Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Surface Passivation of Lead Sulfide Nanocrystals with Low Electron Affinity Metals: Photoluminescence and Photovoltaic Effects

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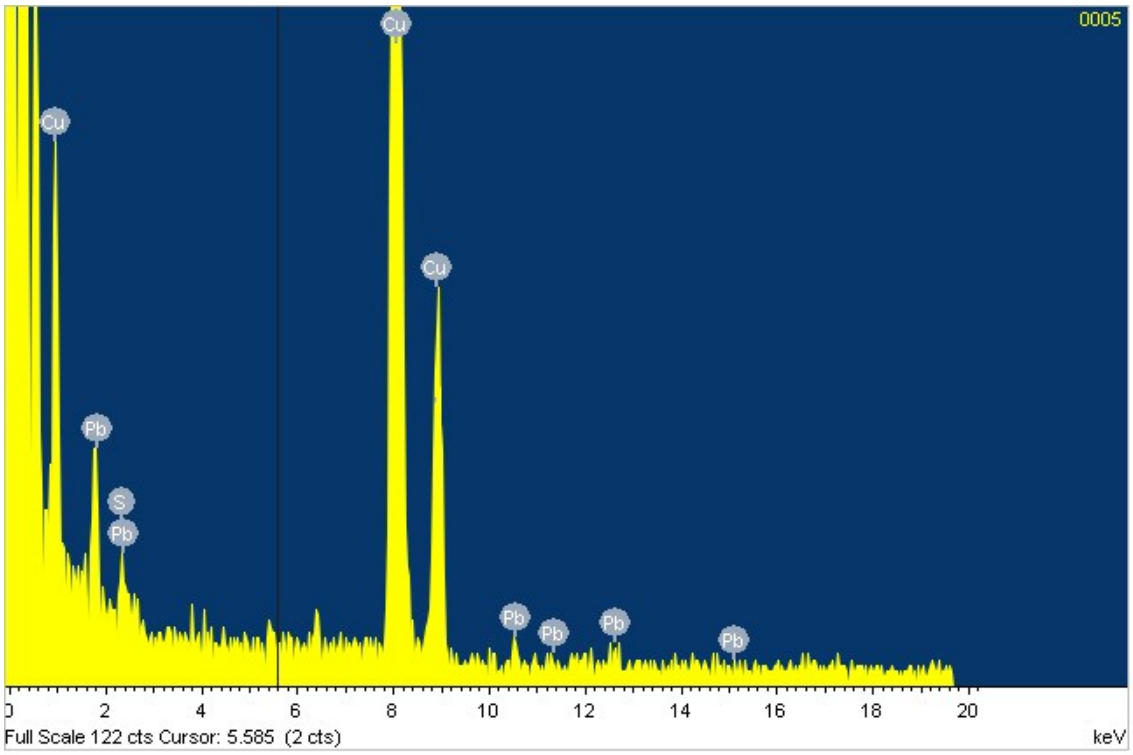

Figure S1. The EDS analysis of PbS QDs supports its elemental composition.

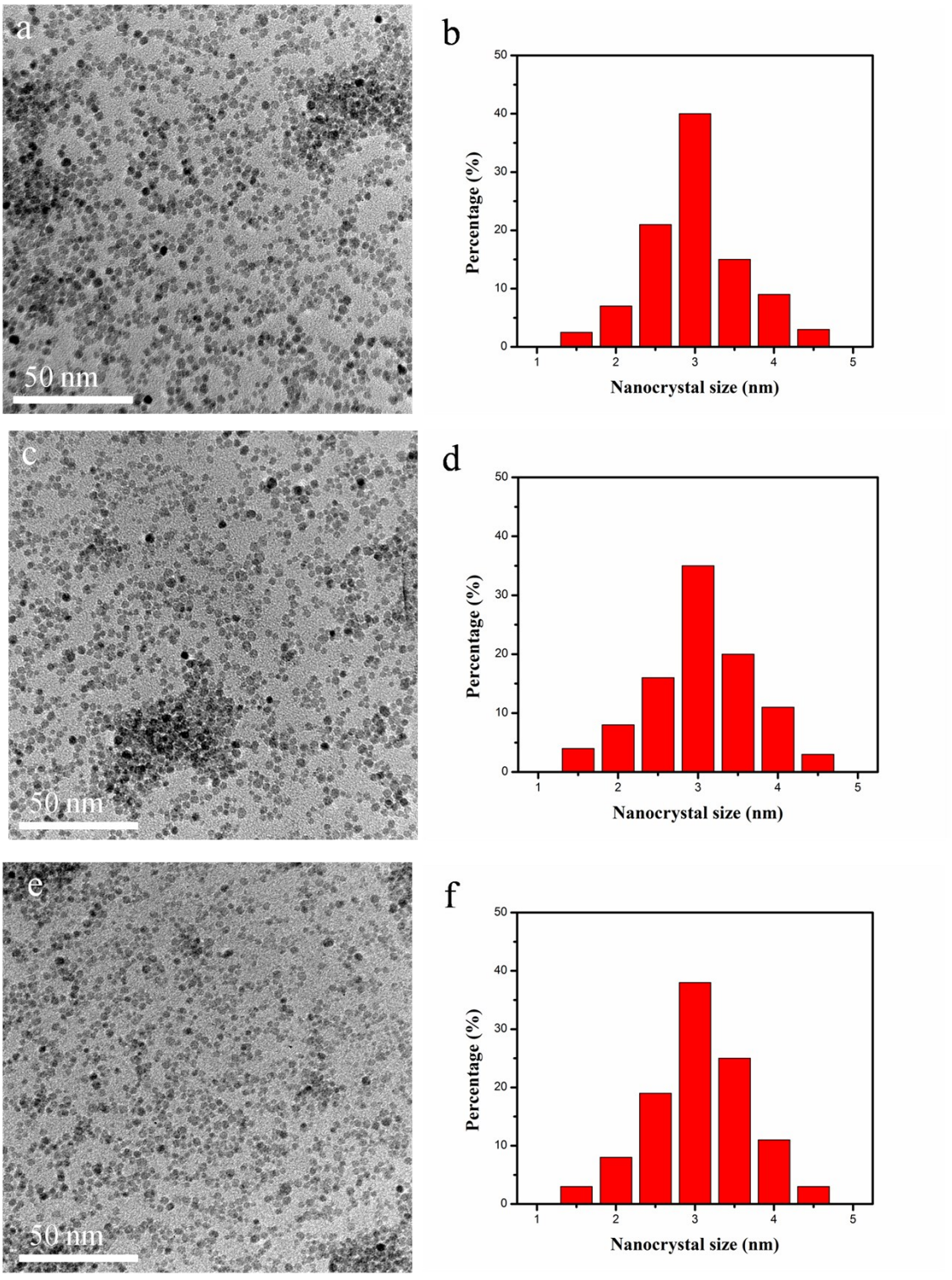

Figure S2. The TEM images and size distribution graphs of PbS nanocrystals after doping with Cd (a,b), Ca (c,d), and Zn (e,f).

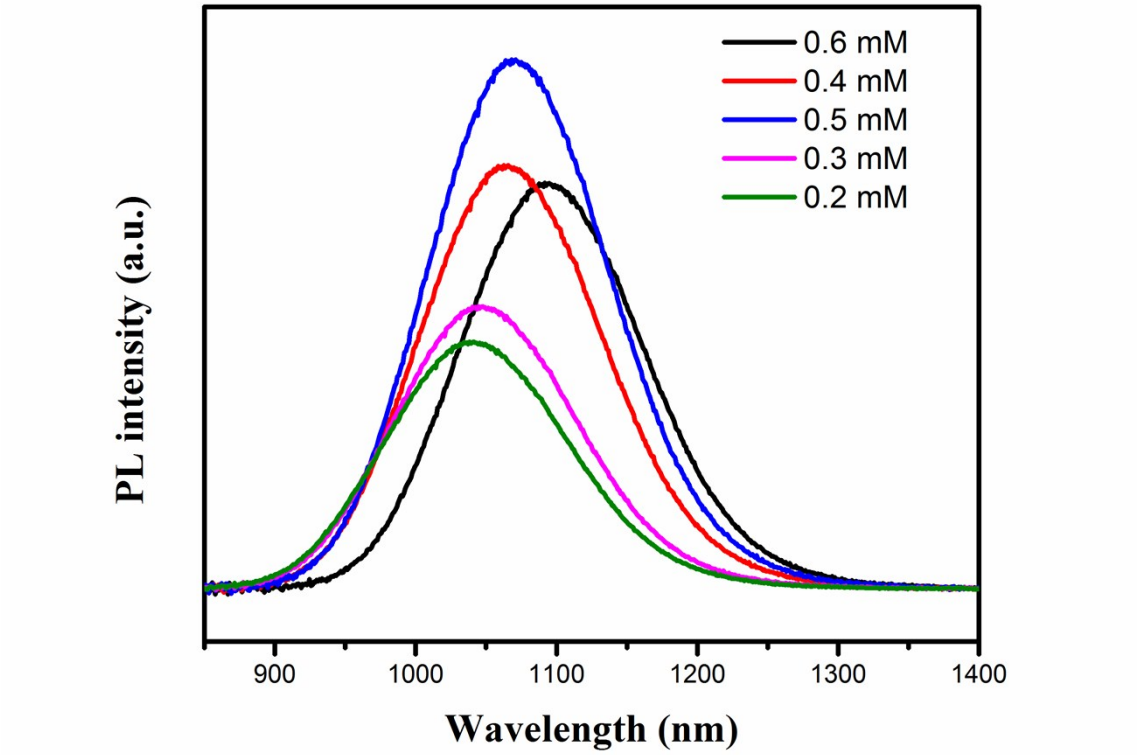

Figure S3. The effect of $CdCl_2$ concentration on the steady-state photoluminescence spectra.

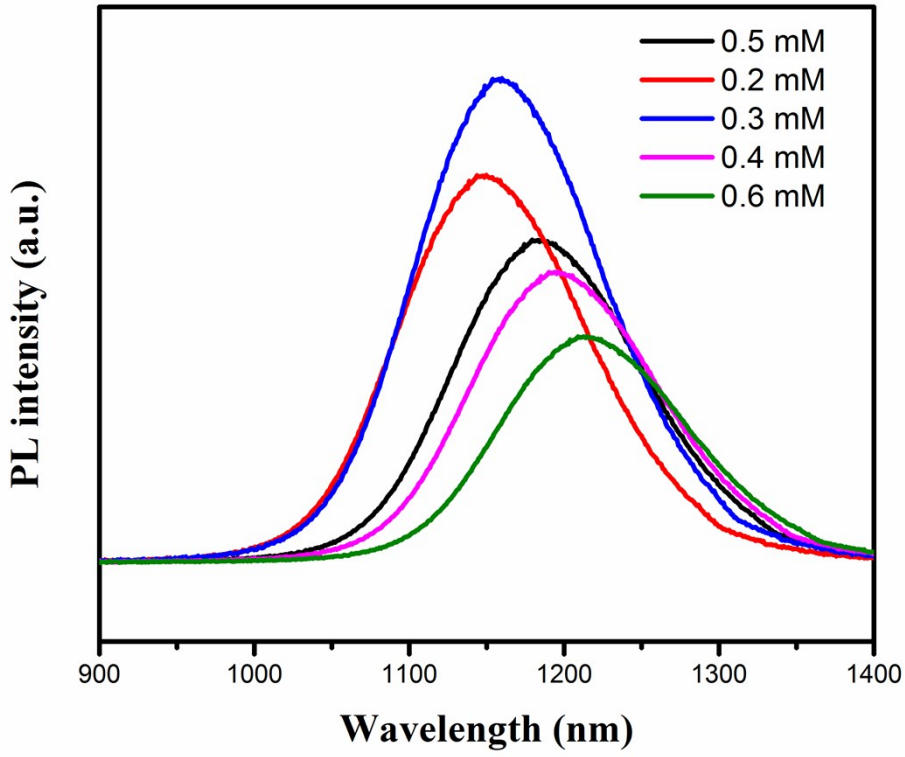

Figure S4. The effect of $ZnCl_2$ concentration on the steady-state photoluminescence spectra.

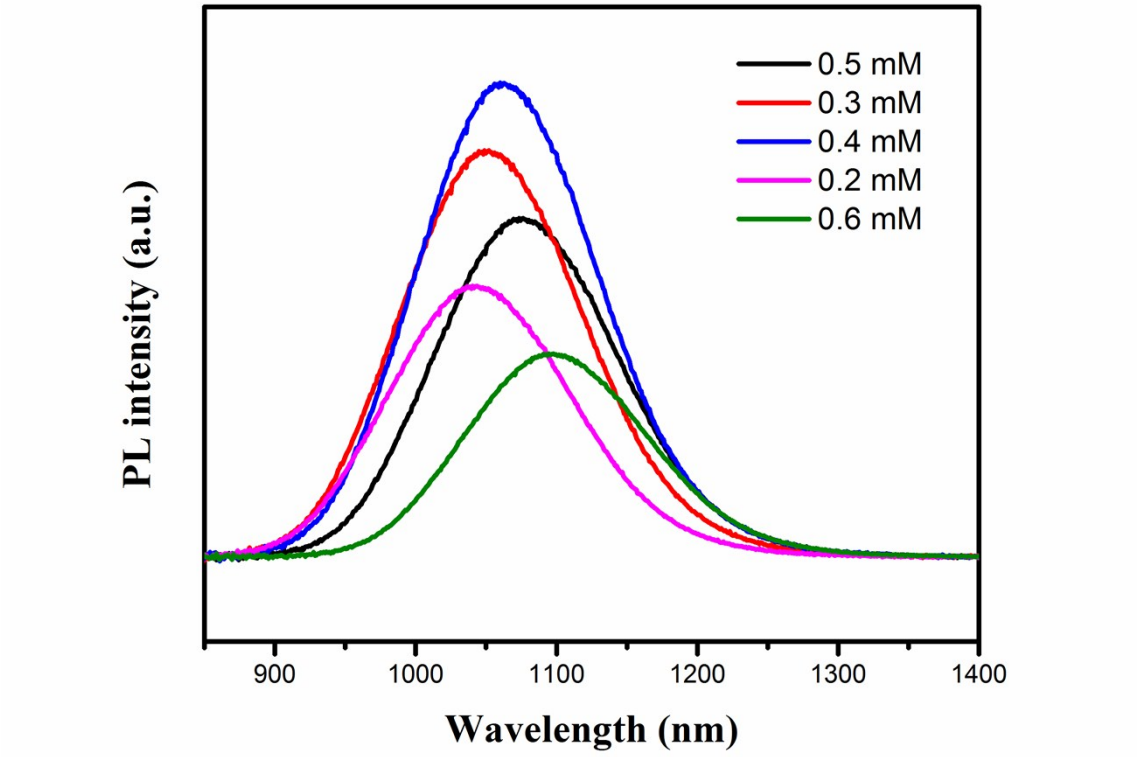

Figure S5. The effect of $CaCl_2$ concentration on the steady-state photoluminescence spectra.

Table S1. Fitting parameters of the corresponding PL decay curves

Sample	τ (μs)	β	χ
PbS/G QDs	0.78	0.91	1.02
Cd-dopped PbS/G QDs	1.41	0.85	1.06
Ca-dopped PbS/G QDs	1.24	0.88	1.05
Zn-dopped PbS/G QDs	1.12	0.89	1.04

Table S2. Effect of M-doping on the average PLQY of PbS CQDs

Doping	**PbS**	**PbS/Ca**	**PbS/Zn**	**PbS/Cd**
Average value (%)	27%	28.7%	27.5%	32%

PbS QD Modeling

The structure of PbS QDs were modeled according to the literature (ref. 4). In this model, the truncated crystal structure has three types of planes, *i.e.,* {100}, {110}, {111}. Regarding to the PbS core model, the surface of {111} planes are completely covered by Pb atoms. Doping of the cations is considered in these planes in accordance with literature (ref.19). Figure S6 shows the PbS QD model.

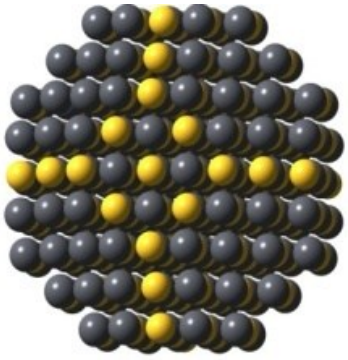

Figure S6. The DFT model of PbS QD without passivation.

For Cd doping, the surface Pb atoms on the planes {111} were replaced by Cd atoms. In order to find the maximum number of Cd atoms for doping, we did another simulation only on the surface of {111} planes. We studied the energy of system after Cd doping, as shown in Figure S7. The results show that the most stable structure of PbS QD was attained using 3 $CdCl_2$ molecules on the surface of {111} planes.

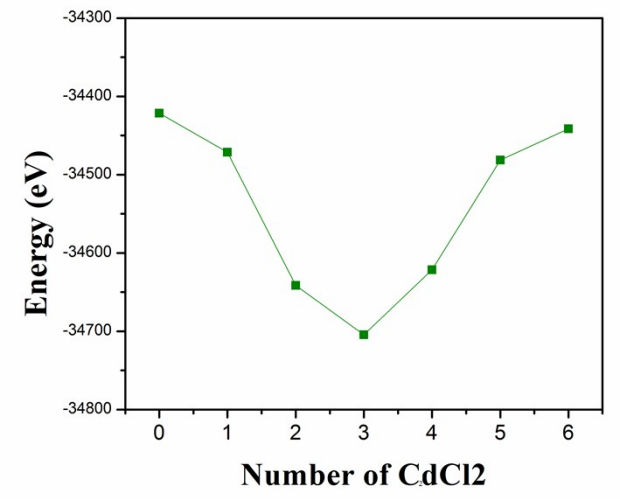

Figure S7. The results of DFT simulation of Cd-doped PbS QD passivated using different number of $CdCl_2$ molecule.

Others planes, i.e. {100} and {110} of PbS QD were passivated with MPA molecules. In this regard, we studied the different conformation of MPA molecule on the surfaces of PbS QD (Fig. S8). We have found that the bended form of MPA molecule has the lowest energy on the surfaces of PbS QDs.

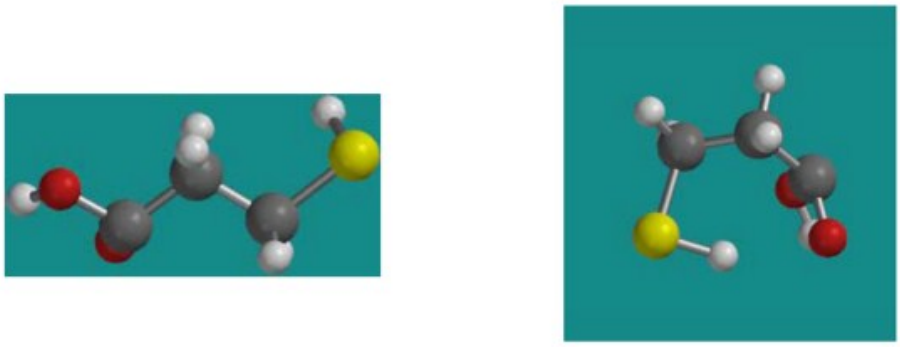

Figure S8. The two different conformations of MPA molecules, (a) straight molecule, and (b) the bended one.

Next, we passivated the {100} and {110} planes by MPA molecules and studied the number of MPA molecules energetically. As shown in Figure S9, the results demonstrate that the most stable structure of PbS QD was attained by passivation of {100} and {110} planes with 4 and 2 molecules, respectively.

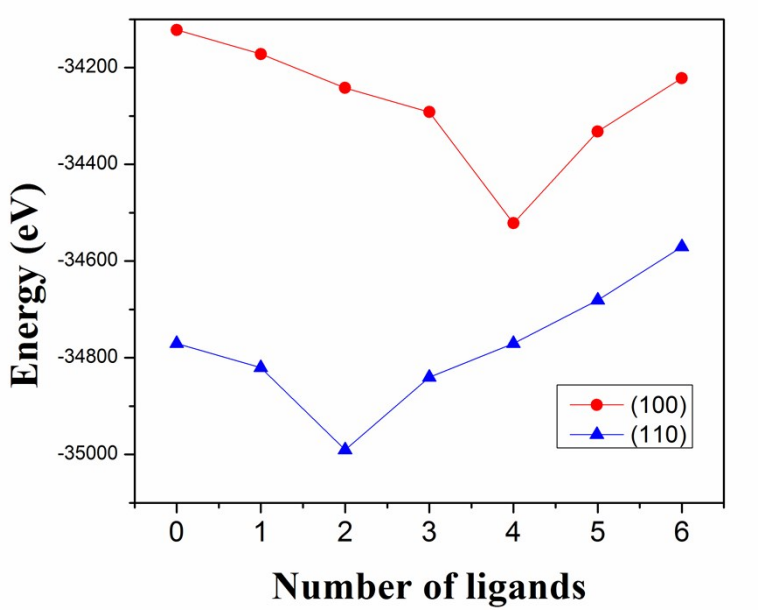

Figure S9. The simulation results of surface passivation of {100} and {110} planes of PbS QDs using different numbers of MPA molecules.

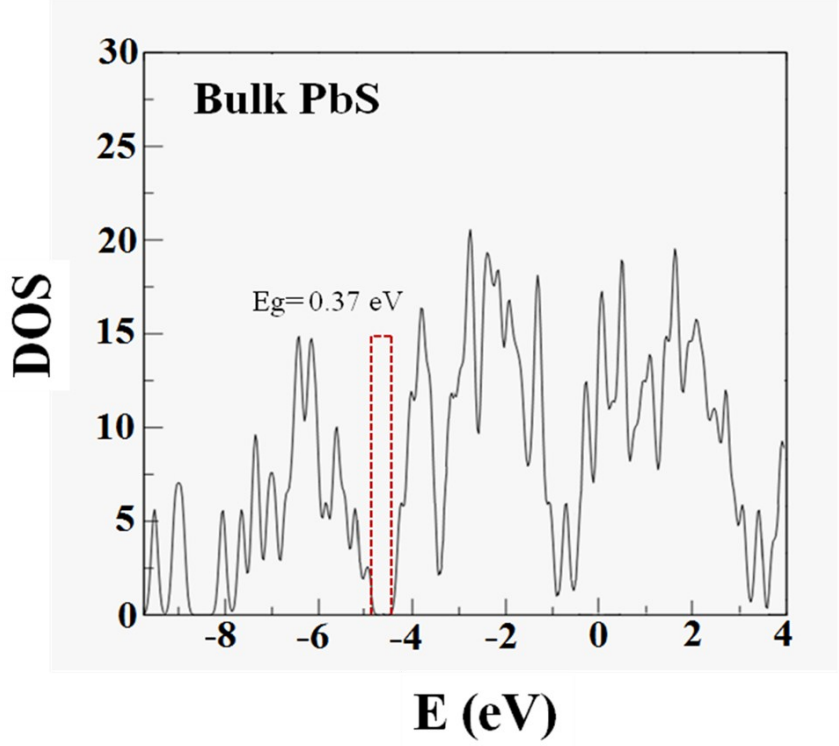

Figure S10. DFT simulation result of DOS for balk PbS.