XANES: observation of quantum confinement in the conduction band of colloidal PbS quantum dots

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Abstract. The presented investigations aimed at development of inexpensive method for synthesized materials suitable for utilization of solar energy. This important issue was addressed by focusing, mainly, on electronic local structure studies with supporting x-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis of colloidal galena nano-particles (NPs) and quantum dots (QDs) synthesized using wet chemistry under microwave irradiation. Performed x-ray absorption near edge structure (XANES) analysis revealed an evidence of quantum confinement for the sample with QDs, where the bottom of the conduction band was shifted to higher energy. The QDs were found to be passivated with oxides at the surface. Existence of sulfate/sulfite and thiosulfate species in pure PbS and QDs, respectively, was identified.

1. Introduction

Development of inexpensive methods for synthesized materials that demonstrate both visible light activity and high solar energy utilization along with stability is still a challenge. Here we propose to explore structures based on lead sulfide (PbS) as one of the promising materials for photovoltaic (PV) applications considering its tuneable broad band absorption in the quantum regime, equal confinement of electrons and holes and a long lifetime of the excited states. Such low-dimensional semiconductor structures have recently provoked an increasing interest due to their peculiar optical and electronic properties as compared to bulk materials [1]. The size of QDs limits the electron energies available within them due to quantum mechanics considerations. The latter, in turn, define the position of energy bands and, consequently, material bandgaps and optical properties depending on QDs shape and composition [2]. One of the advantages of QDs is an ability to grow them easily up to a desired size. This means they can be tuned across a wide variety of bandgaps without changing an underlying material or synthesizing techniques. Such easy bandgap tuning makes them desirable for solar cell use. In this respect QDs are similar to the existing, but expensive, GaAs tandem cells having the calculated efficiency of the same order. The colloidal QDs, particularly lead sulfide, are expected to further improve this. As opposed to CdS and ZnS, the bandgap width of PbS is very sensitive to finite size effects manifesting the incredibly high rise of optical absorption energy of PbS QDs versus bulk PbS. Variation of the size of PbS QDs could provide the optical bandgap, Eg, to be increased up to 2.8

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against the “bulk” value of \(~0.4\) eV at room temperature [3]. That means the mentioned QDs have bandgaps which can be tuned into the far infrared (IR) energy region that normally remains untapped via traditional materials. Let us note that half of the whole solar energy reaching the Earth is in the IR, mainly in the near IR, region. Embedded into QDs solar cell IR-sensitive materials are just as easy to use as any others, enabling of cost-effective capturing of much more energy. Sensitivity of lead sulfide QDs to the visible and near-IR radiation in 400-3000 nm wavelength range makes them very promising for PV applications. Their additional advantage is the ability to be sprayed onto flexible surfaces, including plastics. It enables the production of less expensive and more durable solar cells compared to the common silicon-based solar cells. This paper presents the preliminary research of electronic local structure of unoccupied states under QDs size modification with supporting investigations of XRD and TEM. To our knowledge this is the first x-ray absorption investigations on these materials, which reveal the detailed local electronic structure of QDs in comparison to the bulk one. That kind of in-depth knowledge of the properties of these materials would be invaluable for their prompt application in solar energy conversion devices.

2. Experimental

Investigated colloidal PbS NPs and QDs were grown by wet chemical and radiation method. Particular details of synthesis routine could be found in [4]. XANES measurements at the sulfur \(K\) edge were performed at room temperature on the 9.3.1 beam line [5] at the Advanced Light Source (Berkeley, USA). X-ray absorption spectra were gathered in the total fluorescence yield (TFY) and the total electron yield (TEY) detection modes with a total energy resolution of \(~0.6\) eV. Bulk sensitive TFY data were collected using a Hamamatsu Si photodiode while rather surface sensitive TEY - by measuring the sample drain current. The samples for XANES measurements were prepared by placing 2 ml of colloidal QDs solution on quartz substrates which were subsequently dried on a hot plate (at level of 100 °C) for 15 min.

3. Results and discussion

3.1. Experimental observations

The results of synchrotron XRD measurements for colloidal PbS QDs confirmed their single-phase character with NaCl structure. The details of XRD and TEM observations and analysis are not presented here due to the article size restriction and could be found elsewhere [6]. According to the synthesis procedure described in [4], nano-particles of different sizes, \(~50\) nm (NPs) and \(~5\) nm (QDs), were grown as was manifested by TEM (data are not presented here). A narrow size distribution of QDs is observed. The high resolution (HR)TEM investigations confirmed the monocrystalline PbS QDs formation. In accordance with synchrotron XRD result, three main \(fcc\) diffraction patterns, i.e. 200, 111, and 220, were identified.

XANES measurements were devoted to directly evaluate the eventual modification of conductive band position/profile of bulk PbS versus PbS QDs. Fig. 1 shows the bonding symmetry for the bulk and QDs of PbS along with PbS(VI)O\(_4\), Na\(_2\)S(IV)O\(_3\) standard samples near the sulfur \(K\) edge spectra recorded in TFY, TEY, and transmission (TR) detection modes. The transitions from an atomic-like S \(1s\) state to the unoccupied S \(3p\) \(\sigma^*\) antibonding orbitals are probed.

For bulk PbS target the self-absorption (SA) effect [7, 8] was visible in experimental data (intensity damping of the first resonance, see Fig. 1 A)). The differences in the spectral profiles for bulk PbS XANES spectra collected in TFY and TEY detection modes in the higher energy region, 2.476-2.486 keV, definitely indicate on the surface oxidation. From comparison of investigated here XANES spectra to PbSO\(_4\) and Na\(_2\)SO\(_3\) standards and the literature data [9], the feature at \(~2.478\) keV can be attributed to the absorption of sulfur in the form of sulfite (S(IV)O\(_3\)), whereas the second resonance at \(~2.482\) keV mainly in the form of sulfate (S(VI)O\(_4\)), Fig. 1 A.

A blue shift, visible for the absorption threshold (inflection point), is about \(1.67\) eV for PbS QDs with respect to the bulk one in consequence of decreasing the conductive band minimum \(p-S\) states contribution, antibonding orbital of \(t_{1u}\) symmetry, at about \(2.470\) keV (see the shoulder marked as 1), Fig. 1 B. Whereas the absorption onset positions for bulk and QDs PbS obtained under the technique
mentioned in [10], so called extrapolation and arctangent subtraction data analysis methods, make possible to conclude that this shift is less than 1 eV.

As it is well known, the energy gap of semiconductor separating the conduction and valence energy bands is its defining feature. In semiconductors of macroscopic sizes the gap width is a fixed parameter determined by the material’s peculiarity. It is changed in the case of nano-scale semiconductor particles smaller than ~10 nm. This size range already corresponds to the regime of quantum confinement, when the spatial extent of the electronic wave function is comparable with the quantum dot size. As a result of such “geometrical” constraints, electrons “feel” the presence of the particle boundaries and respond to the particle size changes by adjusting their energy. This phenomenon is known as the quantum-size effect and it plays an important role in QDs. Here we assume that a blue shift of the absorption threshold (Fig. 1 B) occurs due to quantum confinement. Our suggestion is bolstered up by the fact that contrary to Si, Cu$_2$S, CuInS$_2$, CuInGaSe$_2$ and CuZnInS$_2$ having small Bohr exciton radii and generally preserving their bulk properties, PbS has large Bohr exciton radius, ~ 20 nm [11]. Since the QDs radius of PbS investigated here is much smaller than the Bohr radius of the exciton in the initial bulk material, optical and electronic properties of PbS QDs may exhibit their great enhancement allowing the wide tunability, even producing bandgaps that can reach the red edge of the visible light. It was shown that the optical absorption onset of PbS QDs can be tuned from 3000 nm to < 600 nm as a function of QD size [12]. Precise examination of the TEM data shown in [4] reveals the dimension of the smaller PbS QDs to be of order of 5 nm. If these QDs are the main contributor to the aggregate, they will account for the blue shift in the XANES spectrum of PbS QDs.

Other noticeable differences in XANES spectra were found comparing the above edge regions, around ~2.480 keV, Fig. 1 B. The sharp features around ~2.480 keV in colloidal PbS QDs can presumably be attributed to the absorption of sulfur in the form of thiosulfate [8] versus sulfate/sulfite revealed at the surface of bulk PbS.
As observed there are no differences in TFY and TEY XANES of QDs spectra profiles, except a small discrepancy in the resonances intensity (data are not presented here). As particles become smaller, a bigger fraction of the atoms is located on the surface, resulting in the increased surface sensitivity (we are considering here the influence of “surface atoms” on the final XANES spectral profile) often visible in TEY measurements compared to TFY. As it is shown the investigated QDs have the average size of about 5 nm. For such small objects the contribution of surface component from each QD is hardly distinguishable within the differences between TEY and TFY spectra, since even for the soft X-rays the probing depths for TEY and TFY are at about 5 and 100 nm, respectively [13]. These values are larger for semi-hard X-rays. It makes clear why TFY and TEY XANES spectra for the sample with QDs provide the similar profiles.

Finally, the XRD analysis of PbS QDs does not expose the existence of other, than cubic, phases of PbS with the rock-salt structure [6], whereas all standards, discussed under XANES qualitative analysis, have low-symmetry crystallographic structure, like orthorhombic or monoclinic, which was not detected by the XRD. It is likely that the surface of PbS QDs is oxidized, forming a thin structurally disordered in macro-scale, thus invisible to XRD, passivated layer of $\text{SO}_x$. We cannot exclude the possibility that the thiosulfate comes from the oxidation of unreacted $\text{S}^2$ in the system. Qualitative analysis of PbS QDs and thiosulfate [8] XANES spectra allows us to preliminarily conclude, that the surface sulfur atoms in the state of thiosulfate have a minor contribution into the spectrum profile close to conduction band minimum. To conclusively determine a measure of the surface oxidation and to estimate precisely its eventual influence on the observed blue shift in comparison to the quantum-size effect further photoelectron spectroscopy and high resolution TEM measurements with the following advanced analysis are necessary and are currently ongoing. These results will be published elsewhere.

3.2. **Size effect. FEFF8**

The calculations of PbS cluster of increasing size were done by FEFF8 by adding the successive coordination shells to the central S atom until radius (R) of 9.4 Å. It was found for a cluster of increasing size that the S $p$ unoccupied states form a shoulder at the absorption edge enhancing its intensity (inset in Fig. 1 A) until cluster radius 9.4 Å, where no further modification of near-structure profile was found. Next, the calculations for cluster of fixed diameter of 3.6 nm were repeated taking into account a different number of inequivalent sites of S close to the surface region, defined as sites with different coordination numbers. Such an approach was previously described in details in [14]. It concerned the relation between the total number of atoms in full shell cluster and the percentage of surface atoms. Our result is presented in Fig. 1 B at the bottom. A significant effect of decreasing the shoulder intensity (marked as 1) and increasing the states marked as 2 was observed for the sample with QDs compared to unoccupied states of bulk PbS. Similar dependence is clearly visible in the experimental XANES spectra, establishing, thus, that electronic structure of unoccupied states close to the absorption threshold is very sensitive to size effect and surface atoms contribution in the final XANES profile.

4. **Conclusions**

Presented here preliminary XANES studies seem to be promising tool for the determination of the local structure of our samples. In case of PbS QDs with size of about 5 nm, the sulfur $p$ states at the bottom of the conduction band are blue shifted as compared to bulk PbS. This observation suggests a widening of the energy gap caused by the quantum confinement effect. The QDs were found to be passivated with layer of $\text{SO}_x$ at the surface. Existence of sulfate/sulfite and thiosulfate species in pure PbS and QDs, respectively, was identified. To decide on the surface oxidation further photoelectron spectroscopy and high resolution TEM measurements are necessary.

**Acknowledgements**
The synthesis work was partially supported by the Texas Engineering Experiments Station and the Texas A&M University. X-ray absorption measurements were performed at the Advanced Light Source, which is supported by DOE (DE-AC03-76SF00098).

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