

Simple, low-cost alkali treatment approach to improve photoactivity of $\text{Co}_{0.01}\text{Zn}_{0.99}\text{S}$

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An easy alkali treatment method is designed to enhance the activity of $\text{Co}_{0.01}\text{Zn}_{0.99}\text{S}$ (CZS). After alkali treatment, the surface area of CZS increases by 2.8 times (12.8 versus 3.4 m^2g^{-1}), and the oxidation potential (E_{VB}) of valence band also increases greatly (2.55 versus 2.19 V). After treatment, the UV-light activity has increased by 3.4 times for the degradation of dye. This simple, low-cost method may be extended to mass production for practical applications.

1. Introduction: As an important semiconductor material, the optical [1, 2], magnetic [3, 4] and photochemical [5] properties of ZnS are easily improved by transition metal doping (e.g. Co, Cu, Mn, Ag, Ce etc.) [6–15]. Typically, the luminescent magnetic and photocatalytic properties of ZnS can be effectively adjusted by the Co doping [6]. Bi *et al.* [12] have studied the influence of cobalt doping concentration on Raman spectrum of Co-ZnS, they have found that two wide Raman peaks appear at low cobalt doping concentrations, but the additional peaks will appear with the increase of cobalt concentration. Many researchers have reported that the magnetic saturation (M_s) value of Co-ZnS increases with the increase of cobalt content [6, 11, 14, 15]. Tang *et al.* have reported that when the Co doping amount increases, a red shift of Co-ZnS first occurs that causes a weak visible light absorption, followed by a blue shift [13]. Co-doped ZnS have been prepared by various methods, including hydrothermal [11], solution-phase thermal decomposition [12], thermal evaporation [6], chemical bath deposition [13] and so on. Although the photocatalytic properties of Co-ZnS have also been reported [16, 17], they only discussed the influence of cobalt doping amount on the activity of ZnS; moreover, the effect of cobalt doping on the activity of the sample was not obvious. It is needed to design a new method to further improve its performance.

Herein, $\text{Co}_{0.01}\text{Zn}_{0.99}\text{S}$ (CZS) was treated with an alkaline solution. Significantly, the treated sample showed a higher photoactivity for the rhodamine (RhB) degradation than the untreated one. The method is simple, general, which could be used for the other material.

2. Experimental

2.1. Preparation of CZS: Typically, 0.667 g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 0.279 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.608 g $\text{CS}(\text{NH}_2)_2$ were added in 35 ml distilled water. After being stirred for 30 min, it was poured into the autoclave and processed at 180°C for 24 h. The solid was separated, washed with water and dried at 60°C for 6 h in air.

Alkaline treatment of CZS: 0.2 g CZS powders above was added in 35 ml NaOH aqueous solution and stirred for 30 min. Then, it was poured into the autoclave and processed at 180°C for 24 h.

The similar procedures above were used to obtain the product, which is named as 5M-CZS.

2.2. Characterisations: X-ray diffractometer (XRD) pattern was used to determine crystal phase (Rigaku D/max-2550VB). Light absorption was gauged with UV–vis diffuse reflectance spectroscopy (UV-DRS, UV-2550, Shimadzu, Japan). Scanning electron microscope (SEM, Hitachi SU-1510) was used to scan the surface morphology. Nitrogen sorption isotherms were used to measure surface area (Micrometrics ASAP 2020HD88 sorption apparatus). Steady-state photoluminescence (PL) spectroscopy (Japan, Shimadzu RF-5301PC) was used to investigate charge separation efficiency. Electron paramagnetic resonance spectroscopy (EPR, Bruker ESP 500 spectrometer) was employed to examine defect. X-ray photoelectron spectroscopy (VG ESCALAB MKII XPS system) was employed to analyse surface chemical state. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for element quantitative analysis.

2.3. Electrochemical measurement: Photocurrent, electrochemical impedance spectroscopy and Mott–Schottky curve were measured on electrochemical working station (CHI 660D, Shanghai Chenhua Technology Co. Ltd.). Surface photovoltage (SPV) spectrum was obtained on transient SPV spectrometer (PL-TPV, Beijing PerfectLight Technology Co. Ltd.).

2.4. Activity test: About 0.1 g powder was added into 200 ml 7.5 mg l^{-1} RhB solution. Before turning on, the mixture was stirred in dark for 30 min. Then, the system was irradiated by UV light ($\lambda \leq 420$ nm). UV–vis spectroscopy was used to determine the RhB concentration.

3. Results and discussion

3.1. Morphology and crystal phase: Herein, the CZS samples without and with alkali treatment are labelled as CZS and 5M-CZS, respectively. The XRD patterns of the CZS and 5M-CZS samples are displayed in Fig. 1a. For 5M-CZS, the diffraction peaks well match (111), (220), (311), (200), (222), (400) and (331) planes of ZnS (JCPDS Card No. 80–0020); but for CZS, the (200), (222), (400) and (331) peaks are not obvious because

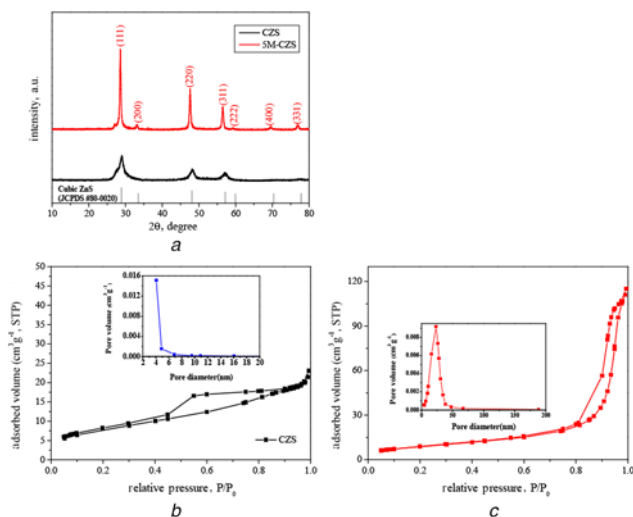


Fig. 1 Physical property

a XRD patterns

b, c Nitrogen sorption isotherms (the inset of pore size distribution)

of the low crystallinity. The diffraction peaks of 5M-CZS become stronger than those of CZS, indicating that the alkali treatment has enhanced crystallisation obviously. Besides, all the peaks of 5M-CZS shift to a lower 2θ values by about 0.3° , which is attributed to the lattice distortion of non-uniform strains [18] caused by the removal of a small amount of Zn. Figs. 1b and c present their N_2 sorption isotherms (the inset of pore size distribution). The sorption isotherms of CZS and 5M-CZS both show the type-IV type. CZS shows a H2 hysteresis loop, which often occurs in pores with narrow necks and wide bodies (often referred to as ‘ink bottle’ pores). 5M-CZS shows a H3 hysteresis loop, which is considered to be a slit pores formed by closely packed plate-like particles. After the sample treated with alkali, the most probable pore size changed from 4.1 nm (CZS) to 23.4 nm (5M-CZS). Besides, the surface areas of CZS and 5M-CZS are determined to be 3.4 and $12.8 \text{ m}^2 \text{ g}^{-1}$ by Brunauer–Emmett–Teller (BET) method. The higher BET surface area would be beneficial to enhance the photocatalytic activity. Fig. S1 (see supplementary information) shows that the samples are both composed of micron particles, which are about $3 \mu\text{m}$ large.

3.2. Zn vacancy analysis: The EPR spectra are shown in Fig. 2a. Compared with CZS, the signal intensity for 5M-CZS increases, suggesting that the Zn vacancies are produced. Furthermore, the atomic percentages of the samples are determined by ICP-AES. Table 1 shows that the amount of Co nearly does not change, while the amount of Zn decreases, indicating the removal of a small amount of Zn. The result is agreed with the XRD and EPR results.

The survey XPS and Co 2p XPS spectra confirm the Zn, Co and S compositions (Fig. S2, see supplementary information). Besides, Figs. 2b and c display the Zn 2p and S 2p XPS spectra. Compared with the CZS, the Zn $2p_{1/2}$, Zn $2p_{3/2}$ and S $2p_{3/2}$ peaks of 5M-CZS all shift to a higher binding energy slightly. Xu *et al.* have confirmed that the presence of bismuth vacancy can cause a blue shift of Bi 4f, which has been attributed to the electron transfer from Bi to O [19]. Hence, we hold that the electron transfer from Zn to Co or S may cause the shift to a higher binding energy for Zn 2p. For S 2p, the shift towards a higher value is due to the removal of a small amount of Zn [19].

3.3. Photoelectrical analysis: Fig. S3a (see supplementary information) shows the UV-DRS spectra of CZS and 5M-CZS. Their absorption edges are both about 420 nm, and their band gaps are

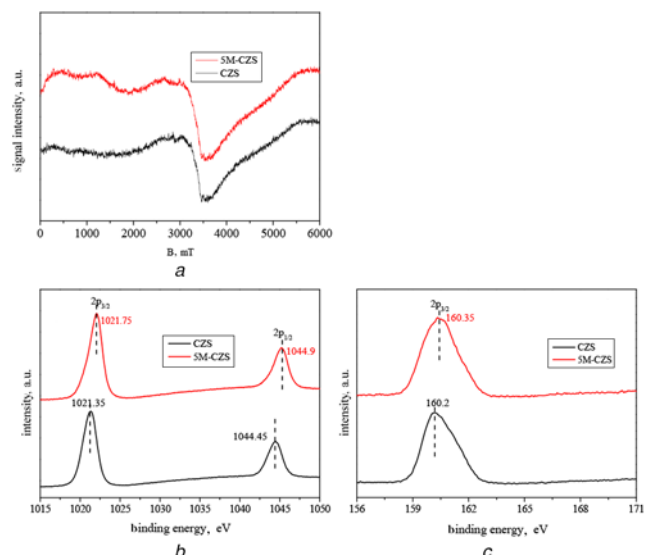


Fig. 2 Formation of Zn vacancy

a EPR spectra

b Zn 2p X-ray photoelectron spectra (XPS)

c S 2p XPS

Table 1 Atomic ratios by ICP-AES analysis

Sample	Atomic percentage (at.%)		
	Zn	Co	S
CZS	65.67	0.65	33.68
5M-CZS	62.67	0.62	36.71

estimated to 2.73 eV. The PL spectra (Fig. S3b, see supplementary information) shows that compared with 5M-CZS, the slightly higher PL intensity at 467 nm suggests a higher charge recombination rate of CZS. The EIS spectra of CZS and 5M-CZS (Fig. S3c, see supplementary information) shows that they have the nearly same charge transfer resistance (R_{ct} , $0.6 \Omega/5\text{M-CZS}$ versus $0.4 \Omega/\text{CZS}$). As shown in Fig. S3d (see supplementary information), the strong positive SPV signal means that the photogenerated holes migrate mainly to the 5M-CZS surface. Herein, we think that the increased Zn vacancy could trap the photogenerated electrons, thus refraining the recombination of hole and electron. As a result, more holes migrate to the surface. For CZS, the weak positive and negative SPV signals mean that less photogenerated holes and electrons transfer to the surface but most of them may have recombined in bulk.

Additionally, Fig. 3a shows the Mott-Schottky plots. Equation (1) [18] was used to determine the potential of conducting band (CB)

$$\Delta E = E_{CB} - E_{fb} \quad (1)$$

The ΔE is -0.3 V , and the flat-band potentials (E_{fb}) are calculated to be -0.24 and $+0.12 \text{ V}$ for CZS and 5M-CZS. The conduction band potentials (E_{CB}) of CZS and 5M-CZS are -0.54 and -0.18 V , and the valence band potentials (E_{VB}) are $+2.19$ and $+2.55 \text{ V}$, respectively. It is obvious that the oxidation ability of VB holes increases but the reducing ability of CB electrons decreases. Furthermore, Fig. 3b shows that the higher photocurrent of 5M-CZS suggests the higher charge transfer and separation efficiency, compared with CZS.

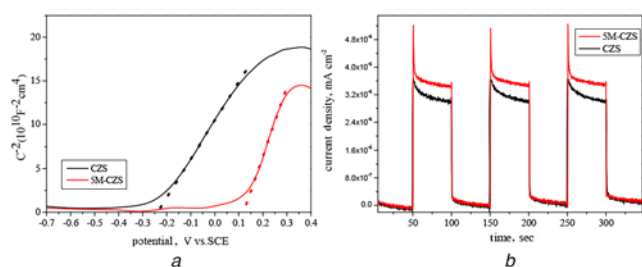


Fig. 3 Photoelectrical properties
a Mott-Schottky curves
b Photocurrent response spectra

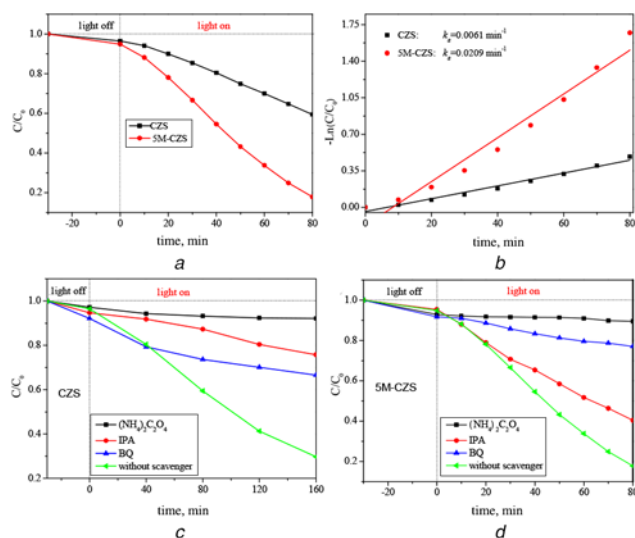


Fig. 4 Photocatalytic activity
a, b RhB degradation curves and apparent reaction kinetic curves under UV-light irradiation ($\lambda \leq 420$ nm)
c, d Trapping experiments

3.4. Degradation activity: Fig. 4a displays the UV-light activity curves for RhB degradation, and the reaction kinetic curves are shown in Fig. 4b. 5M-CZS exhibits an obviously higher photocatalytic activity than CZS. The 5M-CZS shows a 3.4 times higher reaction rate than CZS (0.0209 versus 0.0061 min^{-1}). Based on the results above, the improved activity could be ascribed to the partial remove of zinc, which has improved the BET surface area and the charge separation efficiency.

Furthermore, the trapping experiments were conducted to reveal active oxidation species. Figs. 4c and d show that for both CZS and 5M-CZS, when adding ammonium oxalate, the activity is nearly inhibited, and the activity also decreases obviously with adding IPA or BQ. The results suggest that h^+ , $\bullet\text{O}_2^-$, $\bullet\text{OH}$ are all the major active oxidative species. Furthermore, the cycle stability of the samples has been investigated. As shown in Figs. S4a and b (see supplementary information), after three cycles, the degradation percentages decrease by 7.8 and 7.2% for CZS and 5M-CZS, respectively. After cycles, the crystal phase has not changed, but the crystallinity of the sample has decreased (Figs. S4c and d, see supplementary information). For both samples, the particle surface become rough, even some particles are damaged (Fig. S5,

see supplementary information). These results suggest that the samples have a high stability.

4. Conclusion: The activity of CZS can be obviously improved by the simple, low-cost alkali treatment method. Alkali treatment has increased the BET surface area, improved charge separation efficiency and enhanced oxidation ability of VB holes due to the partial removal of zinc, leading to an increased photocatalytic activity.

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6 References

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