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Research Note

A New Colloidal Technique for the Synthesis of Lead Sulfide Nanoparticles

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In this paper, the use of colloid chemistry in the synthesis of 5 A° lead sulfide semiconductor nanoparticles has been described. Here, hydrogen sulfide gas dissolved in water is used for the chemical reaction, instead of purging the H_2S gas into the solution, which has an influence on particle size. In this technique, the growth of particles was controlled by the addition of EDTA. A fast evolution of the optical absorption spectrum demonstrated the following synthesis. Soon after synthesis reaction, the sample exhibits a structural absorption spectrum with one well-defined peak in a 240 nm wavelength. The absorption spectrum shows a featureless structure, with no tail near the absorption edge being observed.

INTRODUCTION

In the last decade, there has been an increased demand for the nanometer particles of lead sulfide, PbS, due to their unique physical properties. Until now, PbS nanoparticles have been prepared in colloidal solutions [1-7], or embedded in transparent solid media such as glass, zeolite and polymer [8-12]. Bulk PbS has a cubic (rock salt) crystal structure and a narrow direct band gap (0.41ev) at the L point of the Brillouin zone [13,14]. This point is well separated from all the other bands, thus, size quantization will influence, mainly, the valence and conduction band edges. Moreover, the high dielectric constant (17.3), as well as the narrow band and small electron effective mass (< 0.1, m*), create an excition with a large effective Bohr radius (180 A°) and a relatively weak binding energy. The aforementioned properties suggest that size quantization has a strong influence on the electronic properties of PbS nanoparticles. On the other hand, a key objective of research in the field of small semiconductor clusters is to produce such species in a very narrow size dispersion range. Such a material would permit the examination of intrinsic optical and other physical properties of a given cluster dimension unclouded by the averaging effects of having a heterogeneous distribution of cluster size. The results reported for almost all developed techniques so far, show a quite significantly wide dispersion. Previous work on extremely small PbS clusters in zeolite Y [15], shows one of the few that have a narrow cluster size range with a unique observed optical properties. In the present investigation a new colloidal method is introduced for the synthesis of very narrow dispersed lead sulfide nanoparticles.

EXPERIMENTAL

For over 17 years, a range of colloidal techniques has readily prepared small particles of lead sulfide. In this research, based upon the procedure taken from [16], the preparation of lead sulfide nanoparticle solutions was carried out. High quality, pure starting materials are commercially available and were purchased from the Merck Company. The main steps of this procedure, which have been schematically shown in Figure 1, are as follows: 30 μlit of 0.1M $Pb(NO_3)_2$ aqueous solution was added into 30 mlit of water containing 2.29×10^{-3} gr sulfur ions (S^{2-}). Some 30 μlit of 0.1M ethylenediamine tetraaciticacid (EDTA) sodium salt aqueous solution were added to this provided solution, in order to form a complex with Pb^{2+}, which would retard the rate of the subsequent reaction. The solution was then stirred for a few seconds. In order to have a controlled chemical reaction, H_2S gas purging is usually used, the effect of which on particle size is reproduced from [17] and presented in Figure 2. For this reason, H_2S gas dissolved in water was used in this work and

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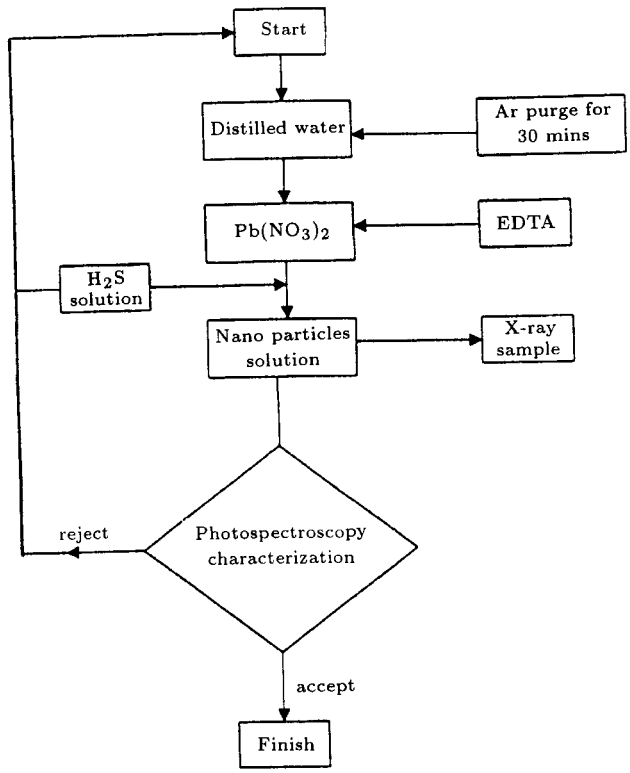

Figure 1. Block diagram of the procedure.

the amounts of S^{2-} in the water were determined by a back titration process (titration with $Na_3AsO_3.12H_2O$) and a direct method. Details of this technique are described in [18]. H_2S gas was prepared from a reaction between ferrous sulfide and hydrochloric acid in a Kipps apparatus. The absorption spectra of the colloidal solutions in visible range were taken using a Hitachi U-3410 spectrophotometer. Most common solvents absorb light strongly in near infrared; therefore, in order to measure the absorption of PbS in this region, it was necessary to use a 200-800 nm wavelength range of photospectroscopy. $MgCl_2$ was added to the solution to induce fluctuation of the nanoparticles and to increase the stability of the colloids. Then, the mixture was transferred to a beaker with a glass slide accommodated at the bottom and the material was allowed to settle onto it. The remaining clear, colorless liquid was then decanted and the relatively uniform film material left on the slide was allowed to air dry. X- ray diffraction was then carried out on the sample.

RESULTS AND DISCUSSION

The reaction took a few minutes to complete, which is time dependent on the initial condition. Light and reactant concentrations have an influence on the rate of the reaction, as well as on particle size. For this reason, a very dark room was used to prepare samples and why a remarkable reproducibility in results was observed. The diffraction pattern obtained confirmed that PbS was the dominant phase. No significant diffraction peak due to $MgCl_2$ was observed. The X-ray diffraction data indicated that nanoparticles of PbS preserve their rock salt crystal structure with a relatively high degree of crystallinity (Figure 3). Due to the aforementioned procedure and despite the agglomeration of particles which occurred during preparation of the X-ray sample, the spectra were still compatible with the results given in [19], in which the particle size was reported to be 18 A°. This clearly shows that, in fact, the particles should be much smaller. One of the absorption spectrum of the PbS nanoparticles colloidal sample is presented in Figure 4, from which a dramatic blue shift

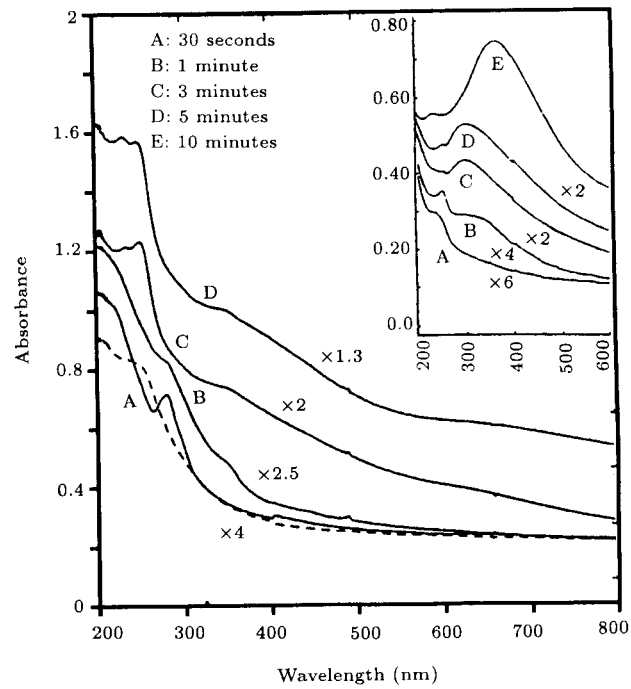

Figure 2. Absorption spectrum of PbS film under H_2S gas purging in various time [17].

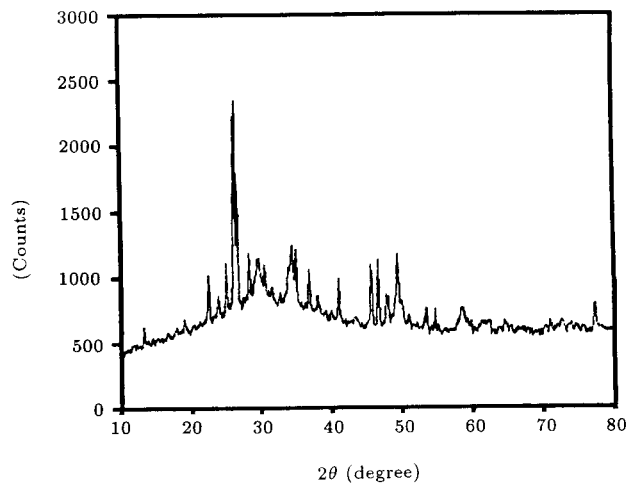

Figure 3. XRD pattern of nanocrystalline PbS.

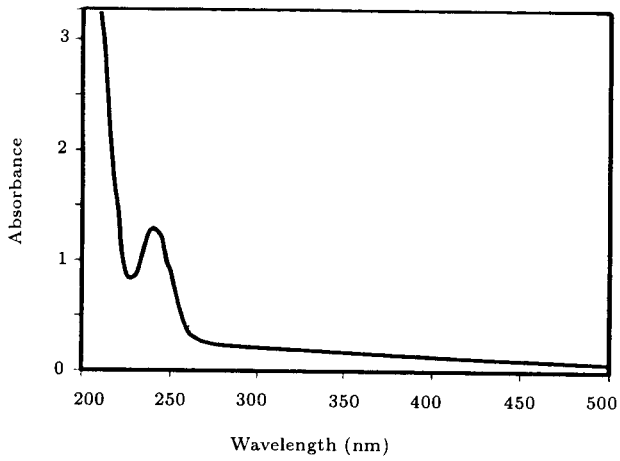

Figure 4. The absorption spectrum of lead sulfide nanostructure colloidal sample.

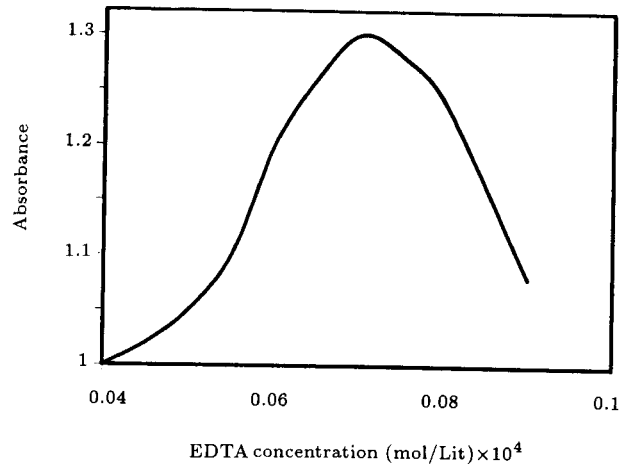

Figure 5. The influence of EDTA concentration in optical absorption spectrum peak.

of the absorption edge, from 3200 nm for balk PbS to 260 nm for the sample, can be seen. The strong absorption peak, which is very close to the expected highest energy of monomolecular PbS itself, is a witness to the success of the proposed method in obtaining uniform nanocrystals. On the other hand, no exitonic absorption structure is observed in the result. This phenomenon only occurs in one of the following cases:

1. Strong excision binding energy,
2. Defects in cluster structure.

It can be concluded that a uniform sample has been provided by this technique. A long tail near the absorption edges, usually seen in results reported from colloidal solutions [1-4], is not observed in our results. This indicates that the PbS clusters formed by the method presented in this paper might have a uniform size distribution and defects might have been reduced due to the surface passivation of oxygen doping from the air. The influence of EDTA concentration on the optical absorption spectrum peak is illustrated in Figure 5. As can be seen from this figure, the optimum concentration is 7 μ mole/lit., which is somewhat different from that reported elsewhere [16]. As the clusters in a colloidal solution are too small, it is difficult to characterize them by using either an ordinary X-ray diffraction apparatus or transmission electron microscopy. Therefore, a theoretical estimation method was applied. For this reason, it seems that the "Tight Bonding Cluster Model", developed and presented by Wang et al. [20], is a reasonable way by which to determine the size of the cluster. Their calculated data for a PbS cluster, as reproduced in Figure 6, has been employed in order to determine our results. The calculation shows an average particle size of 5 A°. As indicated in the introduction, bulk PbS is a narrow band semiconductor with a gap energy of 0.42 ev. Moreover, the top of the valance and

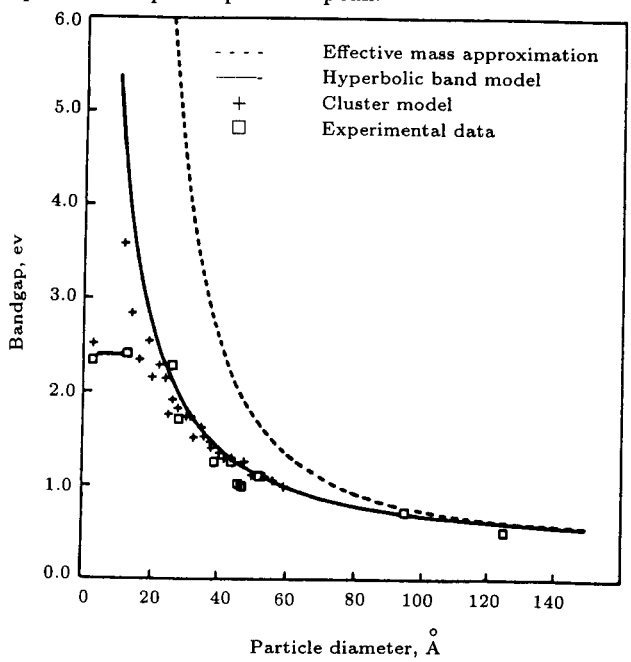

Figure 6. Band gap of PbS as a function of particle size.

the bottom of the conduction band consist of a wave function that is separated from the adjacent ones. Therefore, separation between the band edge can be strongly influenced by the reduction of particle size. Due to the large Bohr radius of the excition in the bulk (about 180 A°), the reduction of particle size to 5 A°opposes strong quantum confinement, which appears as a blue shift of the absorption peak, as shown in Figure 4. According to the discussion which is given by Sitrota et al. [21], the lack of any tail and an excition shoulder at the edge of the tail may be caused by the following: (1) Inhomogeneous broadening, due to the size distribution, (2) Quenching of the excition, due to the large dielectric constant, small effective electron mass and relatively large Bohr radius. On the other hand, comparison of absorption spectra with those of monomolecular PbS demonstrates

the non-contamination of other Pb^{2+} byproducts in the solution. If Pb^{2+} were in the solution, one would have observed an absorption peak at 215 nm. The absence of such an absorption peak in the authors experimental results clearly proves the lack of any Pb^{2+} ions in the solutions. In addition, there is no transition to the excited single molecular orbital $n^3\sigma^2\pi, {}^1\sum^+$ [22].

CONCLUSIONS

1. A new colloidal technique is introduced for the preparation of nanoparticles;
2. H_2S gas dissolved in water has been used instead of traditional h gas purging, in order to control the chemical reaction;
3. Optimum EDTA concentration is almost 7 μmole/ lit, which is different from those reported elsewhere;
4. Optical absorption spectrum of PbS samples shows uniform crystalline nanoclusters provided by this method;
5. The absorption spectrum reveals a featureless structure, due to the absence of a tail near the absorption edge;
6. Based upon the "cluster model", nanoparticle sizes as small as 5 A°can be generated by the proposed technique.

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