

Discovery and optimization of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ -based photocatalysts by scanning electrochemical microscopy and characterization of potential photocatalysts

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Abstract

Scanning electrochemical microscopy (SECM) with a scanning optical fibre was applied to rapidly identify potential $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ -based photocatalysts for water oxidation. Among the photocatalysts studied, the spot with the precursor composition $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ shows the highest photocurrent in 0.1 M $\text{Na}_2\text{SO}_4/\text{Na}_2\text{SO}_3$ solution under both UV-visible and visible light irradiation. The X-ray diffraction and X-ray photoelectron spectrometric analyses reveal that the $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ photocatalyst is comprised of monoclinic Ag_2S and solid solution $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ phases with average crystallite size in the range 18–28 nm. The addition of 30% Ag_2S to $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ photocatalysts enhances light absorption in the visible region. The SECM screening results are also confirmed with bulk film studies. The $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ electrode exhibits highly efficient visible-light photocatalytic activity with an IPCE value above 20% for a light wavelength of 500 nm.

Keywords: Scanning electrochemical microscopy; photocatalyst; zinc cadmium sulfide; silver sulfide; water oxidation.

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Introduction

Photoelectrochemical (PEC) and photocatalytic splitting of water into hydrogen and oxygen has attracted great attention due to its application in solar energy conversion and utilization [1–3]. To enhance the light-absorption efficiency, semiconductors with a proper band gap as photocatalysts are indispensable to absorb visible light for water splitting.

Experimental

● Preparation of photocatalyst arrays

The photocatalyst arrays consisting of mixtures of salt solutions were deposited on FTO glasses using a piezo-based microarray dispenser (CHI model 1550, CH Instruments). The Zn, Cd, and S mixed precursor solutions were first loaded and dispensed in a preprogrammed pattern. The dispenser was then emptied, washed thoroughly, and refilled with the second precursor solutions containing the third metal salts

● Preparation and photoelectrochemical measurements of bulk film electrodes

The potential $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ -based photocatalysts were prepared by the solvothermal coprecipitation method. The solutions containing precursors including AgNO_3 , $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, and thiourea with a specific composition determined from the array results were mixed in a Teflon reactor. This reactor was heated and maintained

at 100 °C during the entire reaction. The pretreated FTO substrates were immersed in the reactor for 12 h.

Results and discussion

In order to confirm that the results observed in the SECM study are applicable to large-scale films, we prepared bulk $\text{Ag}_x\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{1-x}$ electrodes as described in the Experimental section. The current–time transient responses of $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ and $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ electrodes under chopped UV-visible and visible light illumination are shown in Fig. 1 (a).

Fig.2(b) shows photocurrent results obtained from current–time transient measurements of different $\text{Ag}_x\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{1-x}$ electrodes under UV-visible and visible light illumination. The photocurrents of $\text{Ag}_x\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{1-x}$ electrodes under UV-visible and visible light illumination displayed similar trends, in which the $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ electrode exhibited the best photoactivity. With an increase of Ag above 30%, the photocatalytic activity decreased dramatically.

The UV-visible absorption spectra of the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ and $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ photocatalysts are compared as shown in Fig. 3. The $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ photocatalysts display strong absorption in the visible region with an absorption edge of 527 nm, whereas $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ photocatalysts absorb light up to 562 nm

Figure 4 shows IPCE plots of these electrodes over the range 300–600 nm calculated with the equation below:

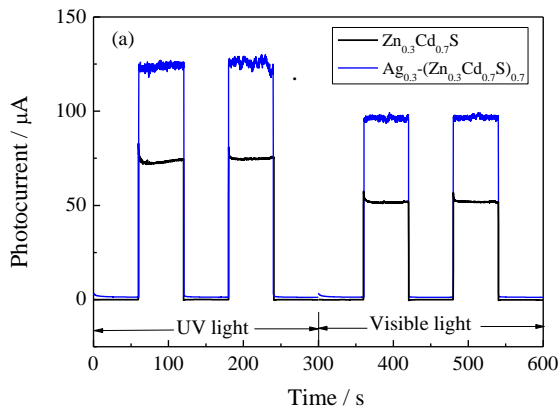


Figure 1: I-T curve of the $(\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S})$ and $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ bulk electrode

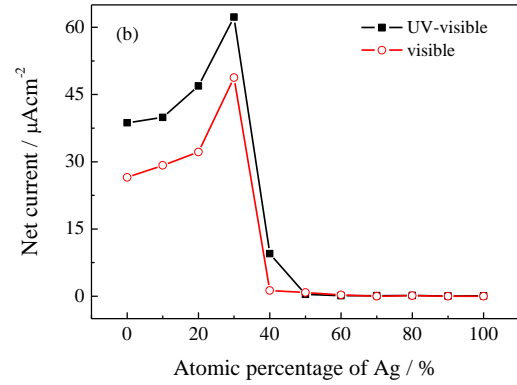


Figure 2: Chopped current time transient response of the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ and $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ electrodes under UV-visible and visible light illumination.

Spot	Ag: $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ (atomic ratio)
$\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$	0:100
$\text{Ag}_{0.1}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.9}$	13:87
$\text{Ag}_{0.2}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.8}$	16:84
$\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$	21:79
$\text{Ag}_{0.4}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.6}$	25:75
$\text{Ag}_{0.5}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.5}$	46:54
$\text{Ag}_{0.6}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.4}$	53:47
$\text{Ag}_{0.7}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.3}$	65:35
$\text{Ag}_{0.8}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.2}$	69:31
$\text{Ag}_{0.9}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.1}$	75:25
Ag	100:0

Table 1: Composition of $\text{Ag}_x\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{1-x}$ spots in the array measured by EDX.

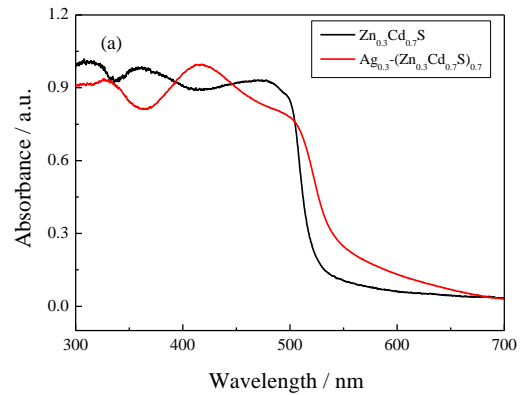


Figure 3: UV-visible absorption spectra of the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ and $\text{Ag}_{0.3}\text{-(Zn}_{0.3}\text{Cd}_{0.7}\text{S)}_{0.7}$ photocatalysts

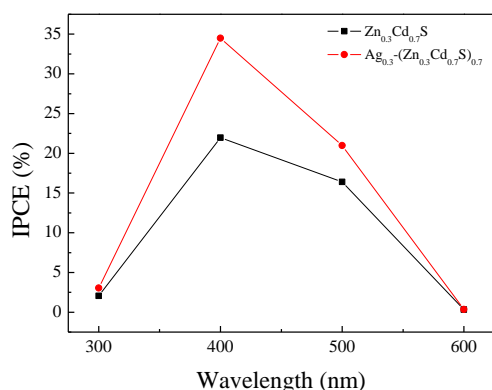


Figure 4: IPCE plots of the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ and $\text{Ag}_{0.3}-(\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S})_{0.7}$ electrodes calculated from the photocurrents at 0 V vs. Ag/AgCl.

Conclusion

Composition optimization of the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ -based photocatalyst systems for the water oxidation reaction was performed by a combinatorial screening method. The $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ -based arrays were prepared by a liquid dispensing method to generate a variety of compositions. Among these arrays, the $\text{Ag}_{0.3}-(\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S})_{0.7}$ photocatalyst exhibited the highest photocurrent in 0.1 M $\text{Na}_2\text{SO}_4/\text{Na}_2\text{SO}_3$ solution under both UV-visible and visible light irradiation. The physico-chemical properties of the best photocatalyst were further examined by SEM, EDX, XRD, XPS, and EIS. The $\text{Ag}_{0.3}-(\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S})_{0.7}$ photocatalyst consisted of monoclinic Ag_2S and solid solution $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ phases with an enhanced visible light adsorption compared to $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$. The IPCE value of the $\text{Ag}_{0.3}-(\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S})_{0.7}$ photoelectrode at 400 nm irradiation was 34.5%, which was 1.6 times higher than that of the $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ photoelectrode.

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