OPTICAL AND ATOMIC FORCE MICROSCOPY CHARACTERIZATION OF PbI$_2$ QUANTUM DOTS

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ABSTRACT

Lead iodide (PbI$_2$) clusters were synthesized from the chemical reaction of NaI (or KI) with Pb(NO$_3$)$_2$ in H$_2$O, D$_2$O, CH$_3$OH, and C$_3$H$_7$OH media. The observation of the absorption features above 350 nm with the help of integrating sphere accessory strongly suggests the quantum dot formation of PbI$_2$ in solution. Spectral comparison between the synthesized PbI$_2$ clusters in solution and PbI$_2$ nanophase by impregnation of PbI$_2$ in four different pore-sized porous silica indicates that the PbI$_2$ cluster size in solution is less than 2.5 nm in lateral dimension. Atomic force microscopy (AFM) measurements show that the PbI$_2$ clusters deposited onto three different molecularly flat surfaces are single-layered. The measured height is 1.0 $\pm$ 0.1 nm. The swollen layer thickness can be attributed to the intralayer contraction from the strong lateral interaction among PbI$_2$ molecules, which is supported by *ab initio* calculation. [1]Raman scattering measurement of LO and TO modes of PbI$_2$ in bulk and in the confined state were also conducted in 50- 150 cm''' region. The observed three bands at 74, %, 106 cm^{-1} are assigned to TO$_2$, LO$_2$, and LO, mode, respectively. The relatively small red-shift in LO modes may be caused by the surface phonon polaritons of PbI$_2$ nanophase in the porous silica.

INTRODUCTION

The study of nanophase materials physically confined in various hosts has attracted much attention in recent years. Depending upon the physical properties of the confining hosts and the nature of the confined materials, many unique mechanical, thermal, and optical properties have been observed and are related to the different types of confinement effects. The physical confinement, interfacial energy at the guest-host boundaries, and the reduction of the confined particle size can lead to, for example, modification of materials' hardness and depression of the melting and freezing transition temperatures. The quantum confinement of the free electrons in metals and the excitons in semiconductors can result in the observation of the colorful surface plasma resonance and the shifts of the band gap. Dielectric confinement due to the confining hosts provides the means to tune the surface plasma resonance frequencies and to enhance the nonlinear optical effects at interface by changing the dielectric constant of the confining hosts. In addition, the observation of the surface phonon polaritons is also due to the dielectric confinement effects. However, it is unfortunate that these fore-mentioned confinement effects are in effect at same time so that a clear fundamental understanding of what exact role of each confinement play is hard to be realized. Further, the often asked question of how these confinement effects modify the physical and chemical properties of the confined materials is not at all conclusive. A clear demonstration of the cross-over effects from bulk state to cluster form has not yet been illustrated.

Heavy metal halides, such as PbI$_2$, form a unique series of layered semiconductor compounds. Besides having potential applications for y-ray detection, the strong intralayer chemical bonding and the weak interlayer van de Waals interaction have made these materials to be good candidates for understanding the cluster formation and growth in confining media and for the study of different types of confinement effects along different crystallographic axes.

Sandroff *et al.*[3] first investigated layered semiconductor clusters in various solvents. Based upon the optical absorption of a solution containing PbI$_2$ and BiI$_3$ clusters and the cluster size distribution from TEM measurements, a single layer platelet-like cluster model was proposed. The *disrupt* blue-shifted absorption bands below 350 nm for PbI$_2$ in different solvents were explained by charge carrier confinement in different-sized crystallite with a single layer thickness. Other research groups[2,3] have re-examined similar systems. Disagreements have been raised in terms of the bands assignments in UV-Vis spectra which may result from the possible I$^-$ or I$_3^-$ presence in solution. However, no efforts have been made to understand how the band gap is truly modified when PbI$_2$ semiconductor changes its physical dimension from small clusters to its bulk. No solid explanation has been put forward to account for the discontinuous blue-shift of the PbI$_2$ clusters in solution. In addition, there has been no direct experimental evidence reported in literature to support the proposed disk-like single-layered semiconductor clusters being formed in the solution phase.

Therefore, the motivation of the present research is: i) to study cluster formation and growth mechanisms in the solution phase, which can provide information on crystal growth on earth and in microgravity;[5] ii) to understand how the confining geometry modifies the physical and chemical properties of the restricted clusters in terms of shape, lattice parameters, as well as the thermal and optical properties; iii) to provide direct experimental evidence of the size and morphology of these layered semiconductor clusters formed in solutions; iv) to study quantum confinement effect when PbI$_2$ is physically confined in four different pore-sized porous glass, which serves as the feed-back to estimate the PbI$_2$ clusters formed in solution.

EXPERIMENTAL

I. Synthesis of PbI₂ Clusters in Solutions

As reported by others,[1,2] The starting materials are $Pb(NO_3)_2$ and NaI or KI which were purchased from Aldrich with purity of 99⁺%. No effort was made to further purify the materials. Two reasons why we chose NaI instead of KI in most of our experiments were the following: 1) synthesized PbI_2 clusters are insoluble in pure alcohol but $NaNO_3$ is. Therefore, the dilution of the colloidal suspended solution will not result in much of the alteration of the formed cluster size; 2) in order to unambiguously identify PbI_2 cluster formation and cluster sizes with AFM, the complete removal of $NaNO_3$ from the surfaces and maintaining the minimal perturbation to the PbI_2 clusters are critical so that SPM images can directly reflect the structural and frictional information on PbI_2 clusters themselves. Both $Pb(NO_3)_2$ and NaI (or KI) were prepared in same solvent with known amount of molar concentration. Lead iodide clusters were synthesized by simply mixing the two solutions in the optical cell before subject to various measurements.

II. Impregnation of PbI₂ in Well-Defined porous Glasses

In order to understand quantum confinement effect on PbI_2 particles, an alternative experiment was planned. That is, to impregnated PbI_2 in well-characterized porous glass. The detailed impregnation procedure has been reported elsewhere. [9] Only a brief outline is given in this paper.

Gelsil porous substrates with 2.5, 5, 10, and 20 nm pore diameters were used for PbI_2 impregnation. The PbI_2 was purchased from Aldrich with 99⁺% purity. The porous glass was first cleaned and then was placed into 10 mm inner diameter and one-end sealed quartz tube. The tube was placed into a vertical furnace. The glass was slowly heated to 450 C in 6 hrs and then was cooled down to 110 C. A sufficient amount of PbI_2 powder was loaded into a smaller glass tube with open ends. Then the tube containing PbI_2 was transported into the bigger tube where the porous glass was dried. The system was heated again very slowly to 450 C. The melted PbI_2 flew out the inner tube and emersed the porous substrates. Upon the 1 hr soaking in the molten state of the PbI_2, the impregnated porous substrate was slowly cooled back to room temperature. The sample tube was properly sealed for characterization.

Hr. Optical Characterization

In order to understand the solution structure and cluster formation kinetics, time resolved and static UV-Vis spectrophotometric measurements were carried out on a Rapid Scan OLIS RSM Spectrophotometer and a Hitichi 3501 spectrophotometer. With OLIS RSM, a series of spectra with time interval of 1-10 ms was collected in the spectral range of 300 - 550 nm. The spectral intensity and frequencies were analyzed as the function of time. The static electronic absorption and extinction spectra were made possible with or without an integrating sphere accessory on a Hitachi 3501 spectrophotometer. All the spectra were measured in 1000-185 mu region with 1 nm resolution.

IV. Atomic Force Microscopy (AFM)

AFM images in TappingMode, constant force, and lateral force modes were obtained with a Nanoscope III atomic force microscope from Digital Instruments. All measurements were performed under ambient conditions with typical relative humidities ranging from 50 - 60%. Well-calibrated E- and A-scanners were used in the present experiments. With A scanner, atomic scale topography images of the hexagonal sheet of SiO_4 in cleavage basal plane of Muscovite mica can be readily obtained on a freshly cleaved mica surface. By comparing the measured value of the nearest neighbor distance of the SiO_4 tetrahedral with the literature value, the lateral resolution of the A-scanner on the atomically flat surface is less than 0.02 nm. Vertical resolution of both A and E scanners in both tapping and constant force modes is less than 0.1 nm. In order to further ensure the consistency in vertical resolution, as we reported elsewhere,[5] a freshly cleaved PbI_2 single crystal surface was imaged which resulted in the observation of half the unit cell distance on c-axis, i.e. a single molecular layer step of PbI_2 along c-axis. The step height was used as an internal height calibration. The measured single layer step height was 0.7 ±0.2 nm which is in good agreement with 0.698 nm in literature.[']

V. Raman Measurement

Raman scattering measurements of PbI_2 in its bulk and confined phase in porous silica were conducted with a Spex Raman spectrometer, which is equipped with a double-grating monochrometer and Ti:Saphire laser pumped with At⁺ laser. The scattered light was collected at 90° to the excitation laser beam. Each spectrum was obtained with 2 cm''' resolution and I second integration time. A water cooled photomultiplier tube was used as the detector. The typical excitation energy of the laser was -100 mW at 770 nm.

RESULTS AND DISCUSSION

I. Optical Characterization of Solution Structure

In order to understand solution structure and to identify of possible species present in solution, efforts were made to systematically study i) solvent effect on reactants, i.e., NaI and Pb(NO$_3$)$_2$; ii) solvent effects on the reaction products, i.e., PbI$_2$ clusters and NaNO$_3$; iii) Pb:I molar ratio effect on reaction products; and iv) concentration effect on the cluster size formation. In the following section, each individual effect will be discussed sequentially.

Fig. 1 illustrates optical absorption spectra of reactants NaI and Pb(NO$_3$)$_2$ in methnaol solution. Both solvent and Pb(NO$_3$)$_2$ did not show any absorption band above 250 nm. However, KI solution did show two absorption bands at 270 and 320 urn, respectively. As pointed out by Wang and Herron[3], the observed two

Fig. 1 Optical spectra of NaI and Pb(NO$_3$)$_2$ in methanol solution, and methanol itself.

peaks at ~325 and 270 nm are primarily due to the absorption of I$_3^-$ species in methanol solution. Similar spectra were also observed for NaI or KI dissolved in H$_2$O, D$_2$O, propanol methanol solution under ordinary light irradiation. Fig. 2 demonstrates the optical spectra of reaction products by mixing of NaI and Pb(NO$_3$)$_2$ with different molar concentration ratio. Three different Pb:I ratios were plotted out in this figure. They were Pb:I = 1:2, 1:3, and 1:4, respectively. As the number of iodine ions increases, the peaks at 270 mu and 320 urn increase accordingly, while a weak peak at 420 nm remained stationary. This observation further suggests that the bands at 270 nm and 320 nm were due to I$_3^-$ complex formed in solution rather than what was believed to be the signature of PbI$_2$ cluster formation in solution.

In order to unambiguously identify PbI$_2$ cluster formation and to clarify true electronic absorption band(s) due to PbI$_2$ clusters in solution, we have collected both extinction and absorption spectra of PbI$_2$ colloidal solution at four different concentrations. The extinction spectra were obtained via simple transmission spectra, while the true absorption spectra were collected with the help of integrating sphere accessory. The extinction spectra, consistent with the work reported in the past,[1-3] showed

Fig. 2 Optical spectra of the reaction products from mixing of NaI and Pb(NO$_3$)$_2$ with different molar concentration ratio.

two bands at 270 nm and 320 urn. However, the absorption spectra clearly showed additional bands above 350 mu, which were not observable in extinction spectra, as shown in fig. 3. In addition, the band position shifts to the red and absorption intensity is enhanced as the PbI$_2$ concentration increases. When the concentration changed from 5.0 to 1.0 mM/l, the electronic absorption band due to PbI$_2$ clusters blueshifted from 505 nm to 420 mu. At 0.5 mM concentration, the electronic absorption due to the PbI$_2$ clusters was expected to overlap with the band at 320 Inn.

It is known that when the physical size or dimension of semiconductors is comparable to or smaller than its exciton Bohr radius (for PbI$_2$, a$_B$ = 1.9 mu), quantum confinement of the electron and hole will result in an appreciable blue-shift from its bulk band gap. Based on the effective-mass approximation (EMA) theory proposed by Brus,[9] the absorption energy E(R) for a nano-sized semiconductor particle (or quantum dot) can be estimated by the following equation:
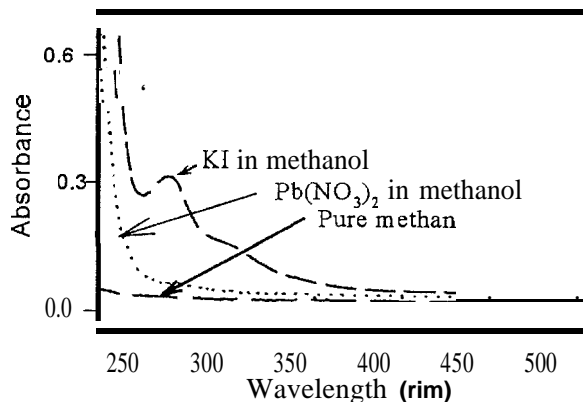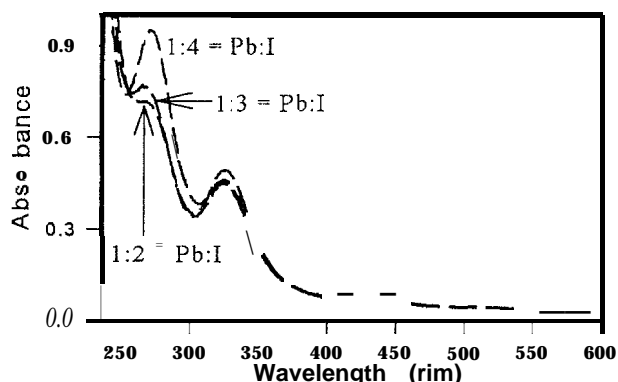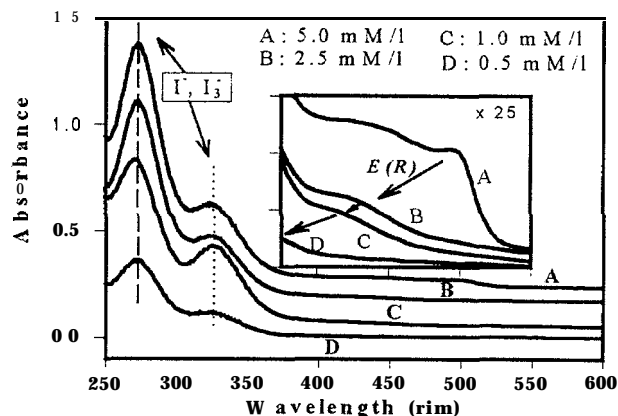

Fig. 3 Absorbance spectra of concentration dependence of PbI$_2$ in methanol solution.

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$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\varepsilon R} + small \ term \qquad (1)$$

where $E(R)$ is the absorption band gap, R *is the size* of the quantum dot, m_e^* and m_h^* are the effective masses of electrons and holes. ε is the dielectric function of the semiconductor. The first term in the equation (1) is the band gap of bulk semiconductor. The second term is due to the quantum confinement of the electron and hole pair. And the third term is Coulomb interaction between the electron and hole. Clearly, the **band gap** of the confined semiconductor is modified by the second ($\propto 1/R^2$) and the third ($\propto 1/R$) terms. Therefore, as the particle size changes, the band gap is changed accordingly. As illustrated in fig. 3, the absorption edge of PbI_2 clusters synthesized in methanol solutions does blueshift gradually as PbI_2 concentration decreases. If it is assumed that the lowest solution concentration has the smallest clusters, then one would expect to observe the largest blueshift in the band gap. Further, as the solution concentration increases, larger clusters are formed that result in an increasing redshift that would ultimately approach the band gap of the bulk material. This trend is consistent with what is predicted by equation (1) and therefore, the absorptions between 550-420 nm for different concentrations are attributed to quantum confined PbI_2 clusters.

I. Confirmation of the Existence of Single-layered PbI_2 Clusters Formed in Solution

Fig. 4 shows one of the typical TappingMode AFM images of the PbI_2 colloidal solution deposited on mica surface. It is clear that all PbI_2 clusters have the same height of 1.0 ± 0.1 nm. In order to eliminate any possible structure alteration due to the mica surface, which can lead to false height information, the same PbI_2 colloidal solution was used to deposits on graphite and SAM derivatized mica surfaces. The same height information was also obtained. Therefore, the 1.0 nm height of the image is considered to be the true height of the PbI_2 clusters. It is also conceivable that the PbI_2 clusters must be disk-like as discussed in previous section and proposed by others.[2,7] Then, the PbI_2 clusters on mica surface are orientated with their c-axis perpendicular to the mica surface. Therefore, the measured image height should reflect the layer

Fig. 4 TappingMode AFM image of lead iodide deposited on a freshly cleaved mica surface. The image height is 1.0 ± 0.1 nm.

thickness of the PbI_2 clusters. Due to the tip convolution problem, no attempt has been made to resolve the lateral dimension of the PbI_2 clusters. As pointed out earlier, the measured single layer thickness of the bulk lead iodide is 0.7 nm, while the height of the PbI_2 clusters was 1.0 nm. The 1.4 times layer thickness expansion seems to be surprising. *Ab Initio* calculation of PbI_2 and BiI_3 clusters, on the other hand, has shown that energy-optimized interlayer and intralayer distances of Pb_6I_{12} were 11% expanded and 1 % contracted, respectively, with respect that of the bulk. A geometry optimization calculation suggests that the equilibrium interlayer thickness expanded 40 % while the intralayer distance was contracted by 3 %. Therefore, the observed 1.4 times of the swollen interlayer is expected. As it was argued by Marino *et al.:* In *the case* of Pb_6I_{12} clusters with D_{3h} point group symmetry, the electron-rich I atoms of the top layer are arranged in head-on configuration with respect to I atoms at the bottom layer. For the bulk PbI_2, however, each I atom in the top layer is located directly above the midpoint between two iodine atoms positioned in the bottom layer. Therefore, it was expected that PbI_2 clusters tend to laterally contract and to vertically expand.

Optical and AFM characterizations have provided sufficient evidence that the PbI_2 clusters formed in methanol solution is single-layered. The lateral size of the disk-like clusters, based on the quantum confinement of the excitons, is comparable or smaller than that of the exciton Bohr radius $a_B = 1.9$ nm.

III. Optical Characterization of PbI_2 Impregnated in Porous Glass

Fig. 5 showed the electronic absorption spectra of bulk PbI_2 and the PbI_2 physically confined in 2.5, 5, 10, and 20 nm pores of silica substrates. As expected, the PbI_2 confined in large pores, the absorption spectrum showed a little blueshift in band gap. However, a noticeable blueshift was observed at - 505 nm when the PbI_2 was confined in 2.5 nm pore, which is consistent with the quantum confinement theory proposed by Brus. 'o By comparing the optical spectrum
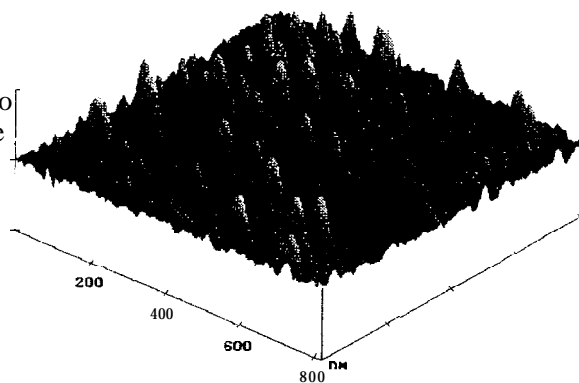
of PbI_2 impregnated in 2.5 nm in fig. 5 with the spectrum of PbI2 clusters synthesized in methanol solution at 5 mM concentration in fig. 3, a same absorption band edge was observed. This observation provided strong indication that the PbI_2 clusters synthesized in the methanol solution was less than 2.5 nm in size. As the concentration decreases, the cluster size gets smaller so that the absorption band of the PbI_2 clusters was further blueshifted.

Fig. 6 illustrated Raman spectra of PbI_2 bulk and confined in four different pore-sized silica host. There were three bands observed in 60 - 150 cm-' region. They are at 75, 96, and 106 cm-', respectively, which had been assigned to TO_2, LO_2, and LO_1 optical phonon modes of PbI_2 crystals. As the pore size decreases, LO modes are broadened and the center frequencies seem to be red-shifted. The red-shift of the band at 106 cm^{-2} is more pronounced. It is speculated that the red-shifts in LO modes may be due to the enhancement of the surface phonon modes resulting from the local electric field at guest-host interface for small panicles. However, the experimental results are further from conclusive to make a claim of surface phonon observation in this system. More experiments are current underway to study surface phonon polartons in layered semiconductor quantum dots.
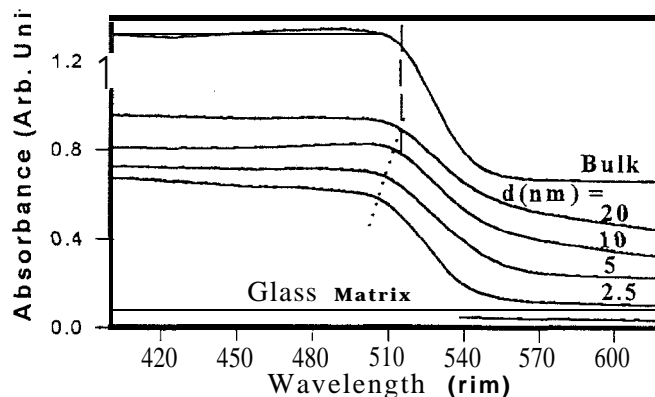

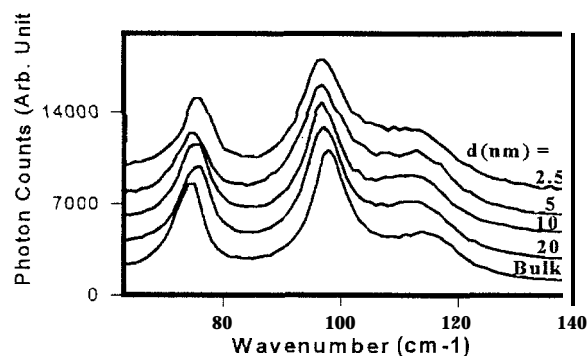Fig. 5 Electronic spectra of bulk and the confined lead iodide in four different pore-sized silica substrates.

Fig. 6 Raman spectra of the bulk and the confined lead iodide In four different pore-sized silica,

CONCLUSION

Optical characterization of PbI_2 clusters synthesized in methanol solution with integrating sphere has unambiguously confirmed the PbI_2 cluster formation. A spectral comparison of the electronic transitions between the PbI_2 clusters synthesized in solution and physically confined in porous glass suggests that the cluster size in solution is less than 2.5 nm in lateral dimension. This observation is consistent with the concept of strong quantum confinement sets in when the particle size is comparable or smaller than the exciton radius ($a_B = 1.9$ mu).

AFM measurements of PbI_2 clusters on mica, graphite, and CH_3 surfaces suggest that the clusters formed from solution synthesis are disk-like. A thickness of 1.0 ± 0.1 nm observed at 0.5 mM concentration confirms, for the first time, that these clusters are single-layered. The 40% expansion of the interlayer distance can be attributed to the finite size effect of the clusters. At small sizes, a strong intralayer chemical bonding can result in the lateral contraction with respect to the bulk value and can lead to the expansion in layer thickness.

LO and TO modes of bulk and the confined PbI_2 were also characterized via Raman scattering measurements. The observed red-shifts and spectral band broadening of LO modes (LO_1 and LO_2) may be attributed to surface phonon polaritons of PbI_2 nanophase in the porous host. However, the experimental results are not yet conclusive.

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