

## Support Information

### **Colloidal synthesis of wurtz-stannite $\text{Cu}_2\text{CdGeS}_4$ nanocrystals with high catalytic activity toward the reduction of iodine redox couples in dye-sensitized solar cells**

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## **Experiment:**

### **Chemical:**

Copper (II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ ; >99.99%), cadmium (II) acetylacetonate ( $\text{Cd}(\text{acac})_2$ ; >99.99%) and trioctylphosphine oxide Trioctylphosphine oxide (TOPO, 99%) were purchased from alfa Aesar; Germanium (IV) chloride ( $\text{GeCl}_4$ ; >99.99%) was purchased from Acros, Oleylamine (OLAm, 70% tech) were purchased from Aldrich. 1-dodecanethiol (1-DDT, 98%) and tert-Dodecanethiol (t-DDT, mixture of isomers, >98.0%) were purchased from TCI. All chemicals were used as received without any further purification.

### **Synthesis of wurtz-stannite $\text{Cu}_2\text{CdGeS}_4$ NCs:**

In a typical synthesis, 1 mmol of copper (II)  $\text{Cu}(\text{acac})_2$ , 0.5 mmol of  $\text{Cd}(\text{acac})_2$ , 0.5 mmol  $\text{GeCl}_4$ , and 1.5 mmol of TOPO were mixed with 10 mL of OLAm in a three-neck round bottom flask and evacuated at 100°C for 30 min to eliminate adventitious water and dissolved oxygen. The solution was then heated to 140 °C under a nitrogen atmosphere and a mixture of 1.5 mmol of 1-dodecanethiol (1-DDT) and 10.0 mmol of tert-dodecyl mercaptan (t-DDT) was quickly injected into the flask. The mixture was subsequently heated to 280°C and maintained at the temperature for 120 min to allow the growth of  $\text{Cu}_2\text{CdGeS}_4$  nanocrystals. Finally, products were precipitated by ethanol and redispersed in organic solvent to form “ink”.

### **Preparation of counter electrodes:**

$\text{Cu}_2\text{CdGeS}_4$  CEs were prepared by spin-coating the as-prepared “ink” onto a cleaned FTO glass substrate (SpinMaster 100, Chemat Technology, Inc.). The thickness of CE active layer can be controlled by the concentrations of the “ink” (i.e., 10, 30, 80 and 150 mg/mL). To remove the long chain ligands from NC surfaces, the  $\text{Cu}_2\text{CdGeS}_4$  NC films were subsequently dipped in 15 mM 1,2-ethanedithiol (EDT) in acetonitrile solution for 30 s and spun (at 3000 rpm for 30 s) to remove the long chain ligands from NC surfaces and reduce interparticle spaces of NCs.<sup>[1]</sup> Subsequently, the films were annealed at 400°C for 30 min under nitrogen atmosphere. For comparison, pyrolytic Pt CE was prepared by drop-casting 50  $\mu\text{L}$  of  $\text{H}_2\text{PtCl}_6$  in ethanol (5 mM) on a  $1.5 \times 1.5 \text{ cm}^2$  FTO glass followed by sintering at 450°C for 30 min in air.

### **Fabrication of DSSCs:**

The N719 (Dyesol)-sensitized devices were fabricated as reported elsewhere. Briefly, the commercial TiO<sub>2</sub> photoanodes (Ying kou Opvtech New Energy Co., Ltd) were first annealed at 500°C for 1 h. After being cooled to 80°C, the TiO<sub>2</sub> photoannodes were immersed in a 0.5 mM ethanol solution of N719 dye (Solaronix SA, Switzerland) for 20 h. DSSCs were assembled by attaching the dye-sensitized TiO<sub>2</sub> electrode with the CEs with a 60-μm thick hot-melt film (Surlyn 1702; DuPont) as spacer and then sealed up by heating. The internal space of the cell was filled with electrolytes using a vacuum pump. The redox electrolyte was used, which composed of 0.03 M I<sub>2</sub>, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-tert-butyl pyridine and 0.1 M of guanidinium thiocyanate with anhydrous acetonitrile as the solvent. Finally, the holes on the back of CEs were sealed with a Surlyn film covered with a thin glass slide. The sealed DSSCs were used for the photocurrent-voltage test with an active area of 0.16 cm<sup>2</sup>.

### **Characterization**

X-ray diffraction (XRD) was performed on a Shimadzu XRD-6000 with CuKα radiation, X-ray tube voltage 40 kV and current 30 mA, respectively. Energy dispersive spectroscopy (EDS) of Cu<sub>2</sub>CdGeS<sub>4</sub> NPs on a silicon substrate was performed to analyze the elemental composition using a Hitachi SU-70 equipped with EDX detector. Transmission electron microscopy (TEM, JEOL, JEM-2100) were used to characterize the morphology and structure. X-ray photoelectron spectroscopy (XPS) was performed with a VG Scientific ESCLAB 220iXL X-ray photoelectron spectrometer. Raman spectra were collected from a Dilor XY Labram spectrometer equipped with an Olympus BX40 confocal microscope under ambient conditions by using a ArHe green laser. The photocurrent-voltage tests of DSSCs were performed under AM 1.5 illumination (100 mW cm<sup>-2</sup>) in ambient conditions on a 94023A Oriel sol3A solar simulator (Newport Oriel solar simulator, newport stratford, inc.) with 450 W xenon lamp as light source. The EIS experiments and Tafel-polarization

curves were measured with dummy cells in the dark by using a Zahner electrochemical workstation (Zahner Co., Germany). The frequency range of EIS experiments was from 0.1 Hz to  $10^6$  Hz with an AC modulation signal of 10 mV and bias DC voltage of 0 V, in dark condition. The resultant impedance spectra were analyzed by means of the Zview software. Tafel-polarization measurements were carried out with a scan rate of  $50 \text{ mV s}^{-1}$ . Cyclic voltammetry was conducted in a three-electrode system in an acetonitrile solution of 0.1 mmol  $\text{LiClO}_4$ , 10 mmol  $\text{LiI}$  and 1 mmol  $\text{I}_2$  at a scan rate of  $50 \text{ mV s}^{-1}$ . Platinum nets electrode served as a CE, and the  $\text{Ag/AgCl}$  couple was used as a reference electrode.

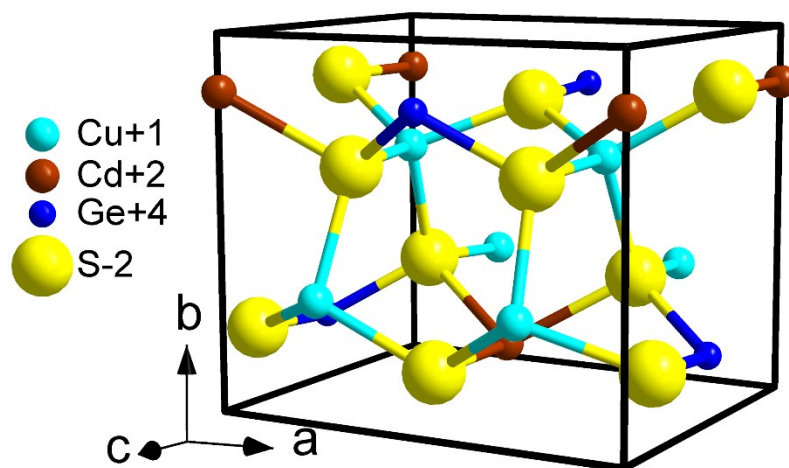


Fig.S1 Crystal structure of wurtz-stannite  $\text{Cu}_2\text{CdGeS}_4$ .

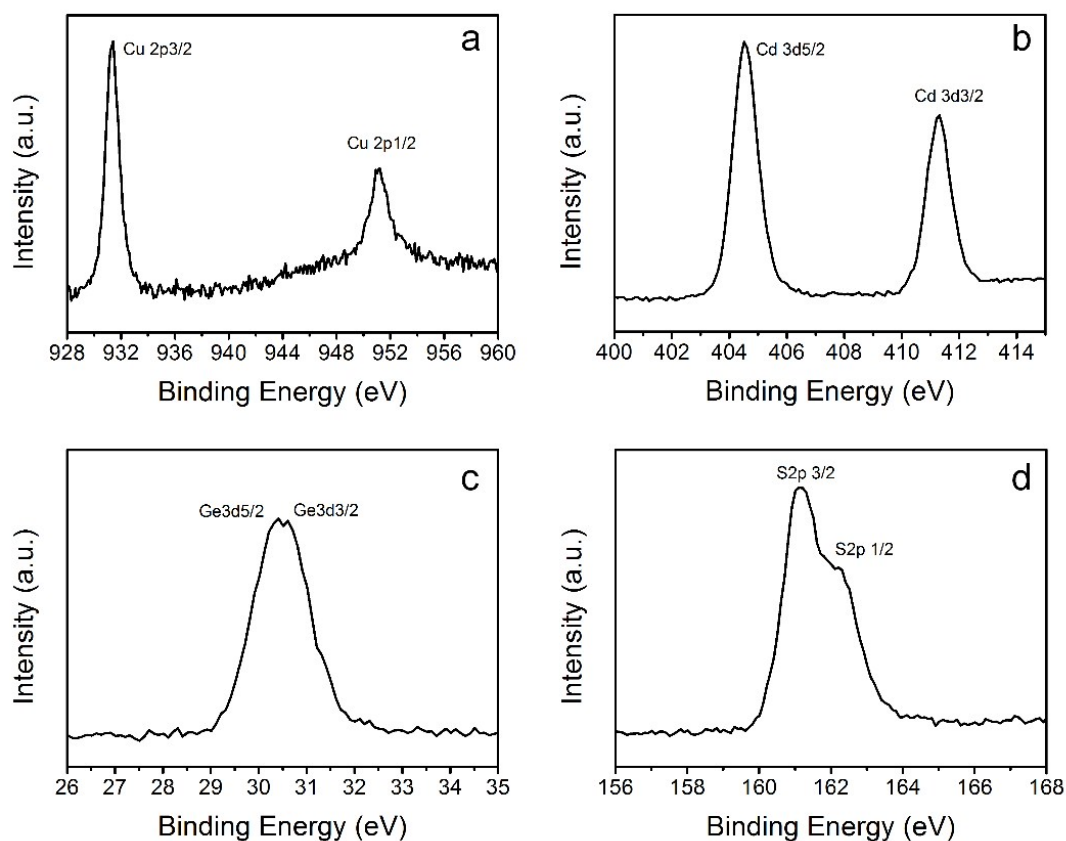


Fig. S2 XPS spectrum of the as-synthesized wurtz-stannite  $\text{Cu}_2\text{CdGeS}_4$  nanocrystals.

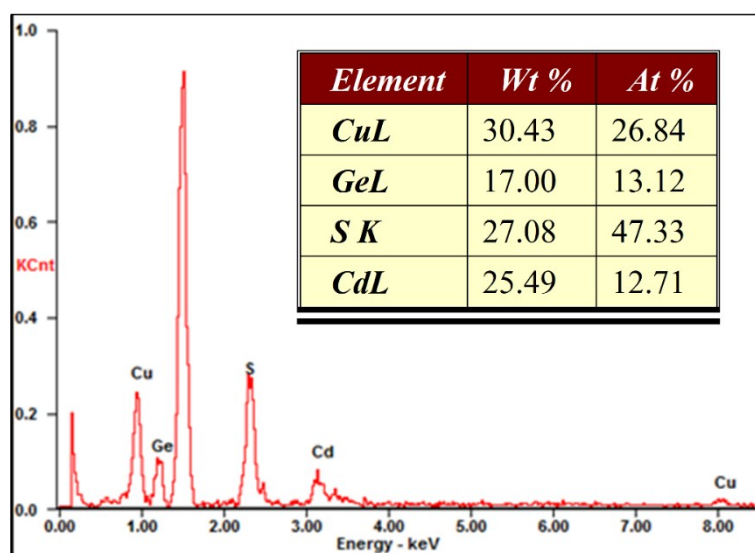


Fig.S3 EDX spectrum of the as-obtained  $\text{Cu}_2\text{CdGeS}_4$  nanocrystals.

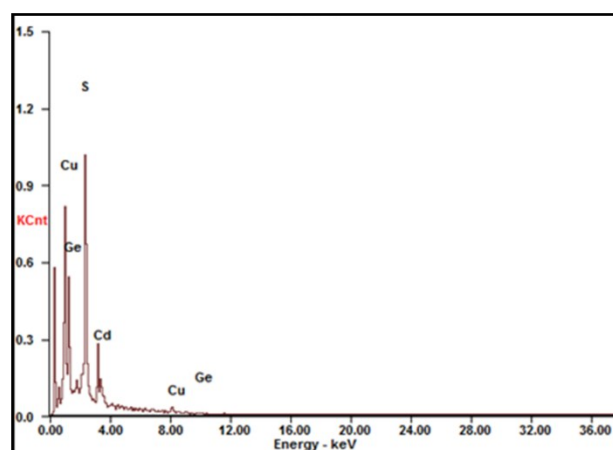


Fig. S4 EDX spectrum of the material obtained after 8 min of reaction.

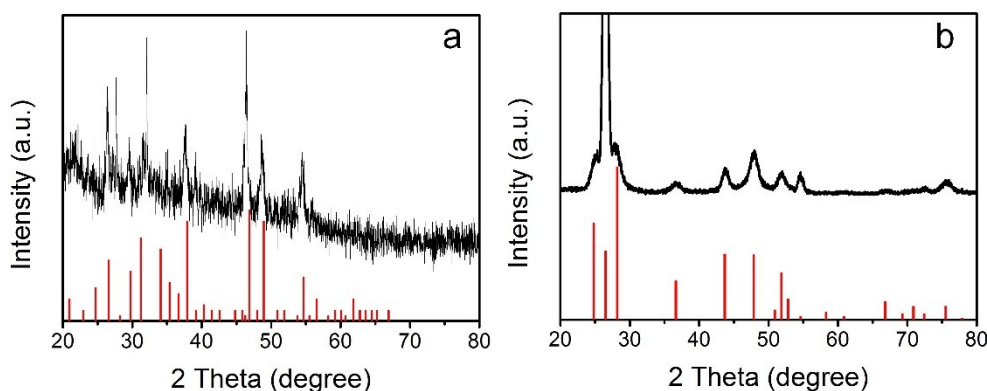


Fig. S5 XRD pattern of the material obtained when  $\text{Cu}(\text{acac})_2$  is heated solely in solution (a) and XRD pattern of the samples obtained when  $\text{Cd}(\text{acac})_2$  is heated solely in solution (b). The red pattern at the bottom is from the standard JCPDS file for monoclinic  $\text{Cu}_7\text{S}_4$  (JCPDS #23-0958) and  $\text{CdS}$  (JCPDS #89-2944), respectively.

To confirm that the formation pathway of  $\text{Cu}_2\text{CdGeS}_4$  starts with the nucleation of  $\text{Cu}_x\text{S}$  and not of  $\text{CdS}$ , we have heated  $\text{Cu}(\text{acac})_2$  and  $\text{Cd}(\text{acac})_2$  separately under similar conditions. A brown product was immediately obtained when alkanethiols (1-DDT and t-DDT) was injected into  $\text{Cu}(\text{acac})_2/\text{OLAm}$  solution, and this has been found to be monoclinic  $\text{Cu}_7\text{S}_4$  from XRD measurements (Fig. S5a). By contrast, heating  $\text{Cd}(\text{acac})_2/\text{alkanethiols}$  solely did not generate any solids until the reaction temperature reach to 320 °C (Fig. S5b). This tells us that under the conditions employed,  $\text{Cu}_x\text{S}$  formed readily whereas  $\text{CdS}$  does not. This strongly supports our hypothesis that the material served as nuclei in the synthesis could not be  $\text{CdS}$  but a  $\text{Cu}_x\text{S}$  phase. Similar phenomenons were also observed in the synthesis of orthorhombic  $\text{Cu}_2\text{ZnGeS}_4$  NCs.<sup>[2]</sup>

Table. S1 Photovoltaic parameters of DSSCs with various CEs under AM 1.5 illumination.

CEs	Thickness ( $\mu\text{m}$ )	$V_{\text{oc}}$ (mV) <sup>[a]</sup>	$J_{\text{sc}}$ ( $\text{mA cm}^{-2}$ ) <sup>[b]</sup>	FF (%) <sup>[c]</sup>	$\eta$ (%) <sup>[d]</sup>
$\text{Cu}_2\text{CdGeS}_4$	0.10	724	14.31	54.9	5.69
	0.20	726	15.54	63.9	7.21
	0.50	723	15.89	66.8	7.67
	1.50	725	15.73	65.6	7.48
Pt	/	726	15.95	65.2	7.54

[a]  $V_{\text{oc}}$ : open-circuit voltage; [b]  $J_{\text{sc}}$ : short-circuit current density; [c] FF: fill factor; [d]  $\eta$ : power conversion efficiency.

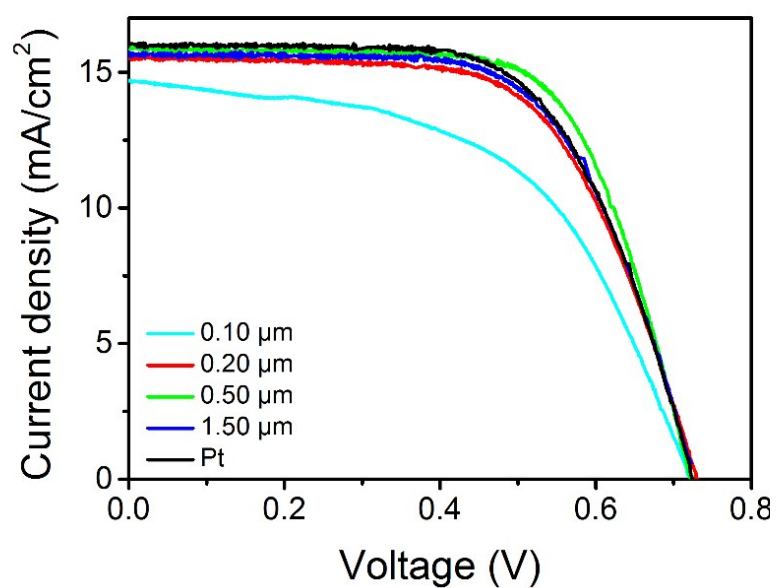


Fig. S6 Current density-voltage characteristics of DSSCs based on different CEs measured at  $100 \text{ mW cm}^{-2}$ .

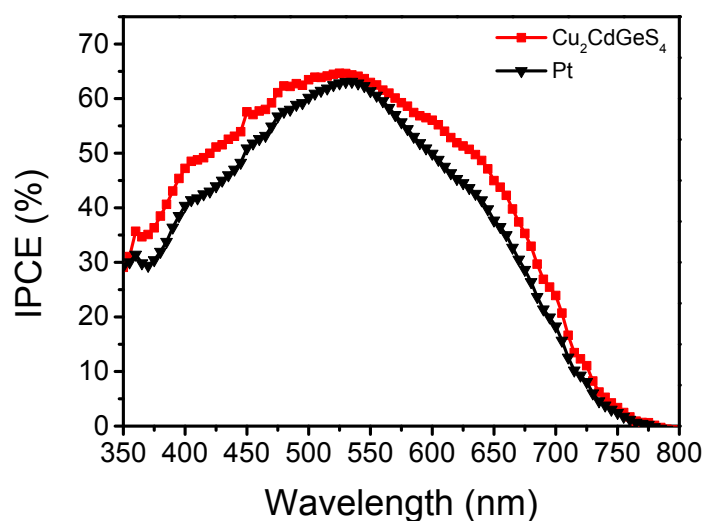


Fig. S7 IPCE spectrum of the DSSCs with different CEs.

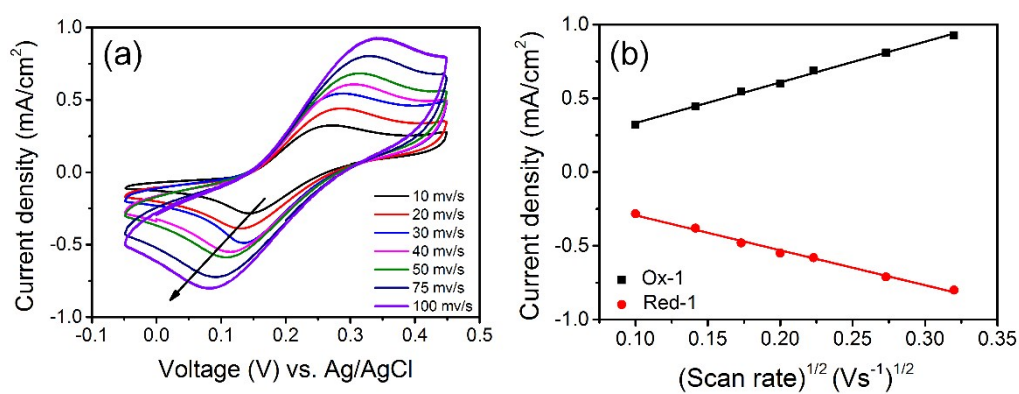


Fig. S8 (a) CV curves of the  $\text{Cu}_2\text{CdGeS}_4$  CE at different scan rate; (b) relationship between the peak current density and the square root of scanning rate of  $\text{Cu}_2\text{CdGeS}_4$  CEs;

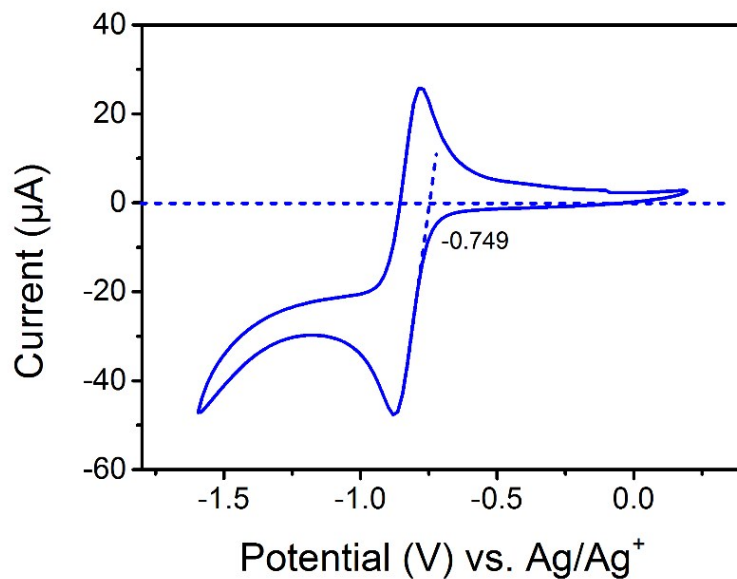


Fig. S9 Cyclic voltammograms of measuring the HOMO and LUMO energy levels of  $\text{Cu}_2\text{CdGeS}_4$  nanoparticles.

The cyclic voltammograms (CVs) were recorded on a Zahner IM6 electrochemical workstation, using 3 mm glassy carbon as the working electrode, a Pt plate as the counter electrode, and  $\text{Ag}/\text{Ag}^+$  (Ag wires with 0.01 M  $\text{AgNO}_3$  in acetonitrile) as the reference electrode; 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) dissolved in acetonitrile was employed as the supporting electrolyte. The  $\text{Cu}_2\text{CdGeS}_4$  nanocrystals (NCs) were purified and redissolved in chloroform. A drop of diluted NCs solution was deposited onto the surface of the working electrode to form a NC film. The electrolyte solutions were thoroughly deoxygenated by bubbling high purity nitrogen for 10 min and a nitrogen atmosphere was maintained over the solution.

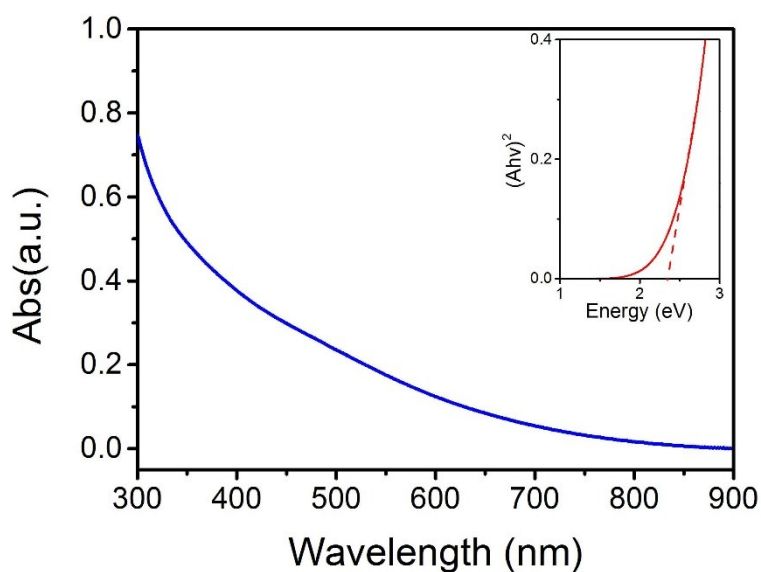


Fig. S10 UV-Vis spectrum of the as-obtained  $\text{Cu}_2\text{CdGeS}_4$  nanocrystals.

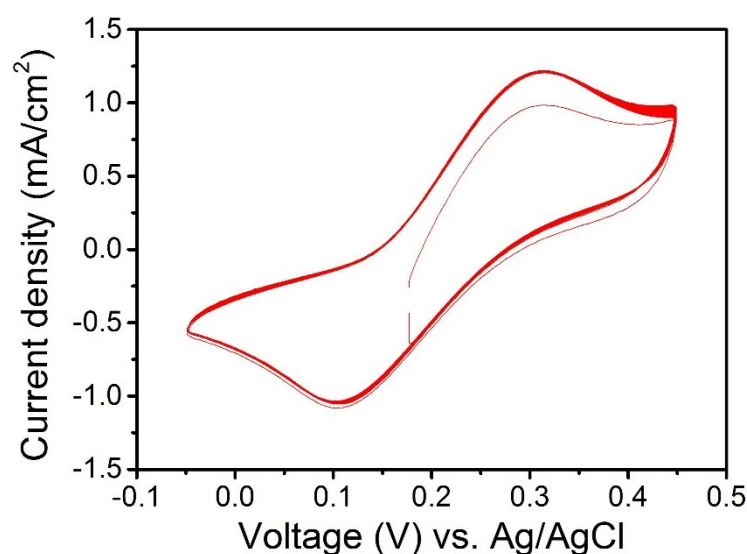


Fig. 11 100 consecutive CVs of  $\text{Cu}_2\text{CdGeS}_4$  nanosheets CE with a scan rate of  $50 \text{ mV s}^{-1}$  in  $10 \text{ mM LiI}$ ,  $1 \text{ mM I}_2$ , and  $0.1 \text{ M LiClO}_4$  acetonitrile.

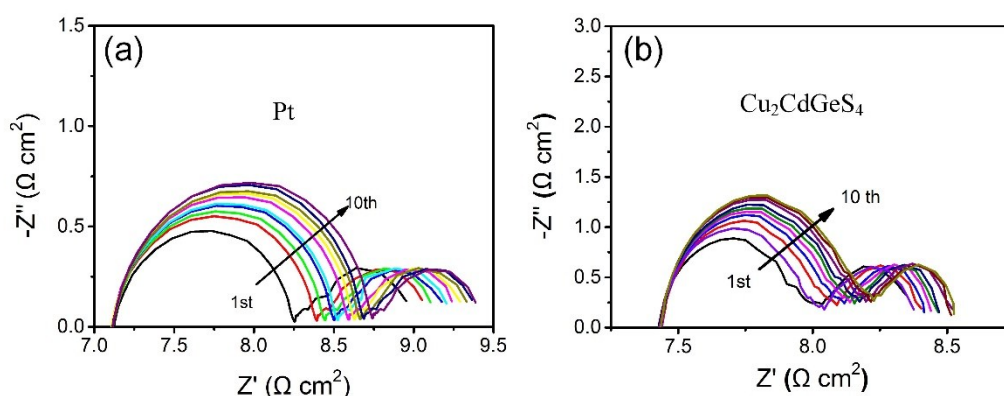


Fig. 12 Nyquist plots of EIS for the symmetrical cells with Pt (a) and  $\text{Cu}_2\text{CdGeS}_4$  (b) CEs. The cell was first subjected to CV scanning from 0 to 1 V and then from -1 to 0 V with a scan rate of  $100 \text{ mV s}^{-1}$ , followed by 60 s relaxation at 0 V, and then EIS measurement at 0 V from 0.1 Hz to 1M Hz was performed. This sequential electrochemical test was repeated 10 times.

[1]. Wang, Y. C., Wang, D. Y., Jiang, Y. T., et al.  $\text{FeS}_2$  Nanocrystal Ink as a Catalytic Electrode for Dye-Sensitized Solar cells[J]. *Angew. Chem. Int. Ed.*, 2013, 52 (26): 6694-6698.

[2]. Fan, C. M., Regulacio, M. D., Ye, C., et al. Colloidal nanocrystals of orthorhombic  $\text{Cu}_2\text{ZnGeS}_4$ : phase-controlled synthesis, formation mechanism and photocatalytic behavior[J]. *Nanoscale*, 2015, 7 (7): 3247-3253.