Supplementary information

Tunable Surface Charge of ZnS:Cu Nano-adsorbent Induced the Selective Preconcentration of Cationic Dyes from Wastewater**

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1. Experimental Section:

1.1 Materials and Instruments.

All of the chemicals were AR reagents obtained from commercial sources and used without further purification.

X-ray diffraction (XRD) was used to identify phase and crystal structure of the obtained samples. Diffraction data were recorded using a PANalytical X' Pert PRO diffractometer with Cu Kα radiation (40 kV, 40 mA) in the continuous scanning mode. The 2θ scanning range was from 10° to 80° in steps of 0.03° with a collection time of 20 s per step. Scanning electronic microscopy (SEM) analyses were used to confirm the particle sizes and to determine the particle morphology. Samples were prepared for SEM study by dispersing the samples onto a holey carbon-coated support. The SEM analyses were performed using a JSM-6700F equipped with an Oxford-INCA energy dispersive X-ray (EDX) spectroscopy. A Shimadzu UV-2550 spectrophotometer was used to record the UV/Vis spectra of various samples. High-resolution transmission electron microscopy (HRTEM) was used to image the morphology, detailed microstructures and phase distinction of individual particles. X-ray photoelectron spectroscopy (XPS) was utilized to analyze the valence state of Cu ions incorporated into the ZnS lattice. The x-ray absorption near-edge structure (XANE) and X-ray absorption fine structure (EXAFS) spectroscopy were collected at Shanghai Syn-chrotron Research Facility (SSRF) beamline BL14W1. To obtain quantitative structural information, the EXAFS data were fitted using the IFEFFIT package[1].

1.2 Preparation of original ZnS microspheres.

The original ZnS microspheres were synthesized by a hydrothermal method as reported in our previous work[2]. In details, ZnO (0.167 g, 2 mmol) was dissolved in a mixture of NaOH (16 M, 12.875 ml) and Na$_2$S (1 M, 2 ml). It was then put into a hydrothermal bomb that was sealed and heated at 230 °C for 12 h. The bomb was forcedly cooled to room temperature rapidly after the heat treatment. The white powder was filtered and washed with excess water and pure ethanol, and finally dried in air at room temperature for 8 h.

1.3 Preparation of the ZnS:Cu adsorbent

The above ZnS microspheres (0.78 g, 8 mmol) were ultrasonically dispersed in 30 ml distilled water. Then, 8 ml NaCl/CuCl solution (Cu$^+$, 0.3 mol/L) was added dropwise and the reaction mixture was stirred at room temperature for 10 min. The black powder was filtered and washed with excess water. Before use, the ZnS:Cu adsorbent has been annealed at 120 ^{o}C for more than 6 h, and finally dried in air at room temperature for 8 h.

1.4 Adsorption isothermal experiments

The preconcentration of low concentration dye. The adsorption column was packed with ZnS :Cu (0.8g, 1 × 1.2 cm). Then a simulated wastewater (10 L) containing 1×10^{-6} mol/L rhodamine B was allowed to pass through the column (flow rate, 0.15 mL/s). When completed, the column was eluted with ethanol (10 ml). The concentrations of the dye were detected by UV-vis adsorbance.

The selective adsorption performance. Simulated mixed dye solutions were prepared to examine the selective adsorption performance of the ZnS:Cu adsorbent. Solution **1** includes rhodamine B, gentian violet, and methylene blue. Solution 2 includes Orange G, malachite green, and methylene blue. All the dye solutions are 1×10^{-5} mol/L. After adsorption, the dye solution was determined by UV-vis a spectroscopy

The adsorption isotherm. A set of rhodamine B solutions with concentrations ranging from 1×10^{-5} to 3×10^{-5} mol/L were prepared before hand. Then, ZnS:Cu adsorbent (10 mg) was added to the dye solution (250 ml) that was immersed in a water bath at 35 ^{o}C. After equilibrium, the concentration of the dye solution was determined by a UV-vis spectroscopy.

2. Results

2.1. Structure of the ZnS raw material

ZnS raw material used for Cu-doping exhibits a flowerlike self-supported structure. As shown in Fig. S1, the microsphere is composed of 10-20 nm thick interwoven nanosheets, with size ranging from 5-10 μm.
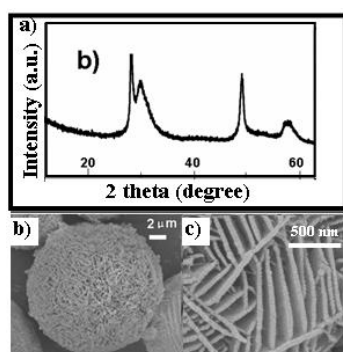
Fig. S1. The XRD pattern (**a**) and SEM image (**b, c**) of ZnS microspheres used for Cu-doping.

2.2. Structure of the nanosheets in a ZnS:Cu microsphere

TEM observations were implemented to investigate the phase of the nanosheets in the ZnS:Cu microsphere. The nanosheets were ultrasonically exfoliated from the microspheres for the observation of the open face of the sheet (Fig. S1-a,b). The Fourier transform (FT) analysis of the image proved that the nanosheet exhibits close packing along the wurtzite [100].
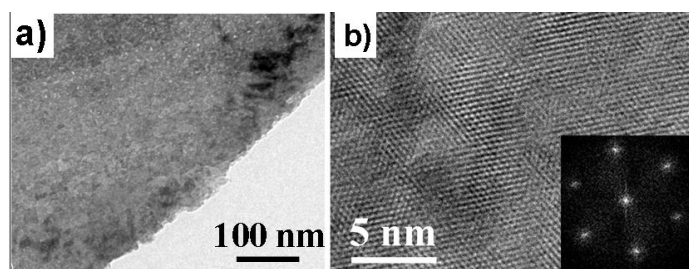

Fig. S2. (**a**) The TEM image of the nanosheet shed from the ZnS:Cu microshpere; (**b**) The HRTEM image of the nanosheet which shows w[100] close packing.

2.3. Explanation of the structure of the ZnS:Cu adsorbent

Firstly, it should be point out that the doping of Cu into ZnS lattice may not change the structure of ZnS. The Cu-S bond is ~ 2.27 Å, which is close to that of the Zn-S bond in ZnS (~ 2.3 Å). When Cu is successfully doped into ZnS lattice, Cu will occupy Zn site without change the parent structure. As a result, it will be no significant difference in XRD, SEM and TEM between ZnS samples before and after Cu doping. Following experimental evidences could support the assumption that the Cu^+ is probably doped into the ZnS lattice.

1)   ICP analysis shows that the ratio of Cu:Zn in ZnS:Cu adsorbent is near to 3:7. If Cu is not doped into ZnS lattice, it may form new compound such as Cu_2S (crystallite or amporphous). However, XRD data show that the diffraction pattern of the ZnS:Cu is almost same as the undoped ZnS. It suggests that little Cu_2S crystallites exit (< 5%). Further TEM and SEM observations (Fig. 1)

show that no phase other than ZnS microsphere is observed. It indicates that no amorphous Cu_2S exit. Since Cu^+ is not exist in Cu_2S or other phase, it is probably doped into the ZnS lattice.

2) Secondly, ξ potential measurements (-40 mV in distilled water) proved that the surface of the adsorbent is negatively charged. If the Cu^+ is physically adsorbed on the surface, it will be positively charged. However, when Cu^+ ion is doped into the ZnS lattice by substituting Zn atoms, it will result in an enhancement of the negative surface charge.

3) Moreover, it was found that with the increasing of the doping level of Cu^+, the saturated adsorption amount (Q_0) to cationic dye is increasing (Table 1), suggesting that the negative charge on the surface is increasing. This result is consistent with the above assumption that the doping of Cu^+ in to the ZnS lattice will lead to enhancement of the negative surface charge.
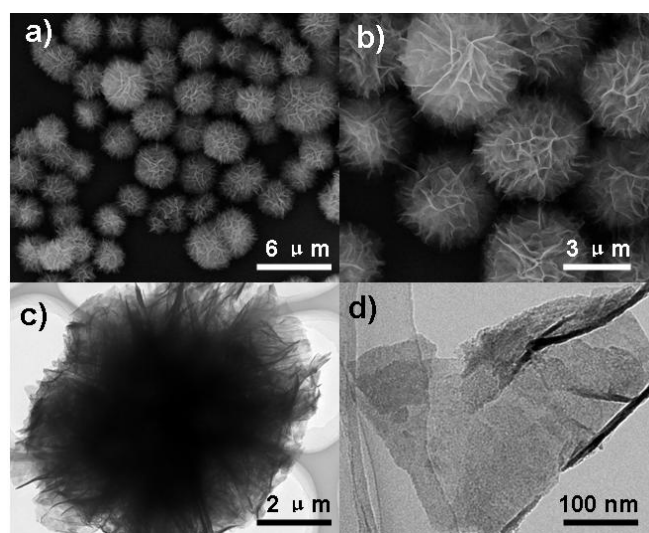

Fig. S3. **a)** The large scale SEM image for ZnS:Cu adsorbent. **b)** A magnified image of **(a)**, **c)** The TEM image of a single microsphere. **d)** TEM image of a nanosheet shed form the microsphere.

Table 1 The Langmuir capacity (Q_0) of Rh B on ZnS:Cu adsorbent with different doping content at 35 °C

Doping content	Q_0 (mg/g)
10% Cu:ZnS	18.68
15% Cu:ZnS	35.03
20% Cu:ZnS	41.56
25% Cu:ZnS	45.70
30% Cu:ZnS	65.01
40% Cu:ZnS	60.31

2.4. Adsorption isotherm

The adsorption isotherm was measured to assess the adsorption capacity and affinity of the ZnS:Cu

adsorbent. Langmuir isotherm equations was adapted to fit the experimental data [3]:

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{C_e Q_0 b}$$

where Q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration

(mg/L). Q_0 is the maximum amount or the saturated adsorption amount (mg/g). b is a constant related

to the binding strength (L/mg). According to the fitting result, the values of Q_0 and b are 65 mg/g and
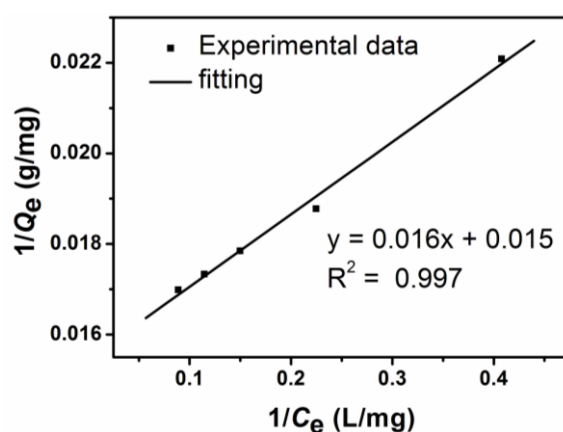
0.95 L/mg, respectively.

Fig. S4. Adsorption isotherms of the rhodamin B on the ZnS:Cu adsorbent.

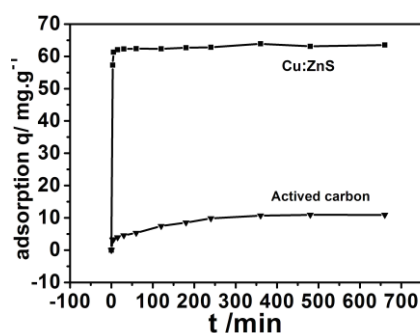**2.5. Control experiments for the adsorption measurements.**

Fig. S5 Control experiments for the adsorption of RhB by using ZnS:Cu and actived carbon

respectively.

As shown in Fig. S5, for the activated carbon it will take ~ 10 h to reach to the adsorption equilibrium. It is much longer than that (5 min) of the ZnS:Cu adsorbent.

The adsorption performance of the un-doped ZnS is measured. The Langmuir capacity (Q_0, RhB) is 10 mg/g. And that of Cu_2S prepared by coprecipitation is also determined, which is 13 mg/g.

2.6. Effect of pH value on the adsorbability of ZnS:Cu.

The pH effect has been investigated. As shown in Figure S6, in the acidic condition the adsorbability is relatively higher (pH = 2, Q_0 = 70.23 mg/g). With pH increasing, the adsorbability decrease slightly. At pH = 10, the adsorbability reaches its lowest value (Q_0 =63.2 mg/g).
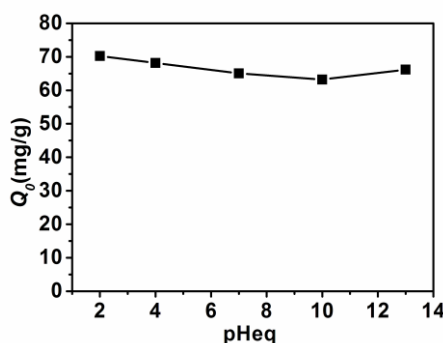

Figure S6. The effect of pH value on the adsorbability of ZnS:Cu adsorbent

2.7 Preliminary assessment of the adsorption efficiency to the real industrial wastewater

In real case, there are many types of industrial waste, such as azo dyes, oxidation dyes, ionic dyes, and etc. The output water from the different textile industries and at different manufacturing stage are not the same. Our adsorbent is aim to dispose the wastewater containing water soluble low concentration ionic dyes. The output water from some textile industries, even after the traditional removal processes, still contains low concentration ($< 1 \times 10^{-5}$ mol/L) of soluble ionic dyes, featuring incomplete decolorization. The composition of the wastewater at this stage is relatively simple. We preliminarily investigated the removal efficiency of the ZnS:Cu adsorbent on the output water from a textile industry in Fuzhou, China, which contains low concentration of cationic dye Brilliont Red (~ 2×10^{-5} mol/L). The pH value is ~ 4. The color removal efficiency for 200 mg/L ZnS:Cu addition is ~ 98%. It has been proved that the sample could be successfully decolorized by ZnS:Cu adsorbent.

Reference:

1   Ravel, B.; Newville, M. J Synchrotron Radiat 2005, 12, 537.

2   D. S. Li, Z. Lin, G. Q. Ren, J. Zhang, J. S. Zheng and F. Huang, *Cryst Growth Des*, 2008, **8**,

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3   I. Langmuir, The adsorption of gased on plane surfaces of glass, mica and platinum, J. Am. Chem.

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