

## Electronic Supplementary Information for

### **Synthesis of metal sulfide nanoboxes based on Kirkendall effect and**

### **Pearson hardness**

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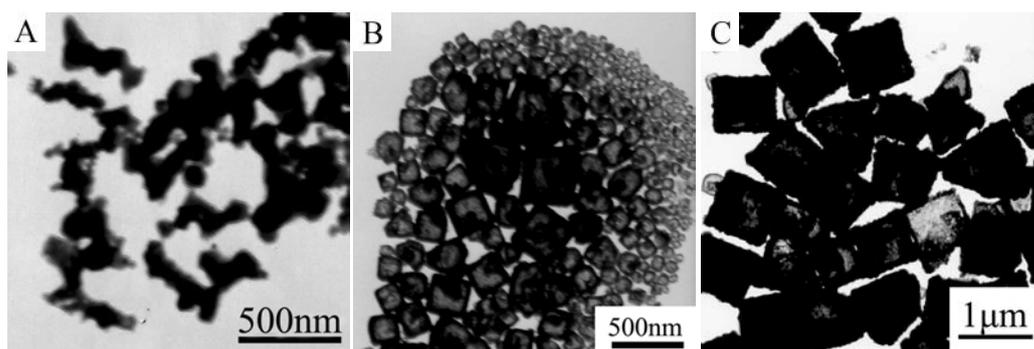
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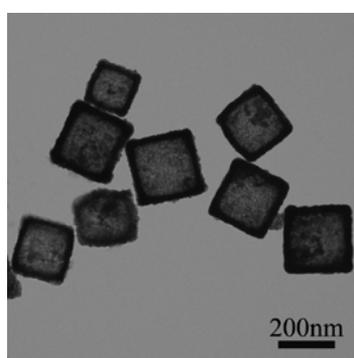
### **Experimental Section**

**Synthesis of metal selenides.** For the synthesis of 0.1 M NaHSe solution, 0.092 g NaBH<sub>4</sub> and 0.9 g selenium powder were added into 10 mL deoxygenated water under magnetic stirring in nitrogen atmosphere. About 10 minutes later, the selenium was consumed and the solution became colorless. Then 1 mL freshly prepared NaHSe solution was injected into AgCl suspension to obtain Ag<sub>2</sub>Se. Followed reaction process is consistent with the above mentioned cation exchange process.

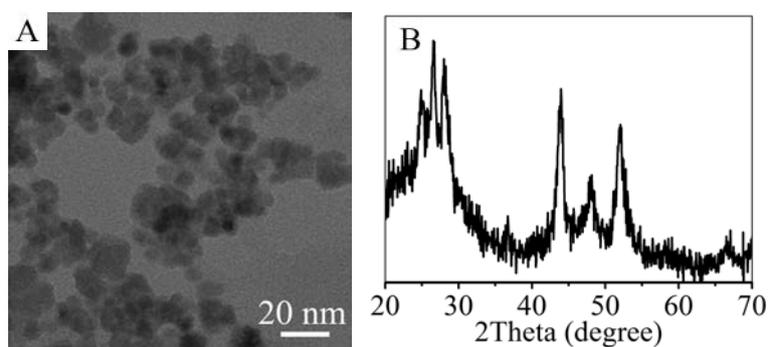
**Synthesis of AgBr as sacrificial templates.** 0.1 g AgNO<sub>3</sub> and 0.084 g KBr were added to 20 mL of chitosan solution (1 wt%, in 0.05 M HNO<sub>3</sub>) under magnetic stirring to form AgBr colloidal solution, and the solution was transferred to 60 °C water bath for an hour. Then 1 mL 0.1 M Na<sub>2</sub>S solution and 1 mL 0.1 M freshly prepared NaHSe was injected into 2 mL AgBr suspension to obtain Ag<sub>2</sub>S and Ag<sub>2</sub>Se respectively. After a consistent cation exchange as mentioned above, flake-like CdS and CdSe were obtained.



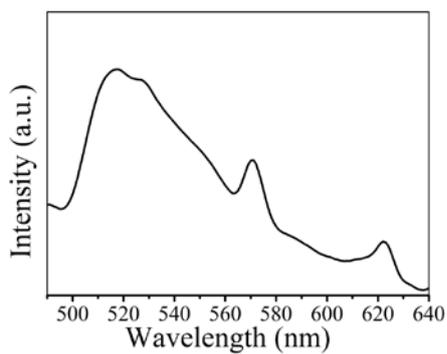
**Fig. S1** TEM images of  $\text{Ag}_2\text{S}$  derived from different  $\text{AgCl}$  templates: (A) PVP, (B) trisodium citrate, (C)  $\text{Fe}^{3+}$  is absent in the aging process of  $\text{AgCl}$ , respectively.



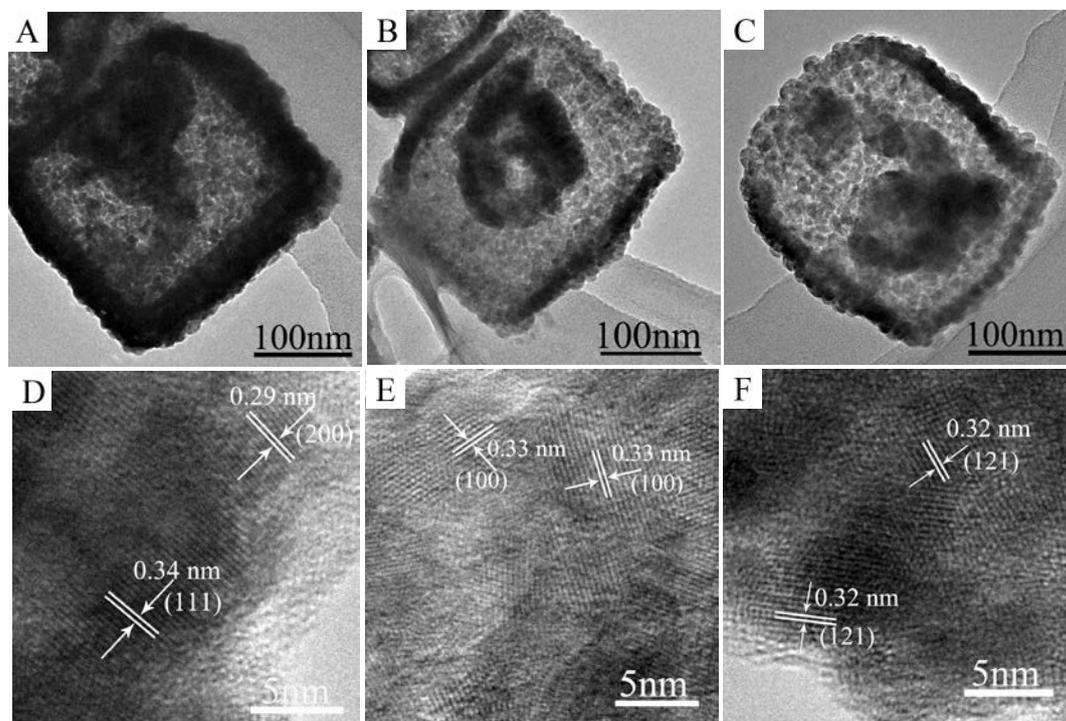
**Fig. S2** The obtained hollow  $\text{Ag}_2\text{S}$  nanoboxes prepared by adding  $\text{Na}_2\text{S}$  solution to  $\text{AgCl}$  suspension dropwise.



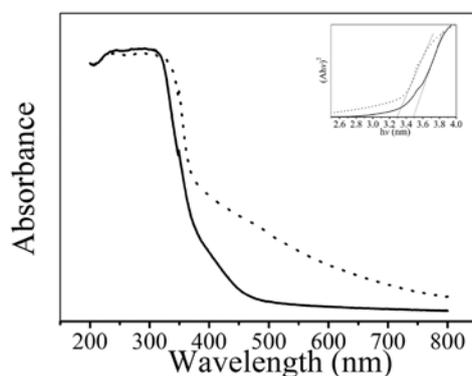
**Fig.S3** (A) The obtained  $\text{CdS}$  nanoparticles by the mixture of cadmium oxide and thiourea under solid reaction at  $140\text{ }^\circ\text{C}$ , (B) the XRD pattern (JCPDS: 49-1049) of the corresponding  $\text{CdS}$  nanoparticles.



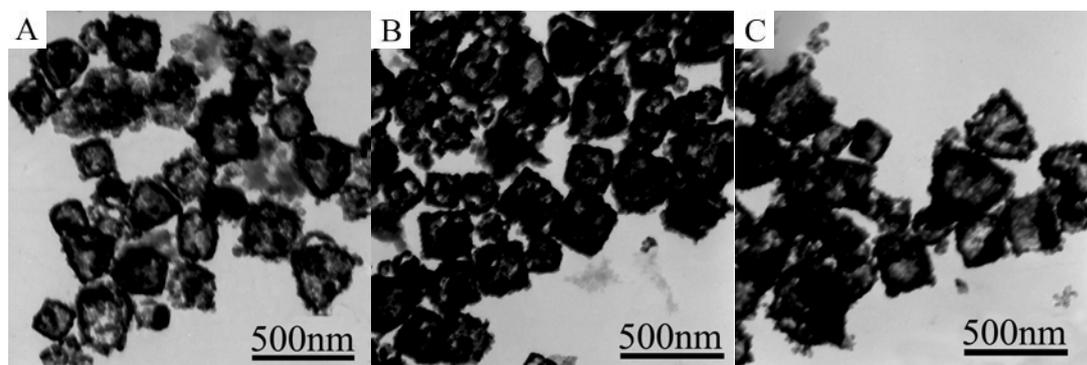
**Fig. S4** Photoluminescence spectra of monodisperse CdS nanoparticles with excitation at 450 nm.



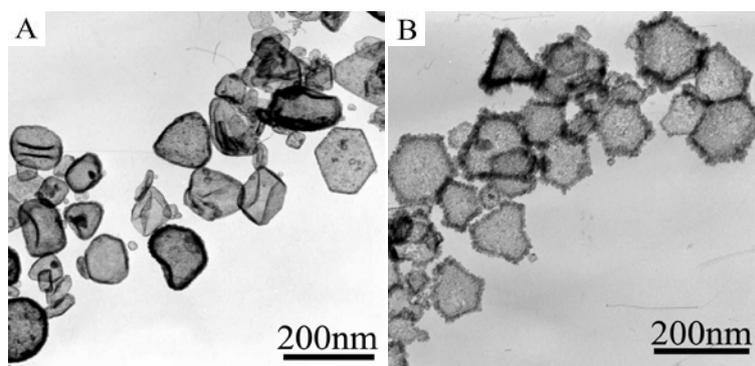
**Fig. S5** Enlarged TEM view of a single nanobox and HRTEM images of the prepared metal sulfides: (A, D) PbS, (B, E) ZnS and (C, F) AgInS<sub>2</sub>.



**Fig. S6** Uv-vis diffusion reflectance spectra of ZnS nanoboxes and individual ZnS nanoparticles. The inset is the calculated the corresponding calculated band gap of ZnS nanoboxes and ZnS nanoparticles. The dashed and solid lines correspond to nanoboxes and nanoparticles, respectively.



**Fig. S7** TEM images of CdSe (A) PbSe (B) and ZnSe derived from AgCl templates. The morphology is not preserved as well as metal sulfides.



**Fig. S8** TEM images of CdS (A), CdSe (B) prepared via two steps of ion exchange by using AgBr as template.