

Conclusions

In conclusion, the spiro-fused thiophene trimer, SIII, and spiro-fused thiophene heptamer, SVII, with terminal α -TMS and β -CH₃ groups were readily oxidized in CH₂Cl₂ both electrochemically and with FeCl₃. The thiophene heptamer segments in the spiro-fused SVII can be oxidized sequentially with FeCl₃ to produce the mono radical cation, the bis(radical cation), the radical cation/dication, and the bis(dication), respectively. The existence of these intermediate ions was confirmed by vis/near-IR and ESR analyses. It was also concluded that there is some interaction between the neutral and the radical-cation forms in SVII, but there is no significant electronic interaction between the orthogonally positioned heptamer radical cations or the di-

cations except possibly some weak magnetic coupling. With SIII, the trimer segments are oxidized at higher voltages, and the four sequential intermediates are not observed because the less stable cations probably dimerize to form a bis(spiro structure) containing thiophene hexamer cation.

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Surface Structures of PbS Microcrystals Modified with 4-Hydroxythiophenol and Their Influences on Photoinduced Charge Transfer

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Abstract: Quantized PbS microcrystals capped with 4-hydroxythiophenol (ArSH) were prepared using two different concentration ratios of $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ and 3.0 with fixed concentration ratio of $[\text{ArSH}]/[\text{Pb}^{2+}] = 4.0$. The size distributions of the prepared PbS particles were determined. Two different surface structure models of fully occupied and partially occupied surface sites of PbS microcrystals with the capped ArSH are assumed, and chemical compositions of these particles are evaluated by taking the experimentally determined particle size distributions into account. By examining the fitness of the chemical analyses data of the PbS particles to the evaluated compositions, it is proposed that the PbS particles prepared $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ had the capped ArSH in all the surface sites, while PbS particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ had some surface sites free from the modifier. The proposed surface structures of the two kinds of PbS microcrystals were rationalized by experimentally found differences both in agglomeration tendencies of the particles and in the effect of the addition of Pb^{2+} ions on the rate of photoinduced reduction of methyl viologen on the particles.

Introduction

Quantized semiconductor microcrystals have been intensively studied in recent years.¹⁻⁵ Synthetic approaches to obtain monodispersed particles with controlled size have been one of the major research interests, and chemical modification by capping with organic reagents seems to be one of the most effective methods to achieve this. For example, thiol and selenol compounds have been successfully used as the capping reagents to prepare quantized CdS, CdSe, CdSe-ZnS, and CdSe-ZnSe particles⁶⁻¹⁶ with narrow size distributions in quantized regime.

Physicochemical properties of these semiconductor microcrystals capped with organic moieties have been studied.⁶⁻²⁶ In particular, the structure of these particles have been characterized by TEM,^{7,9,11,14} NMR,¹⁷ X-ray diffraction,^{9-11,14,21} XPS,^{13,14} Auger spectroscopy,¹³ and EXAFS.²⁴ However, the characterization of the capped surface in atomic scale has not yet been reported except, for example, using EXAFS, where atomic rearrangements of CdS and CdSe surfaces on capping with benzeneselenol were suggested.

In cases of capped semiconductor microcrystals, it seems very important to clarify the effect of the capping agent on various properties of semiconductor microcrystals, especially in relation

to detailed surface structures of capped semiconductors. However, presently we have no information about this. So far well-docu-

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mented results on surface structures, photochemical properties, and photoinduced electron transfers have been obtained only for Cd- and Zn-benzenethiolate clusters,²⁷⁻³⁵ which may be regarded as models of monodispersed CdS and ZnS microcrystals.

In this paper, we attempt to derive information on the structure of the capped semiconductor surfaces in atomic scale by fitting the experimentally obtained chemical compositions to those expected from modeled surfaces of capped semiconductors, and the importance of the capped conditions on physicochemical properties of the capped semiconductor microcrystals is demonstrated for 4-hydroxythiophenol-capped PbS microcrystals.

PbS of nanometer size exhibits large quantum size effects due to small effective masses of electrons and holes, and by this reason preparations and photochemical properties of this material including thiol-modified PbS have been studied using various approaches.³⁶⁻⁴² However, little is known about the relevance of its photochemical properties to the surface structures.

Experimental Section

All the chemicals used in this study were of reagent grade and purchased from Wako Pure Chemical Industries. Lead acetate trihydrate and sodium sulfide enneahydrate were used as received. Methanol was distilled and 4-hydroxythiophenol (ArSH) was purified by vacuum distillation. Aqueous solutions were prepared using doubly distilled water.

PbS microcrystals capped with ArSH were synthesized by reaction of Pb^{2+} with S^{2-} in the presence of ArSH in methanol at $-88\text{ }^{\circ}\text{C}$. Lead acetate and sodium sulfide were used as the starting materials for Pb^{2+} and S^{2-} ions sources. Lead acetate dissolved in methanol, sodium sulfide dissolved in methanol containing 0.5% water, and ArSH dissolved in

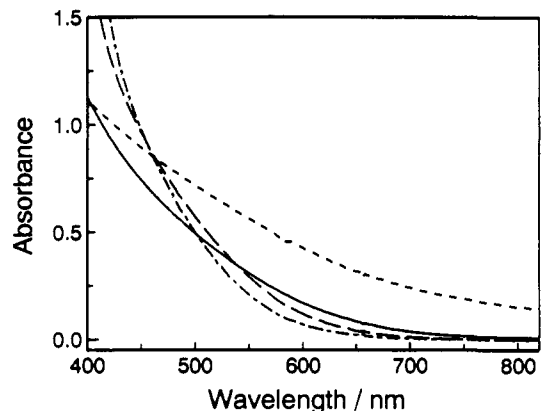


Figure 1. Absorption spectra of 1.25×10^{-4} M PbS colloids after dilution with methanol. The molar ratio of $[Pb^{2+}]/[S^{2-}]$: (---) 1.0, (—) 1.2, (-·-) 3.0, (- - -) 6.0. $[S^{2-}] = 5.0 \times 10^{-4}$ M and $[ArSH] = 1.8 \times 10^{-2}$ M were fixed in the preparation of all colloids.

methanol containing 2.0×10^{-2} M sodium hydroxide were used as the reaction solutions. The concentration of the sulfide was fixed to 5.0×10^{-4} M and that of Pb^{2+} ions and ArSH were varied in such a way that the ratio of $[Pb^{2+}]/[S^{2-}]$ ranged from 1.0 to 6.0 and that of $[ArSH]/[Pb^{2+}]$ from 4.0 to 36.0. A typical procedure for the preparation of ArSH-capped PbS using $[Pb^{2+}]/[S^{2-}] = 3.0$ and $[ArSH]/[Pb^{2+}] = 4.0$ is as follows.

Twenty-five milliliters of 3.0×10^{-3} M lead acetate solution was first mixed with 1.2×10^{-2} M ArSH solution with an equal volume and cooled at $-88\text{ }^{\circ}\text{C}$ with use of dry ice-acetone bath. Then 50 mL of the sodium sulfide solution cooled at $-88\text{ }^{\circ}\text{C}$ was added under vigorous stirring. The mixed solution was kept at that temperature for 2 h and then at $-20\text{ }^{\circ}\text{C}$ for 1 day, resulting in a transparent brown solution. All the procedures including the preparation of each solution, mixing the solutions, and the reaction at the low temperature were carried out under a stream of N_2 .

Absorption spectra of the brown solution were measured at room temperature using a Hewlett Packard 8452A spectrophotometer after 2-fold dilution. The prepared ArSH-capped PbS microcrystals were observed by a transmission electron microscopy (TEM). In order to obtain clear images of ArSH-capped PbS free from any adhered soluble impurities such as Pb^{2+} -ArSH complexes, the brown PbS colloidal solution was concentrated using a 20 Å pore size ultrafilter (Amicon PM-10) under agitation of the solution in the following way. One hundred milliliters of original PbS colloid was filtered until 1 mL of the colloids were left in the cell of the ultrafilter and then 4 mL of deaerated methanol was added to the 1-mL colloid, followed by filtration to leave 1 mL in the cell. The procedures of the addition of 4 mL of methanol and the succeeding concentration to 1 mL of the solution using the ultrafilter were repeated until filtrate showed no appreciable absorption of Pb^{2+} -ArSH complexes. By this procedure, 1 mL of purified PbS colloid was prepared. Then a drop of this colloidal solution was applied to amorphous carbon overlayers on a Cu grid, followed by drying to prepare the TEM samples. High resolution TEM pictures and electron diffraction patterns were obtained at the operation voltage 300 kV (Hitachi, H-9000). During the course of the observations by TEM, however, the microcrystals seemed to be somewhat damaged and aggregated to larger particles. To prevent this undesired event in the determination of the size distribution of PbS microcrystals, observations by TEM under operations with a lower acceleration voltage of 200 kV (Hitachi, H-800) were employed.

To prepare ArSH-capped particles suited for chemical analysis and FT-IR measurement, the purified PbS colloidal solutions were filtered using the ultrafilter, and the residues on the filter were collected and dried under vacuum. Elemental analysis and atomic absorption spectroscopy were performed using a Yanaco Model MT-2 analyzer and a NJA AA-8500 Mark II spectrometer, respectively. FT-IR spectra were measured by a JASCO FT/IR-3 spectrometer using KBr discs dispersed with the powder of the PbS particles.

For comparative purpose to the ArSH-capped PbS, Pb^{2+} -ArSH complexes were prepared by mixing 3.0×10^{-3} M lead acetate solution with 1.2×10^{-2} M ArSH solution in an equal volume, referring to literatures.⁴³⁻⁴⁵ By evaporating the solvent under vacuum at room tempera-

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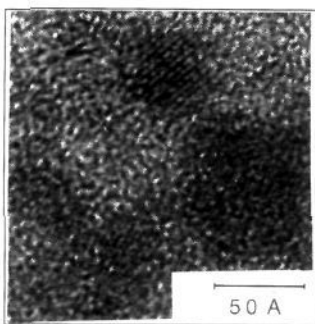


Figure 2. High-resolution transmission electron micrograph of PbS microcrystals prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$. The lattice spacing is 3.43 Å.

ture, yellow powder was obtained, which was used in FT-IR spectra measurements.

^1H NMR spectra of ArSH-capped PbS particles were obtained in CD_3OD at various temperatures. The preparation of this colloidal solution was made by replacing methanol of the above mentioned purified PbS colloidal solution with CD_3OD . The replacement was carried out by repeating a procedure of the dilution of ArSH-capped PbS colloids with CD_3OD and subsequent filtration of the resulting colloids using the 20 Å ultrafilter to leave a little amount of the concentrated colloidal solution. ^1H NMR spectra were recorded on a JEOL JNX-GSX 400 spectrometer equipped with a cryostat operating at 400 MHz with $\text{Si}(\text{CH}_3)_4$ internal reference.

Since ArSH-capped PbS colloids were prepared using methanol as the solvent as described above, it is desired to conduct experiments of photoinduced reduction of methyl viologen (MV^{2+}) on PbS particles in methanol solutions. However, MV^{2+} is apt to be reduced by methoxide ions.⁴⁶ Then photoreduction of MV^{2+} was studied in aqueous solutions. To change the solution environments of ArSH-capped PbS particles from methanol to water, the purified PbS colloids were filtered with the use of the above described ultrafilter, and then the wet residue on the filter was put into a deaerated 0.1 M sodium tartrate aqueous solution (pH 7.5). The resulting PbS suspension was subjected to centrifuge. The wet PbS particles obtained were suspended again in the deaerated sodium tartrate solution containing 1.0×10^{-2} M methyl viologen dichloride so as to give a nominal concentration of 2.5×10^{-4} M PbS. Sodium tartrate was chosen as a hole scavenger. After bubbling nitrogen for 30 min, the colloid was illuminated with a 500W Xe lamp through a UV cut-off filter ($\lambda > 400$ nm).

Results and Discussion

Preparation and Characterization of PbS Microcrystals. In the preparation of the ArSH-capped PbS colloids, the use of a very low temperature such as -88 °C seemed essential. If the synthesis was attempted at room temperature, for example, the bulk PbS particles were produced, indicating that the termination of particle growth by ArSH effectively occurs only at very low temperatures where the rate of particle growth is very low in a relative sense.^{37,47-49} Once the PbS microcrystalline colloids were prepared, they were stable at room temperature for several months as long as oxygen was excluded from the colloidal solution.

Figure 1 shows absorption spectra of PbS microcrystals capped with ArSH, prepared with various concentration ratios of lead ions to sulfide ions which are represented as $[\text{Pb}^{2+}]/[\text{S}^{2-}]$. All the PbS microcrystals were prepared with an excess of ArSH to Pb^{2+} ions, as noticed in the figure caption. A fixed large concentration ratio of $[\text{ArSH}]/[\text{S}^{2-}] = 36.0$ was adopted in the preparation of all the colloids given in Figure 1 to achieve the capping with ArSH as perfect as possible. The synthesis with the use of $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.0$ resulted in turbid PbS colloids which

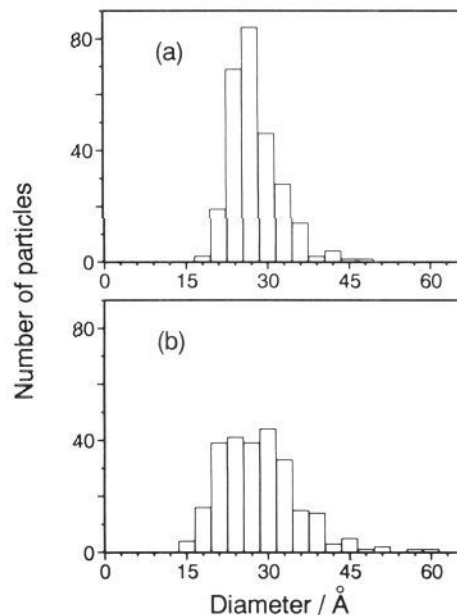


Figure 3. Size distributions of PbS microcrystals prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ (a) and 1.2 (b).

contained agglomerated PbS but with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ or the greater, transparent brown PbS colloids were prepared. When the concentration ratio of Pb^{2+} to S^{2-} was increased from 1.2, the absorption onset was blue-shifted, the degree depending on the magnitude of the concentration ratio, until the concentration ratio increased to 6.0, beyond which almost the same absorption spectra were obtained. In addition, it was found that the colloids prepared with the same $[\text{Pb}^{2+}]/[\text{S}^{2-}]$ ratio gave the same absorption spectra independent of the concentration ratio of $[\text{ArSH}]/[\text{Pb}^{2+}]$, provided that the $[\text{ArSH}]/[\text{Pb}^{2+}]$ was equal to or greater than 4.0.

A high-resolution TEM picture of PbS microcrystals prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$, which is given in Figure 2, shows that the particles are almost spherical and have perfect crystallinity of clear periodic lattice planes with no lattice displacement. Electron diffraction patterns of these particles showed that the PbS microcrystals had a rock salt structure.⁵⁰ Furthermore, the lattice constant of PbS microcrystals obtained from the TEM picture (Figure 2) was 3.43 Å which was in perfect accord with the crystallographic data of the PbS bulk materials. The size distribution of the PbS microcrystals was determined for those prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ and 3.0. In both cases the microcrystals had the same average diameter of 28 Å, but their size distributions were different as shown in Figure 3. The standard deviations of 7.4 and 4.7 Å were obtained for $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ and 3.0, respectively. By applying these results to Figure 1, it is recognized that the narrower size distribution gives the steeper rise of absorption spectrum.

According to Figure 1, the PbS colloids prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ has the absorption onset at around 800 nm (1.6 eV) and those prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ at 700 nm (1.8 eV), being much shorter than the absorption threshold of bulk PbS which is 3200 nm.³⁹

A theoretical equation to predict the diameter of PbS microcrystals from their energy gaps has been derived by Wang et al.³⁹

$$E = [E_g^2 + 2E_g\hbar^2(\pi/R)^2/m^*]^{1/2} \quad (1)$$

$$1/m^* = (1/m_c + 1/m_h)/2 \quad (2)$$

where E is the energy gap of size quantized PbS, E_g is the band gap of bulk PbS (0.41 eV⁵¹), R is the particle radius, and m^* is

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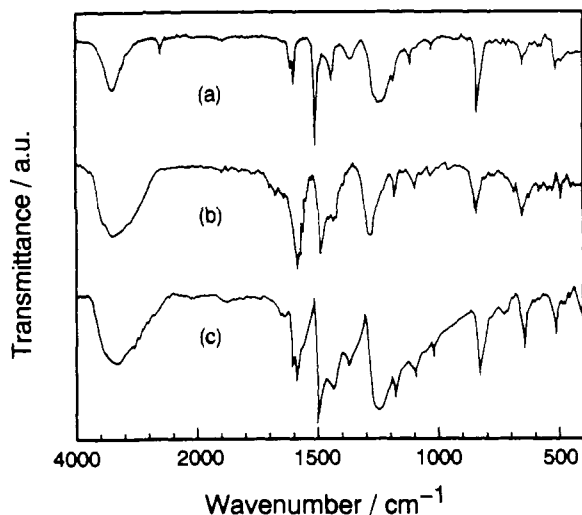


Figure 4. FT-IR spectra of 4-hydroxythiophenol (a), Pb^{2+} -ArSH complexes (b), and PbS particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ (c) taken in KBr pellets.

given by eq 2, where m_e and m_h are the effective mass of an electron and a positive hole, respectively. By applying the above absorption onset to eq 1 and inserting $m_e = 0.080m_0$ and $m_h = 0.075m_0$,⁵¹ where m_0 is the mass of a free electron, the diameters of PbS microcrystals with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ and 3.0 are estimated to be about 39 and 33 Å, respectively. These values are in rough accord with the size of the largest PbS particles of relatively high abundance given in Figure 3, being consistent with the fact that the absorption onset is determined by the largest particles in colloids.⁵²

Figure 4 shows a FT-IR spectrum of isolated ArSH-modified PbS particles, that of 4-hydroxythiophenol and Pb^{2+} -ArSH complexes. The absorption peaks assigned to C-C vibrations of a phenyl ring are observed in a range from 1400 to 1600 cm^{-1} , and a broad peak around 3300 cm^{-1} is assigned to O-H vibrations. However, an absorption due to S-H vibration observed at 2560 cm^{-1} for pure ArSH is absent both for the PbS particles and for the Pb^{2+} -ArSH complexes, evidencing the achievement of capping Pb^{2+} sites of the PbS microcrystal surfaces with phenyl groups through sulfur atoms of 4-hydroxythiophenol.

^1H NMR spectra of ArSH-capped PbS particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ at various temperatures are shown in Figure 5. Unfortunately it was unsuccessful to obtain the ^1H NMR spectrum of PbS particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$, because they were unstable against agglomeration as will be described below in a different section. The resonance of phenyl protons of adsorbed ArSH of PbS particles was split into three groups, two of which appeared at 7.02 and 6.47 ppm as sharp signal groups which superimposed on a broad signal peaking at around 6.3 ppm. Sharp signals observed at 4.85 ppm at 26 °C, which shift toward a downfield with lowering temperature, arise from the resonance of the hydroxyl protons of methanol remained in the CD_3OD solution as an impurity. The resonance of phenyl protons of 4-hydroxythiophenol gave only two sharp signals at 7.13 and 6.67 ppm and that of Pb^{2+} -ArSH at 7.11 and 6.56 ppm in CD_3OD , being downfield compared to that of PbS particles. It is also found that the intensities of the two sharp signal groups were increased and that of a broad signal peak was decreased with lowering temperatures. The broad signal peak must result from slow rotation of phenyl groups of the capped ArSH probably with a high density, while the two sharp signal groups are related to phenyl groups in stationary states. With decreasing temperature, the phenyl groups in rotation are decreased, and those in stationary states are increased. Judging from small temperature dependence of the intensity of the broad signal peak, the capped ArSH have

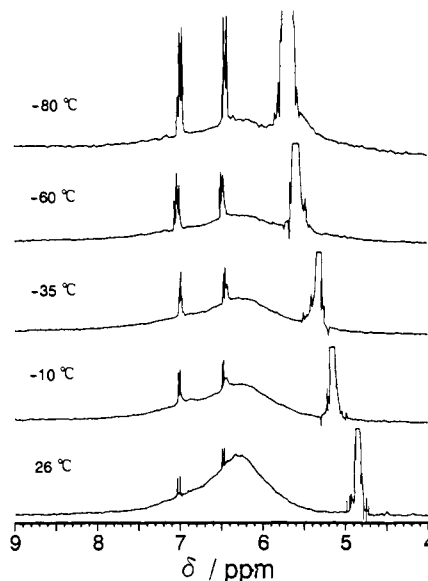


Figure 5. ^1H NMR spectra of a ArSH-capped PbS prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ at various temperatures. The signal intensity is normalized to that of $\text{Si}(\text{CH}_3)_4$ (not shown).

Table I. Analytically Determined Results for PbS Microcrystals Modified with 4-Hydroxythiophenol and Stability Factor Against Agglomeration

preparation condition		composition ^a $\text{Pb}^{2+}:\text{S}^{2-}:\text{ArS}^-$	charge balance ^b	stability factor against agglomeration ^c
$[\text{Pb}^{2+}]/$ $[\text{S}^{2-}]$	$[\text{ArSH}]/$ $[\text{Pb}^{2+}]$			
1.2	4.0	1.30:1:0.65	1.02	<2
3.0	4.0	1.57:1:1.56	1.13	>150

^a Experimentally determined. ^b Calculated by $(2[\text{S}^{2-}] + [\text{ArS}^-]) / (2[\text{Pb}^{2+}])$. ^c The factor of concentration at which the PbS colloid began to agglomerate at room temperature, defined as $C_{\text{conc}}/C_{\text{original}}$, where C_{original} denotes the concentration of PbS present in the original colloids, which were 2.5×10^{-4} M, and C_{conc} denotes that at which the agglomeration began to occur by concentrating the original colloids.

wide energy distributions in their rotations.

Results of chemical analyses of the ArSH modified PbS particles are given in Table I in a relative ratio of $\text{Pb}^{2+}:\text{S}^{2-}:\text{ArS}^-$. Results obtained for carbon and hydrogen are omitted in this table, because the ratio of these two elements agreed with that expected from the chemical composition of 4-hydroxythiophenolate ions (ArS^-) within experimental error. It is seen that the particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ contained larger fractions of Pb^{2+} and ArS^- than those prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$. A good charge balance is achieved at the particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ as shown in Table I, but the particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ had little excess negative charges that may be compensated by other cations such as protons. The amount of protons used for the charge compensator in such cases, however, are negligible compared to the total amount of hydrogen of ArSH used in capping of PbS microcrystals. Considering that the average size and size distribution of the ArSH-modified PbS microcrystals are not greatly different between the two kinds of PbS microcrystals, chemical composition should be almost the same unless there is a remarkable difference in the structure of the capped PbS surfaces. Since the chemical analysis results show that there are large differences in the composition between the two kinds of PbS microcrystals, the structure of these capped PbS surfaces must be different.

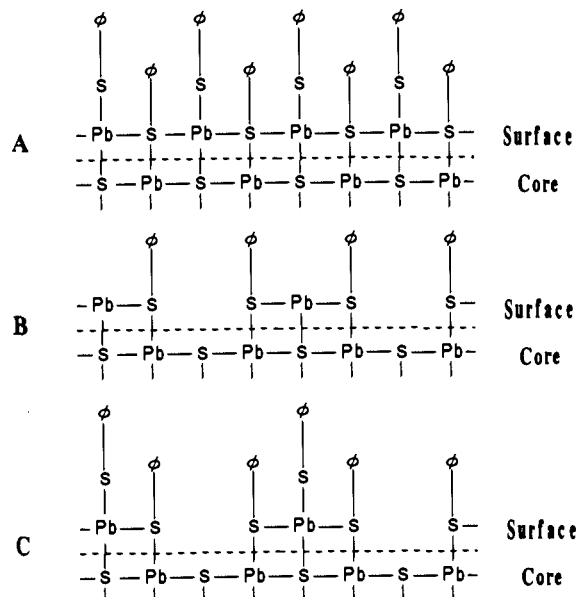
Surface Structure of the PbS Microcrystals. We have attempted to derive information on the surface structures of the PbS microcrystals in an atomic scale. Three different surface structures as illustrated in Figure 6 are first assumed. In this figure, the surfaces are illustrated as plane surfaces but the actual surfaces must be curved, because the prepared microcrystals were spherical, as noticed from Figure 2. In these models, we divide a surface

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Table II. Number of Pb²⁺, S²⁻, and ArS⁻ Constituting a Particle of Various Diameters Having Structures A, B, and C and the Experimentally Determined Size Fraction

diameter (Å)	structure A			structure B			structure C			size fraction [Pb ²⁺]/[S ²⁻] ^a	
	Pb ²⁺	S ²⁻	ArS ⁻	Pb ²⁺	S ²⁻	ArS ⁻	Pb ²⁺	S ²⁻	ArS ⁻	1.2	3.0
9	31	10	58	21	10	21	21	10	40	0	0
12	48	18	78	33	18	30	33	18	54	0	0
15	86	41	112	63	41	45	63	41	79	0.016	0
18	128	68	144	98	68	60	98	68	102	0.062	0.007
21	182	98	198	140	98	84	140	98	141	0.151	0.070
24	249	144	242	197	144	105	197	144	174	0.159	0.256
27	326	201	286	264	201	125	264	201	206	0.151	0.311
30	434	277	354	356	277	157	356	277	255	0.171	0.170
33	547	370	396	458	370	177	458	370	287	0.128	0.104
36	700	484	480	592	484	216	592	484	348	0.058	0.052
39	860	607	556	733	607	253	733	607	405	0.054	0.007
42	1043	752	636	897	752	291	897	752	464	0.011	0.015
45	1256	928	712	1092	928	328	1092	928	520	0.019	0.004
48	1508	1136	804	1322	1136	372	1322	1136	588	0.004	0.004
51	1754	1340	890	1547	1340	414	1547	1340	652	0.008	0
54	2052	1592	988	1822	1592	460	1822	1592	724	0	0
57	2385	1872	1096	2128	1872	513	2128	1872	805	0.004	0
60	2776	2193	1240	2484	2193	583	2484	2193	912	0.004	0
63	3160	2528	1342	2844	2528	632	2844	2528	987	0	0
66	3592	2916	1432	3254	2916	676	3254	2916	1054	0	0
69	4108	3352	1596	3730	3352	756	3730	3352	1176	0	0
72	4600	3784	1720	4192	3784	816	4192	3784	1268	0	0

^a Experimentally obtained size fraction of PbS particles calculated from Figure 3.

**Figure 6.** Models for surface structures of PbS microcrystals modified with 4-hydroxythiophenol.

region of PbS microcrystals into an adsorbed layer and a core. The core is the particle observed by TEM.

Structure A assumes that S²⁻ sites of the core surfaces are fully occupied by adsorbed Pb²⁺ ions, and both Pb²⁺ sites of the core surfaces and the adsorbed Pb²⁺ are occupied by bound ArS⁻ to give the complete coverage of PbS microcrystals surfaces with the organic modifier. Structure B assumes that Pb²⁺ sites of the core are completely covered with ArS⁻ and to compensate excess negative charges due to the bound ArS⁻ a limited amount of Pb²⁺ ions adsorb on the core surfaces. Structure C is a modification of structure B in the point that ArSH species are bound to adsorbed Pb²⁺ ions.

The number of Pb²⁺, S²⁻, and ArS⁻ ions constituting PbS microcrystals of different sizes was calculated for the above mentioned structures by assuming that all of the particles have the same rock salt structure of the lattice parameter of $a_0 = 5.9362$ Å.⁵⁰ In this calculation, a computer was used to count the number of the constituents in building up a particle of a desired size. The procedures of the calculations are given in the Appendix. The

Table III. Analytically Determined Compositions and Theoretical Compositions Given by Structures A, B, and C

[Pb ²⁺]/ [S ²⁻]	component ^a	relative composition			charge balance
		Pb ²⁺	S ²⁻	ArS ⁻	
1.2	anal. ^b				1.02
	structure A	433	286	332	1.51:1:1.16
	structure B	359	286	147	1.26:1:0.51
	structure C	359	286	239	1.26:1:0.84
3.0	anal. ^b				1.13
	structure A	378	241	311	1.57:1:1.29
	structure B	309	241	137	1.29:1:0.57
	structure C	309	241	224	1.29:1:0.93

^a The number of each component containing a PbS particle having the average diameter, calculated by eq 3. ^b Analytically determined results given in Table I.

results are shown in Table II. By taking the size distributions given in Figure 3 into account, the average number ($\langle N_x \rangle$) of Pb²⁺, S²⁻, and ArS⁻ of a PbS particle, defined by eq 3, was obtained for particles prepared with [Pb²⁺]/[S²⁻] = 1.2 and 3.0 where $F(d_i)$

$$\langle N_x \rangle = \sum_i N_x F(d_i) \quad (3)$$

is a fraction of PbS microcrystals with a diameter d_i in the colloids and N_x is the number of the constituents ($x = \text{Pb}^{2+}$, S²⁻ or ArS⁻) of a particle of the same radius having structure A, B, or C. The results are given in Table III.

It is seen that differences in the surface structure are reflected more clearly in the composition of ArSH-capped PbS microcrystals rather than in the charge balance. This implies that experimentally determined compositions can be used as a diagnostic criteria to deduce the surface structure of prepared ArSH-capped PbS. It is not unreasonable to think that there are many different surfaces in a prepared ArSH-capped PbS microcrystal as already discussed above on ¹H NMR spectra of the capped ArSH, but, by comparing the experimentally determined compositions with those given in Table III, we can derive information on what surface structure is predominant in the prepared microcrystals. It is found from comparison of the calculated values with analytically determined results that the composition of the PbS particles prepared with [Pb²⁺]/[S²⁻] = 1.2 is in excellent agreement with that predicted by structure B and that of the particles prepared with [Pb²⁺]/[S²⁻] = 3.0 is fitted to structure A, although a little deficiency of ArS⁻ is noticed for analytically determined result.

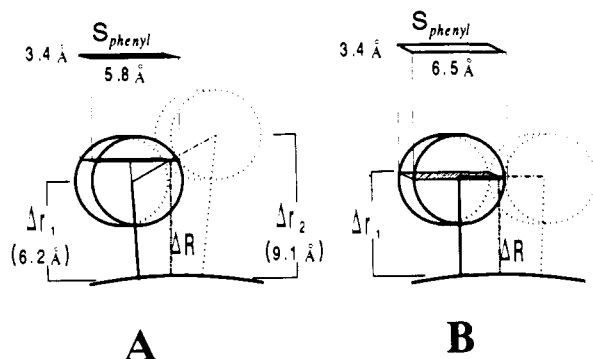


Figure 7. Geometrical configurations of the capped ArSH for structure A and B.

At this stage it seems important to discuss the validity of the proposed surface structures. It is suggested from considerations based on the molecular size of the capped ArSH that the proposed surface structures are impractical for bulk single crystals due to steric hindrance of the phenyl groups of the capped ArSH. However, the problem of steric hindrance is relaxed with decreasing the particle size, because the capping of ArSH occurs on a convex surface of the particles and the degree of the curvature is higher for smaller particles. The critical diameter of ArSH-capped PbS particle having such structures is roughly estimated in the following way.

The number of the capped ArSH on the core surface of a PbS particle of the diameter d_i is not greater than that obtained by dividing the surface area of the capped PbS particle by the cross section of the phenyl group. This threshold number is represented here as N_{\max} , which is given by eq 4 where ΔR is the distance from

$$N_{\max} = 4\pi(\Delta R + d_i/2)^2/S_{\text{phenyl}} \quad (4)$$

the surface of the PbS core to the point where a capped phenyl group comes in contact with an adjacent one, and S_{phenyl} is the cross section of the phenyl group at the distance ΔR (see Figure 7). In the following calculation, the values of 3.0, 1.8, and 1.4 Å are used as the bond length of Pb-S, S-C, and C-C,^{45,50,53} and a phenyl group is assumed to be a disk of 6.5-Å diameter and 3.4-Å thickness which was estimated based on the crystal structure of benzene and van der Waals radius of a carbon atom.^{54,55}

If the 4-hydroxythiophenolate ions are linearly bound to Pb atoms of the core surfaces and to the Pb^{2+} ions adsorbed on S atoms in the core surface, then 6.2 ($=\Delta r_1$) and 9.1 Å ($=\Delta r_2$) are obtained, respectively, for distances between the centers of the bound phenyl groups and the surface of the PbS core as illustrated in Figure 7. S_{phenyl} for that structure is calculated to be 19.6 Å² by using Δr_1 , Δr_2 , and the diameter of phenyl groups, and ΔR is an average value (7.7 Å) of Δr_1 and Δr_2 . In the cases in which all of the ArS^- ions are bound to Pb sites of the core surfaces as in structure B, the phenyl groups make contact with each other at the distance Δr_1 from the PbS core surface as also illustrated in Figure 7. Then, ΔR is equal to Δr_1 and S_{phenyl} is calculated to be 22.1 Å².

The largest particles that were experimentally obtained for structure B were those having the diameter of 60 Å. By inserting this value together with ΔR and S_{phenyl} into eq 4, we have $N_{\max} = 745$, which is much greater than the number of capped ArSH given in Table II for structure B. Thus structure B is practical. In the case of structure A, we have a serious geometrical restriction. By inserting the above described ΔR and S_{phenyl} values into eq 4 for a variety of d_i , it is found that PbS particles having the diameter equal to or smaller than 27 Å give N_{\max} greater than the number of ArSH given in Table II. Accordingly structure A is practical for particles having the diameter less than 27 Å.

According to results shown in Figure 3, the largest particle experimentally obtained with high abundance for $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ had the diameter of 33 Å, being greater the largest limit described above from the geometrical consideration for structure A. However, if N_{\max} of eq 4 is calculated for a particle of 33 Å, it is found that N_{\max} of about 6% less than that given in Table III is obtained. Therefore it seems reasonable to conclude that structure A is predominant in the particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$.

Recently, EXAFS studies²⁴ on phenyl-capped CdSe and CdS have revealed that the crystallographic structures of CdS and CdSe microcrystal surfaces are deformed by capping with benzenethiol and benzeneselenol. If similar things happened in the ArSH-capped PbS, perfect coincidence of the experimental results with the calculated results would not be anticipated.

Stability to Agglomeration. According to the above identification of the surface structures of ArSH-capped PbS, the PbS particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ have partially unmodified surface sites that allow contacts with solution, and they have no net charge in the surfaces. In contrast those prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ are almost completely covered with ArSH and have negative charges on the surface. Then it is expected that the latter colloid is stable against agglomeration as compared to the former colloid, because of the presence of negative surface charges and of more hydroxyl groups of organic modifier than the former. The hydroxyl groups assist in solvation with polar solvents, making the microcrystal stable. Such expectation was demonstrated in the following experiments.

When 100 mL of the transparent brown PbS original colloid ($[\text{PbS}] = 2.5 \times 10^{-4}$ M) prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ was filtered using the ultrafilter (pore size 20 Å) under agitation, the colloid became turbid at the time when about one-half of that colloid solution was filtered, while the colloidal solutions prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ kept its brown transparency even when the colloid was concentrated to 1/150 (Table I).

Photoreduction of Methyl Viologen. PbS microcrystals of 30 Å or less have potentials negative enough to reduce methyl viologen^{40,42} whose redox potential is -0.45 V vs NHE.⁵⁶ PbS microcrystals prepared in the present study should have capabilities for reducing methyl viologen, as judged from the size quantization based on their particle size.

As expected, illumination with a 500 W Xe lamp of the ArSH capped PbS suspensions containing methyl viologen (MV^{2+}) in the presence of sodium tartrate as a hole scavenger resulted in methyl viologen radical cations ($\text{MV}^{•+}$), which were recognized from the characteristic absorption peaks of $\text{MV}^{•+}$ at 396 and 606 nm⁵⁷ both of which superimposed on the absorption spectrum of the PbS colloid. During the course of the illumination, the absorption spectra of the two kinds of PbS colloids prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ and 3.0 were not changed at all, suggesting that the PbS microcrystals were not photocorroded.

Figure 8 shows the time course of changes in absorbance at 396 nm caused by photoinduced formation of $\text{MV}^{•+}$. It was found that the rate of $\text{MV}^{•+}$ production was remarkably hindered by the addition of 5.0×10^{-5} M $\text{Pb}(\text{CH}_3\text{COO})_2$ for the PbS colloids prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 1.2$ as shown in Figure 8b, while little effect of the addition of Pb^{2+} ions was noticed for the PbS colloids prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$ (Figure 8a). As already discussed above, the former PbS has unmodified surface sites (sulfur sites) on which Pb^{2+} ions can adsorb. If the adsorbed Pb^{2+} scavenges a fraction of photoexcited electrons, the rate of reduction of methyl viologen must be decreased, as observed. In contrast, the adsorption of Pb^{2+} ions must occur with less extent for the PbS particles prepared with $[\text{Pb}^{2+}]/[\text{S}^{2-}] = 3.0$, because surface sites of the particles are fully occupied by ArS^- .

It has been reported that PbS microcrystals modified with 3-mercapto-1,2-propanediol emit a strong fluorescence in a visible region.⁴² However, this was not observed for the ArSH modified PbS microcrystals prepared in this study. Accordingly it is

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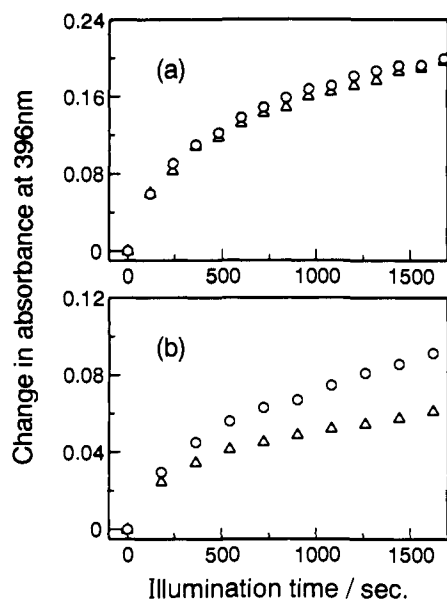


Figure 8. Time course of changes in absorbance at 396 nm caused by photoreduction of MV^{2+} . (a) PbS colloids prepared with $[Pb^{2+}]/[S^{2-}] = 3.0$ and (b) those prepared with $[Pb^{2+}]/[S^{2-}] = 1.2$. 2.5×10^{-4} M PbS colloids contained 1×10^{-2} M MV^{2+} and 0.1 M sodium tartrate and its pH was 7.5: (O) original suspension and (Δ) with addition of 5×10^{-5} M Pb^{2+} ; light source: 500 W Xe lamp ($\lambda > 400$ nm).

speculated that ArS^- groups bound to the PbS microcrystals surfaces quench the fluorescence. The capped ArSH may transfer its electrons to photogenerated holes in PbS microcrystals. It was found that MV^{2+} was photoreduced in the ArSH-capped PbS in the presence of tartrate as a hole scavenger. However, the photoreduction did not take place in the absence of tartrate. These findings seem to suggest that in the absence of tartrate, the capped ArSH is oxidized by the valence band holes and the oxidized ArSH accepts photogenerated electrons from the conduction band, giving no chance for photoreduction of MV^{2+} . If this were the case, then the capped ArSH might work as a mediator for oxidation of some chemical species in solution.

Conclusion

By changing the relative concentration of Pb^{2+} ions to S^{2-} ions in the synthesis of PbS microcrystals with a fixed $[ArSH]/[Pb^{2+}]$ ratio of 4.0, different structures of the capped surfaces were prepared. The most important discovery in the present study is that such difference in the surface structures greatly effects photochemical and photoelectrochemical properties of the capped PbS microcrystals. Furthermore a suggestion was obtained that the surface organic groups, the capped ArSH, have capabilities of the mediation in the electron-transfer reactions.

Appendix

The x , y , z axes of coordinates are chosen along with the crystal axes of the primitive cubic system. If we choose the center of a spherical particle in such a way that it gives a symmetrical point

against the constituent atoms in the primitive cubic system, we have four different centers $P_j(p, q, r)$ which are given by eq A1 ($p, q, r \geq 0$)

$$P_1(0, 0, 0), \quad P_2(\alpha/2, 0, 0), \quad P_3(\alpha/2, \alpha/2, 0), \\ P_4(\alpha/2, \alpha/2, \alpha/2) \quad (A1)$$

where α is the lattice constant of the primitive cubic system. If an atom X in the primitive cubic system is given by $(l\alpha, m\alpha, n\alpha)$, where l, m , and n are integral numbers, then the distance (P_jX) from a center P_j to the atom X is given by eq A2.

$$P_jX = \{(p - l\alpha)^2 + (q - m\alpha)^2 + (r - n\alpha)^2\}^{1/2} \quad (A2)$$

If P_jX fulfills the condition given by eq A3,

$$P_jX < d_i/2 \quad (A3)$$

then we find that the atom X is included in a microcrystal of a diameter d_i .

In this way, calculations were made for P_jX great enough to cover $d_i/2$. The atoms included in a core having the diameter d_i are selected, and the number of them is counted for every P_j ($j = 1-4$). A different P_j gives a little different number of atoms included in a core of the same diameter d_i . We have chosen the largest number (V_{max}) obtained among the four kinds of P_j . The P_j that gives V_{max} is denoted here as P_{max} . Even if the equation " $P_jX \leq d_i/2$ " is used instead of eq A3 to include atoms on the border of the particle, calculations show that the contribution of the border is minor.

Using the above determined $P_{max}(p, q, r)$ the number of atoms in the adsorbed layers on the core is counted. If an atom X satisfies eqs A4, A5, and A6, then it is regarded to be in the adsorbed layers. In eq A6, $k = 1$ and $k = 2$ represent the situation that

$$P_{max}X \geq d_i/2 \quad (A4)$$

$$\{p - (l + \Delta l)\alpha\}^2 + \{q - (m + \Delta m)\alpha\}^2 + \{r - (n + \Delta n)\alpha\}^2 < \\ (d_j/2)^2 \quad (A5)$$

$$|\Delta l| + |\Delta m| + |\Delta n| = k, \quad k = 1, 2 \quad (A6)$$

the atom X exists in the first and second adsorbed layer above surface core atoms, respectively. The atoms in the first layer are directly bound to the core surface.

Calculation of the number of Pb^{2+} , S^{2-} , and ArS^- in a ArSH-capped PbS particle was made by using these procedures. However, PbS is a rock salt structure, being different from primitive cubic system. Then the constant α used above for primitive cubic system must be corrected with use of eq A7.

$$\alpha = a_0/2, \quad a_0 = 5.9362 \text{ \AA} \quad (A7)$$

Furthermore two kinds of atoms, that is Pb and S, must be discriminated by the sum of $(l + m + n)$. If the odd number is chosen for Pb, then S is for the even number. The reverse is also true. Calculations were made for both cases of the presence of Pb^{2+} ion on the origin and of S^{2-} ion on the origin. If we had a little different number of atoms between the two kinds of calculations, the numbers were averaged. The results given in Table II are the averaged ones.