

INFLUENCES OF SOLVENT DIELECTRIC CONSTANT ON PbS SURFACE

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Abstract. *Surface-related properties and influence of solvent play important roles in lead sulfide nanocolloids which have been attracted numerous researches due to their wide range of applications from optoelectronics to biology. This paper represents our ab initio study on geometry and electronic structure of PbS surface. Here the influence of solvent was statically included using the conductor-like screening model (COSMO). The results show that the screening charges from solvent increase the surface rumpling but reduced surface relaxation. Interaction between solvent dipoles and surface electric charges enhances the distortion of electron cloud of surface atoms as well as polarizes surface bonding. However, such solvent effects tend to saturate when the dielectric constant increases.*

I. INTRODUCTION

Nanocolloids have been being an attractive subject in material science owing to its wide scope of applications ranging from optoelectronics to biology. Both fabricating and applying studies devoted to this kind of materials usually face to the complicated interactions between nanocrystals and other components including surfactant, solvent, electron-donor and acceptor agents. The interactions between solvent and nanoparticles have been intensively examined. These interactions were believed to be the driving forces of crystal growth in solution according to the Oswald ripening mechanism formulated by I. M. Lifshitz and V. V. Slyozov [1]:

$$\langle R \rangle^3 - \langle R \rangle_0^3 = kt \quad (1)$$

$$k = \frac{8\gamma V_m^2 c_{r=\infty}}{54\pi\eta a N_a} \quad (2)$$

Here, k is the crystal growth rate constant, γ is the surface energy, V_m is the molar volume, $c_{r=\infty}$ is the equilibrium concentration at a flat surface, η is the solvent viscosity and a is the solvated ion radius. Experiments on preparation typical nanocrystalline materials such as ZnO, CdS in various solvents were fitted very well with Lifshitz and Slyozovs formulation [2, 3]. However, because such model only takes thermodynamic parameters of the system into account, effect of electronic interaction is still in a black box. Meanwhile, the experiments demonstrated the strong increase in surface energy with increasing solvent dielectric constant [2]. This implied that the electrostatic interaction between surface charge of nanoparticles and solvent dipole moments on surface stabilization is an importance part of the black box. The electrostatic interaction was also shown to act on optical properties of nanoparticles. The increase of solvent dielectric constant gave rise to the blue shift of photoluminescence peak of Si and 3C-SiC nanoparticles according to the

far-field electrostatic screening of energy states [4]. The charge transfer rate from PbS nanoparticles to stabilizer molecules was increase with increasing dielectric constant [5].

In this work, we aimed at examining the effect of electrostatic interaction at solvent/solid interface on the solid surface in the framework of density functional theory. The surface of choice was the infinitive flat one of lead sulfide PbS. This rock salt crystalline material has narrow band gap $E_g=0.29$ eV (at low temperature) [6] and strong quantum confinement effect with Bohr radius $R_B=18$ nm [7] which promote it to the first rank in fabricating hybrid nanocomposite optoelectronic devices. Atomic geometry and electronic structure of PbS surface in vacuum have been intensively investigated with various methods including Xray standing wave (XSW) spectroscopy [8], X-ray photoemission spectroscopy (XPS) at room [9] and low temperature [10] and many *ab initio* calculations [11-14]. However, its behaviors in polar solvents have not reported yet. Here, atomic geometry and electronic structure of PbS surface were examined in various solvents with relative dielectric constant ranging from 1 (vacuum) to 78.54 (water). The effect of solvent was added using conductor-like screening model (COSMO) [15] which only takes the electrostatic interaction between embedded solid and solvent dipole moments into account.

II. Modeling details

Because (001) surface is the most dominating surface for "rock-salt", it has been chosen as calculated model. A supercell composed of a vacuum slab stacked on a PbS slab along (001) direction was generated as quasi-2D simulation of such surface (Figure 1a). The vacuum slab thickness was about four times of the unitcell size, i.e 24 Å so that the interaction between neighbouring PbS slabs vanishes. The PbS slab was consisted of 3 PbS atomic layers which will be mentioned in this report as surface layers and center layer. Molecular orbitals (MOs) were built up via linear combination of atomic orbitals (LCAOs), in which, each atomic orbital, in turn, was a linear combination of numerical atomic-like (NA) wave functions [16]. Owing to the neatness of NA basis set, contribution of all electrons can be included in the electron potential. The relativistic effects were also taken into account in the electron potential. Local density approximation (LDA) type exchange correlation potential formulated by Perdew and Wang (PWC) was utilized [17].

In order to get the solvation effect involve, a dielectric continuum model called conductor-like screening model (COSMO) was used [15]. In dielectric continuum model, solute molecule is embedded in a dielectric continuum with relative dielectric constant ϵ . It forms a cavity within the continuum of which, the surface is called "solvent accessible surface" (SAS) (see Figure 1b). The response of solvent dipoles to the charge distribution of the solute due to statistical electric interaction the electrostatic interaction between solvent dipoles and charge distribution of the solute molecules establishes a screening charge density $\sigma(r)$ on SAS:

$$4\pi\epsilon\sigma(r) = (\epsilon - 1)n(r)E^-(r) \quad (3)$$

Here, $n(r)$ is the surface normal vector at r , $E^-(r)$ is the total electric field at the inner side of SAS at r . The problem is that how SAS can be defined to calculate and $E^-(r)$ arises from unknown screening charges themselves and solute charge distribution.

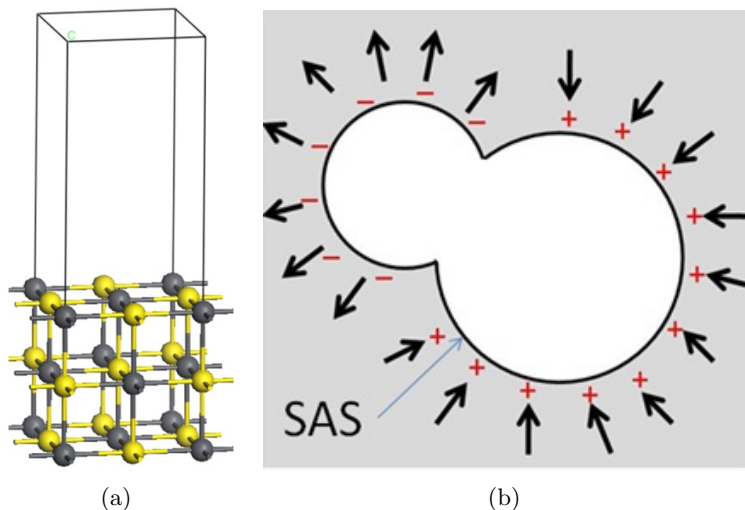


Fig. 1. (a) Supercell model used in surface calculations and (b) solvent accessible surface (SAS) with red minus and plus signs denoting screening charges which originate from the response of solvent dipole to the charge distribution of solute.

In COSMO method, SAS is obtained as a superimposition of spheres centered at the atoms without interior parts. The radii of the spheres are determined as the sum of the Van der Waals radii of the atoms of the molecule and the probe radius of the solvent molecule which depend on the solvent geometry and can be determined experimentally. Concerning the second problem, COSMO method utilizes the approximate boundary condition of vanishing potential on the surface of a conductor to determine screening charge:

$$q = -A^{-1}BQ \quad (4)$$

where q is vector of screening charges, A and B are Coulomb matrices and Q is vector of total solute charges. Once screening charges are determined, an electrostatic COSMO potential can be formulated and added to Kohn-Sham potential in every self-consistence field cycle. The calculation details of COSMO can be found in the original article [15].

III. Results and discussions.

III.1. Surface atomic geometry and electronic polarization of surface ions.

In order to characterize the surface structural reconstruction, surface relaxation δz and rumpling Δ were defined as following:

$$\delta z = (Z_{S_s} - Z_{Pb_s})/d_0 \quad (5)$$

$$\Delta = 1/2 * (Z_{Pb_s} - Z_{S_c} + Z_{S_s} - Z_{Pb_c})/d_0 \quad (6)$$

Here, z specifies Cartesian coordination of atom on the direction perpendicular to surface; S_s , Pb_s are S and Pb atoms in the surface layer; S_c , Pb_c are S and Pb atoms in the center layer; d_0 is the calculated PbS bond length of bulk model. In table 1, these parameters

Table 1. A comparison of surface rumpling δz , surface relaxation Δ (in %), Surface core level shifts (SCLSs) $\Delta\varepsilon_s$ of Pb 5d and S 2p states (in eV) between difference theoretical results and experimental observations

	δz	Δ	$\Delta\varepsilon$ of Pb 5d
Theoretical methods			
Core-shell model (up to more than ten surface layers)[18]	2.1	-3.5	-
Madelung potential estimation [17]	-	-	0.26
Ab initio calculations on 11-atomic layers			
PP/Gaussian basis set/LDA [21]	-3.0	-4.1	-
Ab initio calculations on 7-atomic layers			
PP/PW/GGA [11]	0.03	-5.1	-
PP/PW/GGA [12]	-1.3	-8.4	-
FP/LAPW/GGA [14]	2.9	-7.1	-
Ab initio calculations on 3-atomic layers			
FP/DNP/LDA (Our work for bared surface)	0.91	-2.20	0.26
Experimental measurements			
XPS on PbS at low temperature T=100K [10]	-	-	-
XPS on PbS at room temperature [9]	-	-	0.0±0.1
XSW on PbS at room temperature [8]	< 1%	< 1%	-
LEED*** on PbTe [19]	7	-4	-

from our all electron full potential calculation (FP-NA/LDA) were compared with results of previous works. Despite of the divergence of surface rumpling values and average surface relaxation by different theoretical methods, all of them led to the same trends that the most-top atomic layer possesses the largest surface relaxation ranging from $-3.5\% \div -8.4\%$. Concerning the surface rumpling, full potential-linear augmented plan wave (FP-LAPW) method [11] and core-shell model [18] were in good agreement to predict that in the most-top atomic layer S atoms considerably shift outwards in comparison with Pb atoms (S atom at the top of the surface) but the use of pseudo-potentials (PP-LAPW) predicted insignificant positive rumpling [13] or even flipped the rumpling trend with Pb atom at the top of the surface [14]. Experiments were involved to clarify the surface structural reconstruction trends. Unfortunately, X-ray standing wave (XSW) measurements on PbS at room temperature could not help to exactly estimate surface relaxation [8]. Basing on these measurements, surface relaxation was thought to be less than 1%. The better method to observe surface structure, the low energy electron diffraction (LEED), was only carried out on PbTe, an isoelectronic counterpart of PbS [19]. What can be drawn from such experiment was that surface Pb atoms were experimentally confirmed to shift inwards in comparison with non-metallic atoms. Then it was believed that full potential calculations by I. G. Batyrev *et al* [11] and our group should be more reliable than the one with pseudopotentials. However, our values are much smaller than the FP/LAPW/GGA ones. It should be noted that those values from literature were corresponding to 7-atomic-layer PbS slab model, meanwhile our calculation model was only 3-atomic-layers thick.

Then we increased the slab thickness up to 7-atomic-layers. The thickness-dependences of surface rumpling and surface relaxation are represented in Figure 2. According to this, those values decreases with the increasing of the slab thickness and at the same slab thickness, our method predicts smaller surface reconstruction than literature in [18].

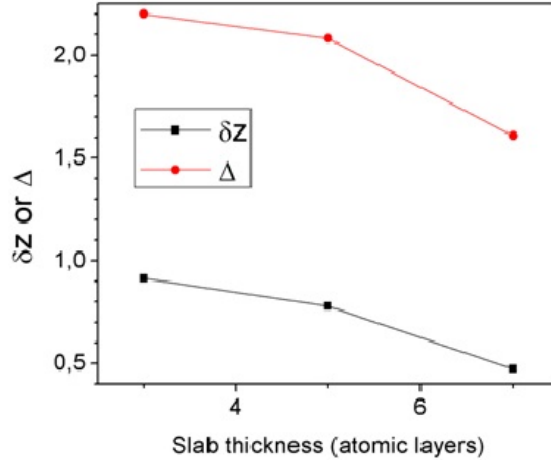


Fig. 2. The slab thickness dependence of surface relaxation and rumpling from our calculation.

III.2. Surface structural reconstruction, surface coordination imperfection and interaction between electronic dipoles of surface atoms.

To gain a deeper insight into the rumpling effect, we recalled the simplest theory for cohesion in ideal ionic crystal which includes only inter-ionic Coulomb interaction and the strong short-range core-core repulsion due to Paulis principle. According to this, the surface relaxation is purely corresponded to the reduction of Madelungs constant at the surface due to the reduction of the coordination number. Then, the surface relaxations at every Pb and S site should be the same. That means the surface rumpling should be absent for ideal ionic crystals.

If one used the core-shell model, additional short-range effects were involved, i. e. intra-ionic core-shell interaction, shell-shell, core-shell interactions between first and second neighbors [18]. These interactions correspond to electron polarization potential of each ionic shell and overlap potential of wave functions at different sites, which usually occur in covalence bonding. The quantitative agreement between full-potential methods and core-shell model rumpling suggested that the surface rumpling may originate from the electronic polarization of surface ions due to coordination imperfection and covalent bonding.

The left panel of Figure 3 is (010) cross-section of the electron deformation which is the difference between electron density of PbS slab and total electron density of isolated

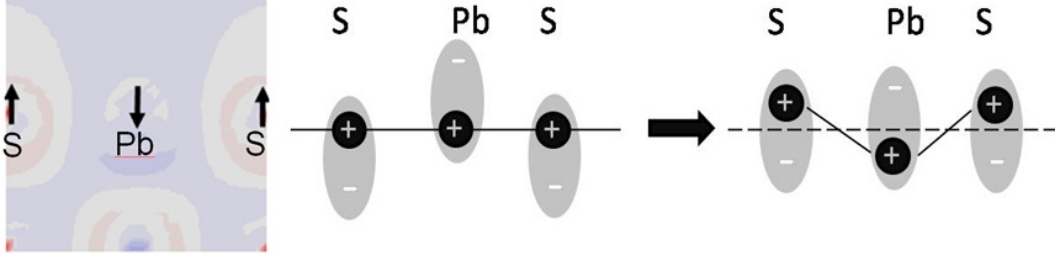


Fig. 3. The formation of surface dipole due to the surface coordination imperfection (left) and the rumpling of surface layer to optimize dipole-dipole interaction energy (right).

atoms. The red color denotes electron-enhanced region and the blue color denotes electron-reduced region. According to this, there were distortions of electron clouds at the surface which gave rise to the formation of surface electronic dipoles (see inserted arrows). Then, it was believed that the geometrical rearrangement of surface ion corresponding to the surface rumpling tended to optimize the dipole interaction energy (see right panel of Figure 3). On the other hand, the softy of electron potential in pseudo-potential methods seemed to underestimate the electronic polarization. As a result, they failed to predict the rumpling of PbS surface.

III.3. Effects of polarized solvent on PbS surface.

Figure 4a shows the developments of surface relaxation and rumpling up on increasing solvent dielectric constant. Figure 4b is the corresponding changes in electronic dipoles of surface atoms. It was suggested that the solvent screening charges enhanced the surface electronic polarization which, in turn, increased the surface rumpling. At the same time, the screening potential could be considered to compensate the coordination imperfection at the surface when it reduced the surface relaxation. However, these two quantities showed clear convergences to about 2% (surface rumpling) and 1.7% (surface relaxation) when the solvent polarizes as strong as water with dielectric constant 78.54.

The enhancement of surface electronic polarization with increasing solvent dielectric constant was accompanied by the enhanced polarization of surface bonding. The concentrated atomic charge of surface and center atoms calculated on the base of Mullikens population analysis [20] exhibited difference solvent dependences (See Figure 5a). The absolute charge values of surface atoms increased up to 9% while the center ones changed less than 2% when the solvent polarization increases. This demonstrates that the solvent effect the polarization of bonding in surface layer only. In experiment, the change in bonding nature at the surface is usually evaluated on the base of SCLSs. It has been proposed that the larger ionicity give rise to the smaller SCLSs [21]. The SCLSs of PbS surface has been attracted both experimental and theoretical studies because of different smearing effects which were believed to make it difficult to observe SCLSs at room temperature. The temperature smearing or phonon broadening was evidenced to dominate the SCLSs of 2p S band which could be only observed at low temperature (~ -0.3 eV) [10]. However, even at low temperature, the SCLSs of 5d Pb band was still unobservable. It was believed

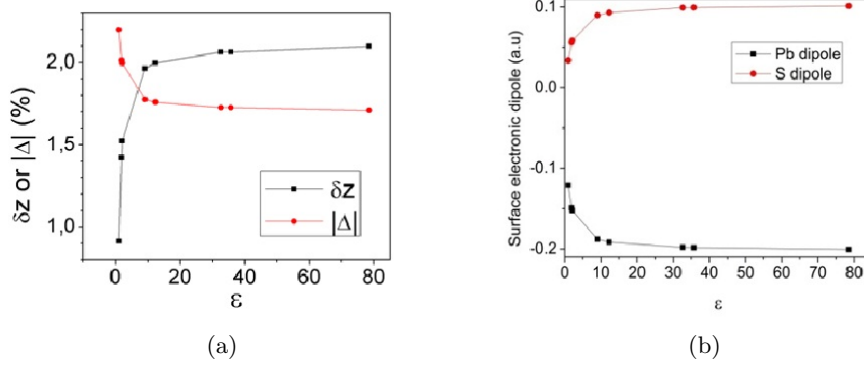


Fig. 4. The developments of surface geometry parameters (a) and electric dipoles of surface ions up on increasing solvent dielectric constant.

to be so small that the natural broadening (Lorentzian broadening) could overlay it. In our calculated energy range, only 5d Pb can be observed. Figure 5b represents the dependence of SCLSs of 5d Pb band on dielectric constant. The calculated SCLSs values are very small (below 2%) and reduce quickly when the dielectric constant increased. This is in consistent with the increase of ionicity according to the dielectric constant.

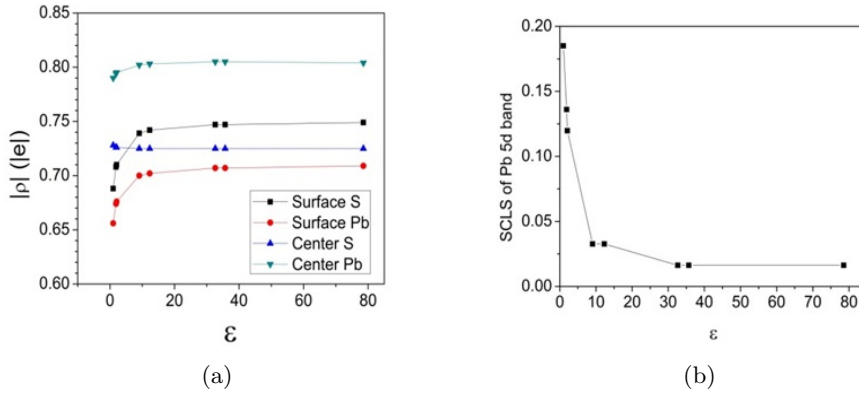


Fig. 5. The dependence of concentrated atomic charges (a) and surface core level shifts of Pb 5d band (b) on dielectric constant.

IV. Conclusions.

Solvent effects were studied electrostatically by incorporating a continuum solvation model into Kohn-Sham Hamiltonian of density functional theory. It was shown that the surface rumpling originates from the electronic polarization of surface ions. Solvent

screening charges enhanced the polarization as well as surface bonding. As a result, the surface rumpling was increased but the SCLS of 5d Pb states was reduced. Besides, the potential induced by screening charge seemed to compensate for the surface coordination imperfection, suppress the surface relaxation.

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