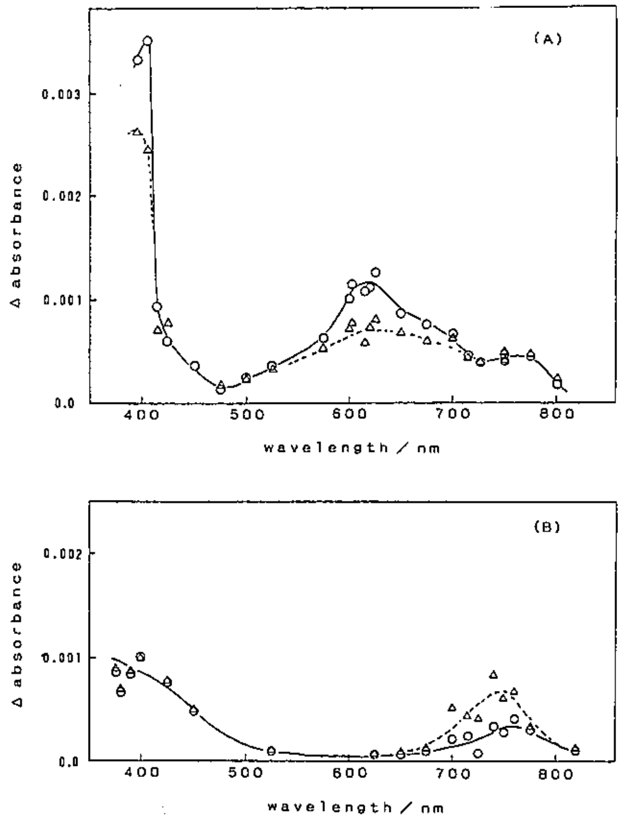

Fig. 3. Transient spectra observed immediately (△) and 15μs (○) after the laser pulse for deaerated 0.2 mM PbI_2 methanol solution (A) in the presence (50 μM) and (B) in the absence of benzylviologen (BV^{2+}).

at about 750 nm, which can be assigned to I_2^-.[15] The absorption band at shorter than 480 nm is the 385-nm band of I_2^-. In Fig. 3B, the 385-nm band remains constant while the 750-nm band changes, suggesting that a recovery of the bleached PbI_2 absorbance compensates for the decay of the I_2^- absorbance at 385 nm. When the electron acceptor BV^{2+} is present in the solution, the 750-nm band does not decay. On the other hand, in the absence of BV^{2+} the band decays in 15 μs but the absorbance is maintained for more than milliseconds. This observation indicates that some reducing species for BV^{2+} react with I_2^-. The quantum yields (Φ) for the formation of BV^{2+} and I_2^- are calculated to be 0.08 and 0.17 by adopting ε (602 nm) = 14000 M^{-1} cm^{-1},[16] and ε (725 nm) = 2600 M^{-1} cm^{-1},[15] respectively.

A slower increase of BV^{2+} in Fig 3A indicates the initial formation of a relatively stable reduced species besides the oxidized species, I_2^-. Thus, an oxidation product, I·, is most likely formed at first as indicated by eqs 1 and 2. Since I· reacts rapidly with I^- as shown by eq 3[17], I_2^- is formed as an oxidation product. Here I^- is presumably supplied from a reversible reaction, eq 4.

$$Pb_nI_{2n} + h\nu \longrightarrow e^- + h^+ \qquad (1)$$

$$Pb_nI_{2n} + h^+ \longrightarrow Pb_nI_{2n-1}{}^+ + I\cdot \qquad (2)$$

$$I\cdot + I^- \rightleftharpoons I_2^- \qquad (3)$$

$$Pb_nI_{2n} \rightleftharpoons Pb_nI_{2n-1}{}^+ + I^- \qquad (4)$$

$$Pb_nI_{2n-1}{}^+ + e^- \longrightarrow Pb_nI_{2n-1}\cdot \qquad (5)$$

$$Pb_nI_{2n-1}\cdot + BV^{2+} \longrightarrow Pb_nI_{2n-1}{}^+ + BV^{+}\cdot \qquad (6)$$

$$Pb_nI_{2n-1}\cdot + I^- \longrightarrow Pb_nI_{2n-2} + I_2^- \qquad (7)$$

$$Pb_nI_{2n-1}\cdot + I_2^- \longrightarrow Pb_nI_{2n} + I^- \qquad (8)$$

Parallel to the I· formation, reduced particles, $Pb_nI_{2n-1}\cdot$, may be produced (eq 5). Then the reduction (eq 6) occurs for "adsorbed" BV^{2+}, at first, and for free BV^{2+} in 15 ms, after diffusion. In the absence of BV^{2+}, a larger amount of I_2^- was formed immediately after the pulse, indicating that I_2^- formation competes with the $BV^{+}\cdot$ formation, as shown by eqs 6 and 7. The observation of I_2^- decay in Fig. 3B can be explained by eq 8. This process is essentially radical recombination when the equilibrium of eq 3 is applied.

After the laser experiments, the absorption spectrum of Pb_nI_{2n} is slightly changed if BV^{2+} is present in the solution. The absorbance increases at 290 nm and decreases at 320 nm. The redox potential of I_2^- (0.2 V vs. NHE)[18] is smaller than that of I^- (1.3 V)[18], and I_2 equilibrates with I_3^-.[19]

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (9)$$

Therefore, the increase at 290 nm shows the formation of I_3^-, and the decrease at 320 nm is explained by the degradation of Pb_nI_{2n}.

As for HgI_2, the absorption spectra show concentration dependence, and consist of many molecular and ionic species.[9] Thus details of the photoinduced reaction of the HgI_2 solution are not discussed in the present paper.

Effect of Viologen Concentration on Photoreduction Yield

The two-step reduction of BV^{2+} observed in Fig.3A is explained by partial association of BV^{2+} molecules with PbI_2 particles, which has been observed for an MV^{2+} – TiO_2 system.[4] The electron transfer quantum yield, Φ, immediately after the laser pulse, was measured by changing BV^{2+} concentration and plotted in Fig. 4. The dependence can be analyzed in terms of a Langmuir-type adsorption, where

$$\Phi = \Phi_0 \cdot K_{app}[BV^{2+}] \,/\, (1 + K_{app}[BV^{2+}]) \qquad (10)$$

The values of K_{app} and Φ_0 are shown in Table 1, where those for the other viologens are also listed. Although no

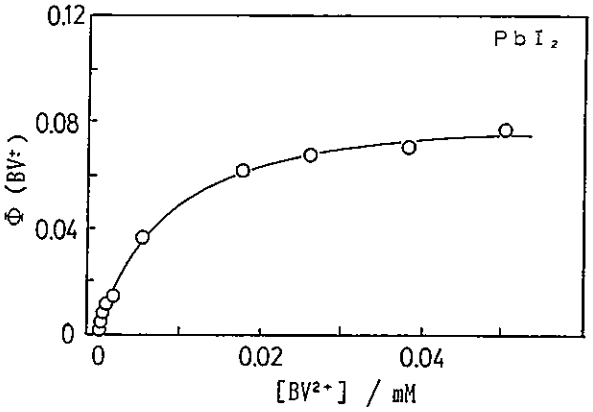

Fig. 4. Quantum yield (Φ) of BV$^{+\cdot}$, observed immediately after the laser pulse is plotted as a function of concentration of BV^{2+} in the solution.

significant difference in Φ_0 was observed, a larger K_{app} for BV^{2+} compared with SPV may be the result of a difference in the viologen charge.

For HgI$_2$ and BiI$_3$, the values of K_{app} are similar to those for PbI$_2$, as shown in Table 1. On the other hand, the Φ_0 value for HgI$_2$ is larger and that for BiI$_3$ is smaller than that for PbI$_2$ of corresponding viologen. This difference may originate in the electronic characteristics of the metal ions.

Effect of Incident Light Intensity on Photoreduction Yield

The yield of photoinduced BV^{2+} reduction was measured for various incident laser-pulse intensities. Figure 5 shows the yield Φ as a function of photon density in semiconductor solid. The observed Φ was nearly constant at photon densities down to 3×10^{18} cm^{-3} for both PbI$_2$ and HgI$_2$. An apparent increase in Φ at a lower photon density may be attributed to experimental errors, insofar as the laser-induced absorption change was less than 10^{-4}. By assuming that one semiconductor particle consists of 100 molecules, a particle absorbs more than one photon only when the photon density is larger than 8×10^{19} cm^{-3} as an averaged value. When the photon density is smaller than this value, the electron–hole recombination will not affect Φ.[3] Therefore, Fig. 5 indicates that the relatively low Φ observed is not attributable to the direct electron–hole recombination in the particles.

Table 1. Parameter values for viologen photoreduction by metal iodide in methanol solution

Metal iodides	Viologens	(E° in V)[18]	K_{app}/M^{-1}	Φ_0
PbI$_2$	BV^{2+}	(–0.37)	1.4×10^5	0.08
	SPV	(–0.38)	1.2×10^4	0.05
	MV^{2+}	(–0.45)	2.6×10^4	0.06
HgI$_2$	BV^{2+}	(–0.37)	1.7×10^5	0.24
BiI$_3$	MV^{2+}	(–0.45)	2.4×10^4	0.03

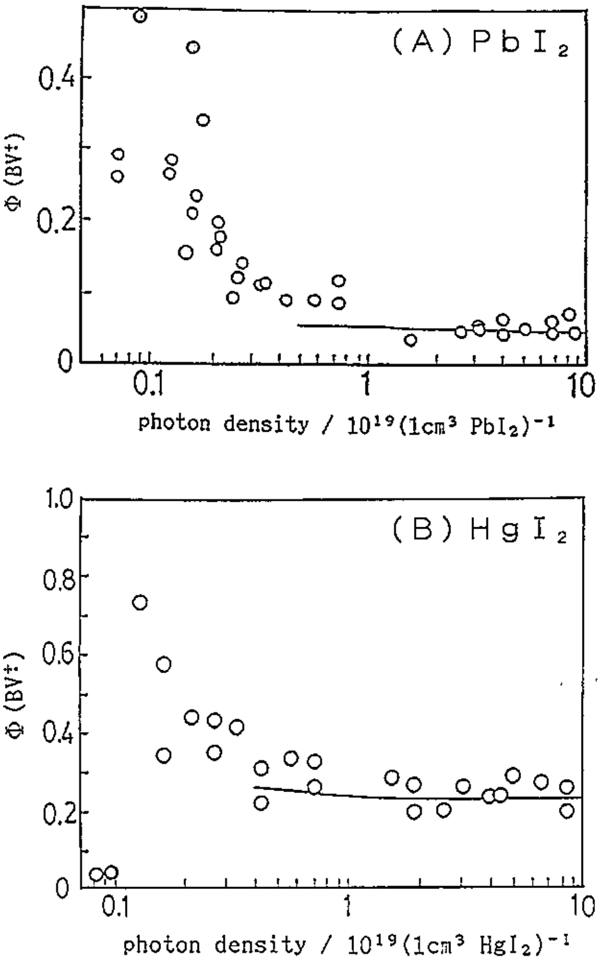

Fig. 5. Quantum yield (Φ) of BV$^{+\cdot}$ as a function of laser-induced photon density in the particles: (A) for 0.2 mM PbI$_2$ with 44 μM BV^{2+} and (B) for 0.2 mM HgI$_2$ with 45 μM BV^{2+}.

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