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# **Supporting Information**

## Quantum capacitance of CuS:Ce<sup>3+</sup> quantum dots as high-performing

## supercapacitor electrodes

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### **Experiment section**

### Materials characterization

The compositions of samples were investigated using energy-dispersive X-ray spectroscopy (EDS) attached to a scanning electron microscope (MAagellan-400). The valence states of the elements were analyzed by using X-ray photoelectron spectroscopy (XPS, ESCALAB MK II). Fourier transform infrared spectroscopy (FTIR) was recorded by a Nicolet Impact 410 FTIR Infrared Instrument using the KBr pellet technique.



Fig. S1. The growth mechanism schematic of CuS:Ce<sup>3+</sup> QDs.

The green ball represents the S<sup>2-</sup>, the blue ball represents the Cu<sup>2+</sup>, the red ball represents the Ce<sup>3+</sup>, the black ball represents the PVP, the black ball in tandem with the blue ball represents the complex of PVP-Cu<sup>2+</sup> and the black ball in tandem the red ball represents the complex of PVP-Ce<sup>3+</sup>. The growth mechanism of CuS:Ce<sup>3+</sup> QDs mainly consists of three steps: (1) the preparation of the reaction solution, (2) rapid nucleation of the CuS:Ce<sup>3+</sup> QDs, and (3) crystal grain growth of the CuS:Ce<sup>3+</sup> QDs. A large number of Cu<sup>2+</sup> cations and Ce<sup>3+</sup> cations in the reaction solution can be easily attracted by the oxygen in the lactam ring of PVP. Thus, the complexes of PVP-Cu<sup>2+</sup> and PVP-Ce<sup>3+</sup> are formed by PVP combining with Cu<sup>2+</sup> cations and Ce<sup>3+</sup> cations in the process of mixing the reaction solutions. A weak alkaline environment is beneficial to the H<sub>2</sub>S gas dissolved in the reaction solution. However, the alkalinity of the reaction solution cannot be too large; otherwise it will lead to the reaction of the blue Cu(OH)<sub>2</sub> precipitation directly, which hinders the generation of CuS in the following steps. Thus, the PH value of the reaction solution is adjusted to 8.0-8.5 in the experiment. In the rapid nucleation stage, the complexes of PVP-Cu<sup>2+</sup> and PVP-Ce<sup>3+</sup> undergo gradual decomplexing with the emergence of the S<sup>2-</sup> anions from H<sub>2</sub>S, and the ionic bonds are formed between the  $Cu^{2+}/Ce^{3+}$  cations and  $S^{2-}$  anions, which eventually leads to  $Ce^{3+}$  cations doping into the host CuS lattices and forming the multiple nucleation of CuS:Ce<sup>3+</sup>. There are a large number of S<sup>2-</sup> /Cu<sup>2+</sup> ions and a small amount of Ce<sup>3+</sup> cations that gradually diffuse to the nucleus of CuS:Ce<sup>3+</sup> and control the homogeneous growth of crystal nucleus in every direction. This can be explained by the diffusion control and trapped dopant mechanisms. The nucleation of CuS:Ce<sup>3+</sup> gradually grows by absorbing a great number of surrounding ions. The reaction chamber is placed in an ultrasonic environment which is helpful to prevent agglomeration between these crystal nucleus, and also helps to remove the surrounding PVP. In the crystal growth stage, the crystal nuclei of CuS:Ce<sup>3+</sup> gradually absorb the surrounding ions and grow to immature crystal grains. After the Ostwald ripening process, the immature CuS:Ce<sup>3+</sup> crystal grains gradually grow to stable nanoparticles.



Fig. S2. XRD patterns of CuS and all CuS:Ce<sup>3+</sup> quantum dots :0.24 at. %, 0.53 at. %, 0.86 at. %, 1.26 at. %, and 1.63 at. %, respectively.

It can be seen that the (118) peak positions of the CuS:Ce<sup>3+</sup> slightly shift to lower angles (higher d value) with increasing Ce ion concentration, which reveals the successful incorporation of the rareearth metal Ce ions and their dispersion into the host matrix.



Fig. S3 Energy dispersive X-ray (EDX) spectra of CuS:Ce<sup>3+</sup> QDs (0.86 at. %).

The EDS spectra only shows the Cu, S and Ce elements, indicates that the synthesized samples are pure phase.

Elements Line		Apparent	k ratio	Atomic	Standard sample	
	Туре	Concentration		percent	label	
S	К	0.49	0.00419	45.63	FeS <sub>2</sub>	
Cu	L	0.87	0.00870	53.51	Cu	
Ce	L	0.02	0.00017	0.86	CeO <sub>2</sub>	
Total :				100.00		

Table S1. The composition of each elements of CuS:Ce<sup>3+</sup> QDs (0.86 at. %).

The tables shows the composition of each elements of CuS:Ce<sup>3+</sup> QDs (0.86 at. %). From the table, it can be see that the atomic percent of S and Cu are 45.63% and 53.55%, which the ration between Cu atom and S atom is about 1:1. The result indicates that our synthesized samples are CuS materials. The atomic percent of Ce is 0.86 % indicates that Ce element is successful doping into CuS structures.



Fig. S4 XPS spectra of CuS:Ce<sup>3+</sup> (0.86 at. %) QDs: (a) S 2p, (b) Cu 2p, (c) Ce 3d, (d) all the elements of CuS:Ce.

The elemental composition and chemical status of the surface compositions of CuS:Ce<sup>3+</sup> (0.86 atom%) were analyzed by XPS. The XPS spectrum of the as-prepared products is shown in Fig. S4. Fig. S4a and Fig. S4b show the XPS spectra for S 2p and Cu 2p, respectively. Two peaks with binding energies at 162.4 eV and 163.9 eV belong to S  $2p_{3/2}$  and S  $2p_{1/2}$  in the CuS:Ce<sup>3+</sup> QDs. In the XPS spectrum of Cu 2p, there are two peaks with binding energies

at 934.4 eV and 954.4 eV due to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  in the CuS: Ce<sup>3+</sup> QDs. It is found that S and Cu are in the S<sup>2-</sup> state and Cu<sup>2+</sup> state according to the standard binding energy of S and Cu, respectively. The XPS spectrum of the Ce 3d are shown in Fig. S4c. The binding energies for Ce  $3d_{5/2}$  and  $3d_{3/2}$  are 884.3 eV, 901.2 eV and 858.6 eV, 906.4 eV. This result indicates that Ce is in the Ce<sup>3+</sup> state compared with the standard binding energy of Ce 3d. Fig. S4d is the XPS of all the elements of CuS:Ce<sup>3+</sup> QDs. The binding energies of Cu 2p and S 2p were calibrated by referencing the C 1s peak (284.8 eV). The peaks of O and C may come from H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub> adsorbed on the surface of the sample, due to exposure to the air, and from adventitious hydrocarbons from the XPS instrument itself.



Fig. S5. FTIR spectra of CuS and all CuS:Ce3+ QDs.

The FTIR spectra of CuS and all the CuS:Ce<sup>3+</sup> QDs in the range of 400–4000 cm<sup>-1</sup> are compared in Fig. S3. The peaks at 619.6 cm<sup>-1</sup> and 1108.8 cm<sup>-1</sup> of the CuS and CuS:Ce<sup>3+</sup> QDs can be attributed to the typical absorption of Cu–S stretching modes from CuS, which were consistent with previous reports. For the pure CuS and all the CuS:Ce<sup>3+</sup> QDs, the characteristic peak at 1382.8 cm<sup>-1</sup> and 1016.8 cm<sup>-1</sup> can be attributed to the C=O and C–O stretching vibration, while the vibration peaks at 1611.4 cm<sup>-1</sup> are associated with the O-H stretching vibration of the adsorbed water molecules. A relatively broad absorption band is observed at 3532.2 cm<sup>-1</sup> for all the CuS:Ce<sup>3+</sup> QDs, indicating the

presence of the interaction of  $Cu^{2+}$ ,  $S^{2-}$  and  $Ce^{3+}$ . This is due to the  $Ce^{3+}$  being doped into the CuS QDs, whereas no such absorption band is observed in the case of pure CuS QDs.



Fig. S6. The models of (a)  $Cu_{54}S_{54}$ , (b)  $Cu_{53}Ce_1S_{54}$ , (c)  $Cu_{52}Ce_2S_{54}$ , (d)  $Cu_{54}S_{53}$ , (e)  $Cu_{53}Ce_1S_{53}$ , (f)  $Cu_{52}Ce_2S_{53}$ , respectively.

The vectors a, b, and c represent the direction of the lattice constants. The blue ball represents the S atom. The red ball represents the Cu atom and the purple ball represents the Ce atom. The dotted circle represents the position of the S vacancy. These supercell models were obtained by a 3x3x1 expansion of the CuS primitive cell. The supercell structure of the six models all contain 108 atoms. All six models have been optimized by VASP.

Structure	а	b	С	α	β	γ	Formation
							energy (eV)
$Cu_{54}S_{54}$	9.90974	9.90974	18.99216	90.0000	90.0000	120.0000	
$Cu_{53}Ce_1S_{54}$	10.52001	10.52001	18.66923	90.0000	90.0000	120.0000	3.14
$Cu_{52}Ce_2S_{54}$	10.38451	11.03722	18.72933	95.3594	90.0000	118.0623	0.12
$Cu_{54}S_{53}$	10.29331	10.29331	19.26779	90.0000	90.0000	120.0000	-0.56
$Cu_{53}Ce_1S_{53}$	10.39352	10.79722	18.37964	92.8875	90.0000	118.7707	-1.01
$Cu_{52}Ce_2S_{53}$	10.68431	11.07130	18.29831	83.9284	103.4630	120.7745	-4.63

Table S2. The lattice constants and the minimum formation energy for six supercell models.

The lattice constants of different defect structures are increased. The apparent lattice dilation phenomenon of the CuS:Ce supercell structure is consistent with previous XRD test results. The formula for the formation energy of the intrinsic defect or doping defect of the CuS supercell is defined as follows:

$$E_{f} = E \frac{defect}{tot} - E \frac{perfect}{tot} - \sum_{s=1}^{N} n_{s}^{i} \mu_{s}$$
(1)

Here,  ${}^{E_{f}}$  is the formation energy of the intrinsic defect or doped defect of the supercell structure.  ${}^{E_{f}} {}^{defect}_{tot}$  is the total energy of the supercell structure, including defects.  ${}^{E_{tot}} {}^{erfect}_{tot}$  is the total energy of the ideal system.  ${}^{N_{species}}$  is the number of types of all defective chemical elements.  ${}^{n_{s}^{i}}_{s}$  is the number of s type atoms that are added ( ${}^{n_{s}^{i}} > 0$ ) or removed ( ${}^{n_{s}^{i}} < 0$ ) when a defect is formed.  ${}^{\mu_{s}}$  is the chemical potential of the s type atom. For the hexagonal phase of the CuS system, the chemical potential of Cu and S, referred to as  ${}^{\mu_{s}}$  and  ${}^{\mu_{cu}}$ , must meet the following growth condition:

$$\mu_{\rm CuS} = \mu_{\rm Cu} + \mu_{\rm S} \tag{2}$$

 $\mu_{CuS}$  represents the chemical potential of the hexagonal phase of the CuS system. It is the hydrogen sulfide gas that entered the reaction solution in the experiment. We consider that the chemical

potential of the Cu was obtained through metal Cu in the condition of rich Cu<sup>2+</sup>. We calculate the formation energy of the Cu<sub>53</sub>Ce<sub>1</sub>S<sub>54</sub> and Cu<sub>52</sub>Ce<sub>2</sub>S<sub>54</sub>, Cu<sub>54</sub>S<sub>53</sub>, Cu<sub>54</sub>S<sub>55</sub>, Cu<sub>53</sub>Ce<sub>1</sub>S<sub>53</sub>, Cu<sub>52</sub>Ce<sub>2</sub>S<sub>53</sub> structures as 3.14 eV, 0.12 eV, -0.56 eV, -1.01 eV, and -4.63 eV, respectively, according to formulas (1) and (2). The Cu<sub>53</sub>Ce<sub>1</sub>S<sub>54</sub> and Cu<sub>53</sub>Ce<sub>1</sub>S<sub>53</sub> structures are regarded as the low doping concentration systems, while the Cu<sub>52</sub>Ce<sub>2</sub>S<sub>53</sub> and Cu<sub>52</sub>Ce<sub>2</sub>S<sub>53</sub> structure are the high doping concentration systems. The formation energy of the high doping system is lower than teh low doping system for the Cu<sub>53</sub>Ce<sub>1</sub>S<sub>54</sub> and Cu<sub>52</sub>Ce<sub>2</sub>S<sub>54</sub> structure, which indicates that the Ce atom doped into CuS structure can greatly reduce the defect formation energy. Considering that the chemical reaction in the experiment occurred under the condition of rich Cu<sup>2+</sup>, we also calculated the defect formation energy of the S vacancy structure. The result shows that the formation energy of the S vacancy structure is lower than the formation of the Ce doping system, which indicates that the defect of the S vacancy is more stable than the Ce doping system. Actually, the doping system is not only a pure interposition doping system, but also may have vacancy defects at the same time. Thus, the formation energy of S vacancy with the Ce doping has been calculated under the case of being mainly a doping system. The formation energy of the Cu<sub>53</sub>Ce<sub>1</sub>S<sub>53</sub> and Cu<sub>52</sub>Ce<sub>2</sub>S<sub>53</sub> supercell structures are all lower than the formation energy of a pure doping system, which refers to the Cu<sub>53</sub>Ce<sub>1</sub>S<sub>54</sub> and Cu<sub>52</sub>Ce<sub>2</sub>S<sub>54</sub> supercell structures. It may be easier to synthesize the Cu<sub>53</sub>Ce<sub>1</sub>S<sub>53</sub> and Cu<sub>52</sub>Ce<sub>2</sub>S<sub>53</sub> structures in experimental conditions. This result also indicates that the Ce doping is beneficial to form S vacancy defects in the hexagonal phase of CuS. To sum, the theoretical calculation is significantly consistent with the experimental results.



Fig. S7. The charge density of (a)  $Cu_{53}Ce_1S_{54}$  and (b)  $Cu_{52}Ce_2S_{54}$  structures.

Fig. S7 shows the charge density of  $Cu_{53}Ce_1S_{54}$  and  $Cu_{52}Ce_2S_{54}$  structures. It can been see that the



electrons are mainly localized on the Ce atoms.

Fig. S8. The preparation of the button cell.

CuS:Ce<sup>3+</sup> (0.86 at. %) QDs as an anode material are used in these self-assembled button cells. Fig. S8 shows the detailed preparation of one button cell. In Fig. S8, A is the anode material which is made of CuS:Ce<sup>3+</sup> (0.86 at. %), acetylene black, and polytetrafluoroethylene (PTFE). B is the cathode material which is made of activated carbon, acetylene black, and PTFE. C is the negative battery shell. D is the shrapnel. E is the spacer and the thickness of the spacer is 0.8 mm. F is the diaphragm with the diameter of 19 mm. G is the positive battery shell (CR 2032). It is the installation sequence of button cells from step 1 to step 12. First of all, the shrapnel and spacer are placed in the negative battery shell in sequentially, and then drop a drop of the electrolyte (6 M KOH) on the spacer. The cathode material is placed on the spacer. And then add a drop of the electrolyte on the cathode material. The diaphragm is placed on the cathode material. And then add a drop of the electrolyte on the anode material is placed on the diaphragm. And then add a drop of the electrolyte on the anode material. The positive battery shell is placed on the anode material and then encapsulated under the hydraulic crimping machine (MSK-110). The negative battery shell, shrapnel, spacer and the positive battery shell are soaked in alcohol and acetone for 6 hours and dried before using.



**Fig. S9.** (a) low magnification and (b) high magnification FESEM image of CuS:Ce<sup>3+</sup> (0.86 at. %) QDs. All samples have the similar morphology structure. Fig. S9 shows the morphology structure of



CuS:Ce<sup>3+</sup> (0.86 at. %) QDs.

**Fig. S10.** (a) The SEM image and (b) EDS mapping image of CuS:Ce<sup>3+</sup> (0.86 at. %) QDs. (c), (d) and (e) elemental mapping images of S, Cu and Ce respectively.

Fig. S10 shows the EDS mapping of the CuS:Ce<sup>3+</sup> (0.86 at. %) QDs. It is learned that the distribution of S and Cu elements is well-proportioned. The Ce element is also uniformly distributed in the obtained samples.



**Fig. S11.** Nitrogen adsorption-desorption isotherms of the CuS:Ce<sup>3+</sup> (0.86 at. %) QDs and the inset is pore size distribution.

To study the pore structural and the specific surface area of CuS:Ce<sup>3+</sup> (0.86 at. %) QDs, Brunauer-Emmett-Teller (BET) gas-sorption measurement was carried out. According to the corresponding results present in Fig. S11, it is no doubt that the CuS:Ce (0.86 at. %) QDs, whose isotherm represents a typical type IV curve with a hysteresis loop at relative pressure (p/p<sub>0</sub>) between 0.4 to 1.0, contains some microporous and mesoporous. The total pore volume is 0.276 cm<sup>3</sup>/g and the total microporous volume is 0.0102 cm<sup>3</sup>/g. The specific surface area of CuS:Ce<sup>3+</sup> (0.86 at. %) QDs is evaluated to be 24.322 m<sup>2</sup>/g from data points in the relevant pressure range. A larger surface area of CuS:Ce<sup>3+</sup> QDs can provide more electroactive sites and complete contact with the electrolyte and facilitate rapid electron/ion intercalation. Therefore, superior electrochemical performances can be expected for CuS:Ce<sup>3+</sup> QDs when used as electrode materials for supercapacitors.



**Fig. S12** (a) low magnification and (b) high magnification FESEM image of the working electrode (CuS:Ce<sup>3+</sup> (0.86 at. %) QDs + acetylene black + PVDF) after the life cycle.

Fig. S12 shows the low magnification and high magnification FESEM image of the electrode material after the life cycle. The working electrode is fabricated by mixing the CuS:Ce<sup>3+</sup> (0.86 at. %) QDs, conductive acetylene black, and polyvinylidene fluoride. The distribution of CuS:Ce<sup>3+</sup> (0.86 at. %) QDs are uniformed in the working electrode.



**Fig. S13** XRD pattern of working electrode (CuS:Ce<sup>3+</sup> (0.86 at. %) QDs + acetylene black + PVDF) after the life cycle.

Fig. S13 shows the XRD pattern of working electrode (CuS:Ce<sup>3+</sup> (0.86 at. %) QDs + acetylene black + PVDF) after the life cycle. The XRD diffraction peaks can be indexed to CuS (JPCDS 6-0464,

space group: P-63/mmc (no. 194)), and the sharp peaks reveal the QDs'good crystallinity. The extra XRD diffraction peaks belong to Ni, acetylene black and PVDF. Fig. S13 indicates that the good stability of CuS:Ce<sup>3+</sup> QDs and it can be used in supercapacitor.

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