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Formation of Orderly Organized Cubic PbS Nanoparticles Domain in the Presence of TiO_2

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Formation of an orderly organized cubic-shaped PbS nanoparticles domain in the presence of TiO_2 is described. Dodecylbenesulfonic acid was used as surfactant to extract lead ions and TiO_2 colloidal particles together from aqueous solutions to organic phase. The obtained organosol was further influxed for several hours following treatment with H_2S gas. Uniform cubic particles having ordered arrays in a long-range domain were observed on the carbon-coated grids by transmission electron microscopy. The experimental phenomena indicated TiO_2 particles had an important effect on the kinetic procedure during the formation of PbS nanoparticles.

Considerable interest has been shown in recent years to the study of semiconductor nanoparticles because of the beneficial electrical, optical, and electrooptical properties, which are caused by surface effects and quantum-size effects.[1−3] The phenomena of self-assembly in surfactant solutions play an important role in the synthesis of inorganic materials with well-defined microstructures and morphologies. Surfactant-coated nanoparticles have been prepared by several groups.[4,5] Spreading surfactant-stabilized nanoparticles on aqueous solutions has already been applied to form monoparticle layers, because it provides a means for defining the interparticulate distances and facilitates subsequent transfer of the particulate films to a wide range of solid substrates by using Langmuir−Blodgett (LB) techniques.[4] Comparing with the nanoparticles in aqueous phase, the surfactant-coated nanoparticles can be easily isolated without losing their discrete character, dispersed in organic solvent, and placed in polymer matrix and ultrathin film to investigate their special electronic and optical properties.

The cubic-shaped PbS nanoparticles were synthesized in the presence of TiO_2. First, acidic TiO_2 colloid was prepared by hydrolysis of $TiCl_4$ at low temperature.[6] Briefly, 6.8 mL of fresh doubly distilled $TiCl_4$ was slowly added to vigorously stirred 500 mL of water maintained at 0 °C. The mixture was dialyzed to yield a suspension of 8 g/L TiO_2 particles dispersed in water at pH 2. Then, 100 mL of TiO_2 colloid (4.0 g/L), 5 mL of 5.0×10^{-2} M $Pb(NO_3)_2$ solution, and 80 mL of toluene were poured into a beaker. This solution was stirred, and 80 mL of 0.025 M sodium dodecylbenzenesulfonic acid (DBS) solution was added dropwise. The resulting microemulsion was further stirred for 2 h. 63.1% of lead ions and 46.8% of TiO_2 colloidal particles were extracted into the organic phase during this process. The resulting organosol was refluxed for 1 h and then exposed to H_2S in a sealed container. After 30 h, the organosol changed from slightly yellow through bright yellow to brown gradually. No precipitation emerged during this process. The resulting organosol have a long-time stability.

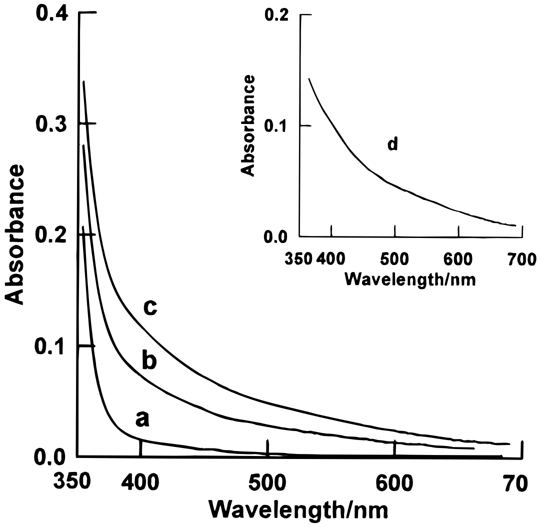

Figure 1. Absorption spectra of the organosol in toluene solvent. (a) Pb^{2+}/TiO_2. (b) PbS/TiO_2 (10 h), and (c) PbS/TiO_2 (30 h), obtained from Pb^{2+}/TiO_2 organosol after exposure to H_2S. Insert (d) is absorption of PbS particles, which was obtained by subtracting (a) from (c).

The UV−vis absorption spectra of the PbS/TiO_2 and Pb^{2+}/TiO_2 organosol are shown in Figure 1. The UV−vis spectra of pure TiO_2[6] and pure PbS[7] nanoparticles are well-known. Comparing curve a with curves b and c, it was found that little absorption emerged in the visible region for Pb^{2+}/TiO_2 organosol, while obvious absorption was found in the same region for another organosol which was obtained from the former organosol after exposure to H_2S. The insert cruve d shows a typical absorption spectrum of pure PbS colloid. The results confirmed the formation of the PbS particles.[7] Compared curves b and c, it is worth mentioning that

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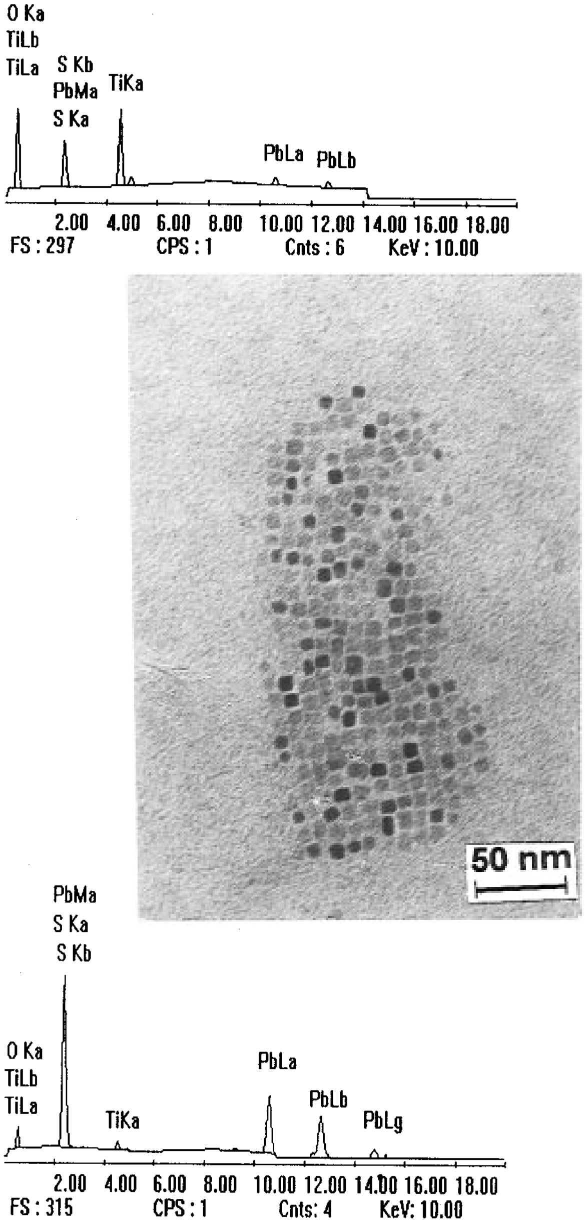

Figure 2. Transmission electron micrograph and EDS results of the sample. The top spectrum represents the composition of the area without cubic-shaped particles. The bottom spectrum represents the composition of the cubic particles area. The sample was supported by a carbon-coated, 200-mesh copper grid.

the red-shift of the bandgap onset occurred when the reactive time was prolonged. This indicated that a slow crystallite growth occurred for a longer reactive time.

Samples for transmission electron microscopy (TEM) were prepared as follows. The nanoparticles-containing toluene solution was dropped on the surface of water, which dispersed to be a layer of film immediately. Carbon-coated copper grids were allowed to float on the organic film for 2 min. Care was taken to avoid deposition of the film on both sides of the grid, after which these grids were allowed to dry under ambient conditions. TEM examination was made on a Hitachi-8100 transmission electron microscope. Electron microscopic examination shows that many domains of particles are present, which occupy approximately 20% of the total areas of the supported film and are uniformly distributed. The particles within the domains are unaggregated and appear to be uniform cubic shape (12 nm, Figure 2), which organize orderly on the carbon-coated grid. The orderly array often takes place on a long-range domain which is usually larger than 4.0 × 10^4 nm^2. The self-assembled action could be due to van der Waals and dispersion forces by analogy with the self-assembly of the docecanethiol-coated Ag_2S nanoparticles in a hexagonal network.[8] The particles were identified as PbS from the selected area electron diffraction pattern (Figure 3). Data obtained from the diffraction pattern are given in Table 1, which establishes a cubic rock salt structure for the PbS particles.

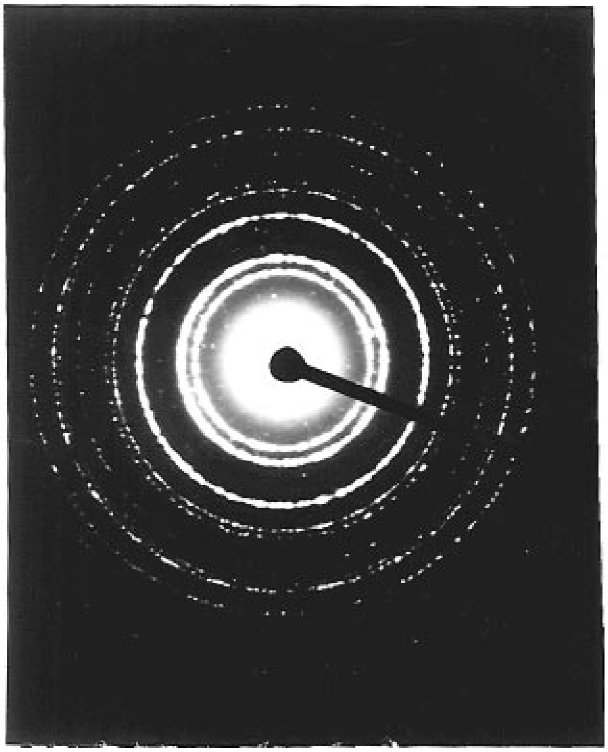

Figure 3. Selected area electron diffraction taken of a region of cubic nanoparticles.

Table 1. Selected Area Electron Diffraction (SAED)

n_d	card vol	calc vol	*hkl*
1	1.790	1.800	311
2	1.484	1.487	400
3 (weak)	1.212	1.2096	422
4	1.0490	1.0486	440
5	0.9386	0.9383	620
6	0.8568	0.8527	444

Energy-dispersive X-ray spectropy (EDS) was employed to identify the composition of the orderly array and the other region. Two different areas are selected: one is a small region among the cubic particles domain (Figure 2, top); the other is a small region without cubic particles (Figure 2, bottom). The results of the analysis in the former region show that the ratio of Pb/Ti is roughly 12:1, while the ratio of Pb/S is 1:1, which further confirmed that cubic particles were mainly fabricated by PbS particles. On the other hand, the results of the analysis in the latter region show that the ratio of Ti/Pb is roughly 7.3:1, which means this region contains

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mainly TiO_2 particles. The results of the analysis show the relatively clear nature of the sample.

The PbS growth habit was well observed under Langmuir monolayer systems.[4,9] Here, it is very interesting that a new kind of cubic-shaped PbS nanoparticles was formed in the presence of TiO_2. It is known for aqueous colloidal experiments that inorganic ions can be adsorbed on metal oxide surface. Studies of many cations, such as Hg^{2+}, Pb^{2+}, and Cd^{2+} adsorbed on TiO_2 or FeOOH, were reported recently.[10] Pb^{2+} may be adsorbed onto TiO_2 at the acidic pH region and form the species $>TiOPb^+$ and $(>TiO)_2Pb$, respectively.[10-12] The possible hypothesis is that lead ions are first adsorbed on the surface of TiO_2, after which the formation of incipient PbS crystallites may occur at molecular level on the surface of TiO_2. We considered that the formation of cubic-shaped particles was controlled by the aggregation process of these small PbS crystallites.

In summary, we have described the formation of orderly organized cubic-shaped PbS nanoparticles domain in the presence of TiO_2. TEM results provide direct evidence that the nanoparticles have well-defined two-dimensional spatial configurations on the carbon-coated grids. The special structure and self-assembled action of the composite have been initially investigated. The existence of TiO_2 and PbS particles is confirmed by EDS and UV−vis spectra.

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