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## Photoelectrochemical studies of H<sub>2</sub> evolution in aqueous methanol solution photocatalysed by Q-ZnS particles

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### Abstract

H<sub>2</sub> evolution photocatalysed by Q-ZnS particles in aqueous methanol solutions was studied in a PEC cell. The photocatalytic activity of ZnS nanoparticles was characterized by short circuit photocurrent measurements. The steady state anodic and cathodic photocurrents were studied as a function of solution pH. An analysis of the transient responses of anodic photocurrent obtained in the different concentrations of methanol solutions indicates that the fast and slow components of the composite anodic photocurrent were correlative with the reactions of photoreduction of H<sub>2</sub> and photooxidation of methanol, respectively. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Photocatalysis; H<sub>2</sub> evolution; Transient photocurrent; Steady state photocurrent

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### 1. Introduction

Photocatalytic water cleavage and chemical pollutant degradation based on the semiconductor particles have been studied extensively due to the potential applications in solar energy conversion and environmental protections [1–4]. Considerable efforts were devoted to examine the photocatalytic activities of a variety of semiconductor particles with sizes ranging from colloids to powders and to understand the influence of the photoactivities of semiconductor particles on the photocatalytic mechanism. Recent works revealed that the photocatalytic behaviors of semiconductor particles can be studied in a PEC cell [5–9], in which semiconductor colloidal solution containing reductant, oxidant or the pollutant species were used as electrolyte and Pt electrode was used to collect charges generated during photocatalytic processes. By determining the photocurrent responses of the charge collective electrode under positive and negative bias, the kinetic mechanism of photocatalytic processes can be analyzed in terms of the anodic and cathodic photocurrents produced from the anodic and cathodic reactions of the PEC cell.

Previous work showed that H<sub>2</sub> evolution with high quantum yield was obtained in the photocatalysis of aqueous methanol solution by Q-ZnS particles [10], but the photo-

catalytic mechanism was not well clarified. In this paper, we report a kinetic mechanism studies of photocatalytic H<sub>2</sub> evolution in a PEC cell by using steady state and transient photocurrents methods.

### 2. Experimental details

Q-ZnS particles were prepared by embedding ZnS in  $\beta$ -cyclodextrin (BCD) cavities with rapid precipitation and subsequent temperature treatment and obtained as the form of inclusion complex Q-ZnS/BCD. The preparation procedures were described elsewhere [10,11]. The microstructural morphology of Q-ZnS/BCD that coated on the surface of highly oriented pyrolytic graphite (HOPG) substrate was imaged by using Tunnelscope 2400 type scanning tunneling microscope (STM) in air. A PEC cell was constructed with two 4 cm<sup>2</sup> Pt foils as working and counter electrodes and SCE as reference electrode. Transparent and colorless electrolyte was employed by peptizing 10<sup>-3</sup> M Q-ZnS/BCD inclusion complex in aqueous methanol solution containing 0.1 M K<sub>2</sub>SO<sub>4</sub>. The PEC cell was irradiated with 245 nm light generated from a 9 W low pressure Hg lamp through a quartz window. A PAR 273 Potentialstate/Galvanostate was used to control the electrode potentials at +0.60 and -0.10 V vs. SCE for collecting anodic and cathodic photocurrents, respectively. The collection of transient responses of photocurrent at light on and light off was recorded at EPR-

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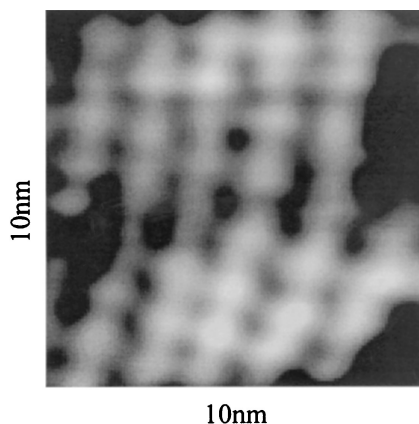


Fig. 1. STM image of Q-ZnS/BCD inclusion complex.

2314 X-T recorder during transient photocurrent measurements.

### 3. Results and discussion

Fig. 1 is the STM image of Q-ZnS/BCD inclusion complex, Q-ZnS particles in a shape of sphericity arranged regularly on the HOPG substrate surface. The sizes of Q-ZnS measured from the image were 9.7–12.2 Å and the BCD could not be distinguished in the image. The photoactivity of Q-ZnS/BCD for photocatalytic H<sub>2</sub> evolution in aqueous methanol solution was examined by measuring the short circuit photocurrents  $I_{sc}$  in a two electrodes cell with 75% methanol aqueous solution (pH=7) as the electrolyte. Fig. 2 shows the  $I_{sc}$  as a function of preparative pH. A maximum  $I_{sc}$  was obtained at pH=8.2 which was consistent with the pH=8.4 obtained by the determination of maximum amounts of H<sub>2</sub> evolution [10]. The preparative pH represented actually the concentration ratio of S<sup>2-</sup> to Zn<sup>2+</sup> which was optimal at pH~8 for preparing Q-ZnS/BCD with high photoactivity. This result indicates that the photoactivity of Q-ZnS/BCD can be examined by measuring the short circuit photocurrents in the PEC cell.

The photocatalysis of aqueous methanol solution by Q-ZnS/BCD consists of the following reactions:

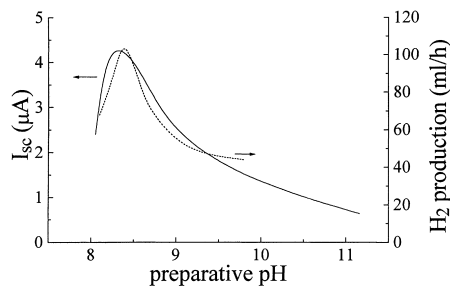
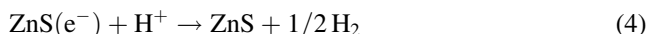
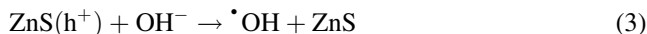
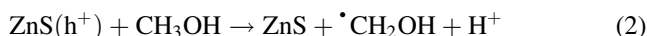
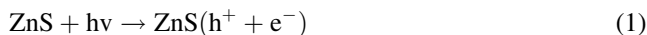


Fig. 2. The dependence of short circuit photocurrents  $I_{sc}$  on the pH of Q-ZnS/BCD preparation measured in 75% CH<sub>3</sub>OH aqueous solution, pH=7, Q-ZnS/BCD 10<sup>-3</sup> M.



The electroactive species such as  $\cdot\text{CH}_2\text{OH}$ ,  $\cdot\text{OH}$  and H<sub>2</sub> produced in the reactions (2), (3) and (4) can be oxidized or reduced at biased Pt electrode to generate anodic and cathodic photocurrents according to the following anodic reactions (5) and (6), or the cathodic reactions (7), (8) and (9) in the PEC cell.

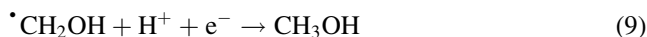
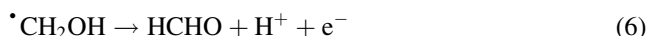


Fig. 3 shows the dependence of steady state photocurrents  $I$  on the applied potentials measured in 33% methanol aqueous solution at pH=7. The transient photocurrent responses of light on and light off recorded at different applied potentials were also illustrated in the figure. It can be seen that the transient responses of net cathodic and anodic photocurrents presented at the potentials -0.10 and +0.60 V, respectively. In the potential +0.10 V, an anodic photocurrent spike produced at the light on, followed with the cathodic photocurrent and cathodic photocurrent spike occurred at the light off were observed.

By measuring the steady state anodic and cathodic photocurrents as a function of solution pH in 75% methanol aqueous solution under the potentials of +0.60 and -0.10 V, respectively, the anodic and cathodic reaction processes can be analyzed. As seen from Fig. 4, the steady state anodic photocurrent  $I_a$  increased with the increase of solution pH, while the steady state cathodic photocurrent  $I_c$  decreased as the solution pH became higher. As we know that the increase of solution pH should be favorable for reactions (2) and (3), leading to the increases of steady state anodic photocurrent due to the anodic reaction of (6), the

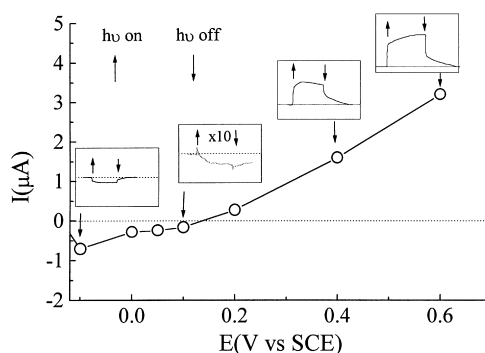


Fig. 3. Steady state photocurrents  $I$  as a function of applied potentials measured in 33% CH<sub>3</sub>OH aqueous solution, pH=7, Q-ZnS/BCD 10<sup>-3</sup> M.

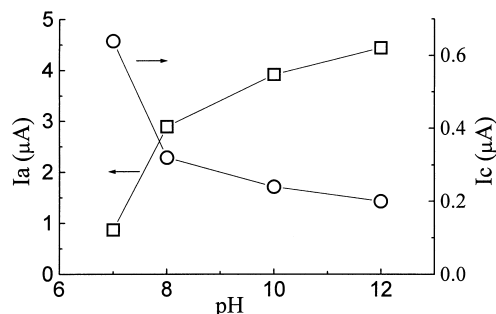


Fig. 4. Steady state anodic and cathodic photocurrents ( $I_a$  and  $I_c$ ) as a function of solution pH measured in 75% aqueous  $\text{CH}_3\text{OH}$  solution, Q-ZnS/BCD  $10^{-3}$  M.

steady state cathodic photocurrent attributed by cathodic reactions of (8), (9) can also increase (or less change). The correspondent experimental results of the increase of anodic photocurrent with solution pH shown in Fig. 4 indicate that the steady state anodic photocurrent arose from anodic reaction (6). However, a decrease of cathodic photocurrent with the increase of solution pH observed in our experiments reveals that the cathodic photocurrent were not dominated by the cathodic reductions of methanol and hydroxide radicals i.e. reactions (8) and (9), probably cathodic reaction (7) was considered to contribute to the generation of cathodic photocurrent.

In order to know the kinetic processes of anodic reactions concerning  $\text{H}_2$  evolution, the transient responses of anodic photocurrent were studied in 75% methanol aqueous solution and 100% water under applied potential of +0.60 V. From the transient photocurrent response plots of Fig. 5, we observed a rapid ascent of anodic photocurrent when light was switched on, attaining to the steady state photocurrent in  $\sim 120$  s, and a fast descent following with gentle decrease of anodic photocurrent when light was switched off. Kinetic information can be obtained from the analysis of transient anodic photocurrent responses of light on and light off.

The analysis was performed by fitting the transient photocurrent response plots with the following double exponential equation

$$I_t = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2),$$

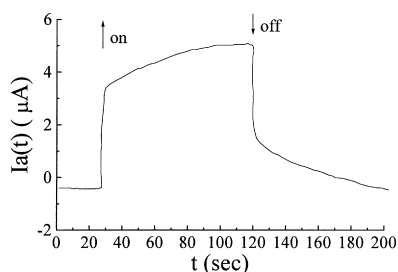


Fig. 5. Transient response of anodic photocurrent  $I_a(t)$  measured in 75%  $\text{CH}_3\text{OH}$  aqueous solution, pH=7, Q-ZnS/BCD  $10^{-3}$  M, applied potential +0.60 V.

Table 1  
Time constants of transient responses of anodic photocurrent

	Fast component (s)				Slow component (s)		
	$\text{H}_2\text{O}$		75% $\text{CH}_3\text{OH}$		$\text{H}_2\text{O}$	75% $\text{CH}_3\text{OH}$	
	On	Off	On	Off		On	Off
pH=10	4.17	1.43	1.38	1.20	–	114	158
pH=12	2.10	2.30	2.69	1.86	–	102	116

where  $A_1A_2$  are the amplitudes of the photocurrent and  $\tau_1\tau_2$  are the time constants.

The fitting results indicate that the transient anodic photocurrents of light on and light off were a composite of fast component and slow component. Table 1 lists the time constants of fast and slow component obtained in 75% methanol aqueous solution and 100% water solution at pH=10 and 12.

As seen from this table that the time constants of fast and slow components in 75% methanol solution were 1.38–2.69 s and 102–158 s, respectively, in both cases of light on and light off and were not affected by the change of solution pH from 10 to 12. In the case of 100% water solution, the transient responses of anodic photocurrent at light on and light off were fitted with a single exponential equation, the time constants were 2.10–4.17 s almost as the same as that of the fast component of 75% methanol aqueous solution.

Fig. 6 shows the amplitudes of fast and slow components of anodic photocurrent at light on as a function of methanol concentrations in pH=10 and pH=12 solutions. It is observed that the amplitude of slow component was increased dramatically with the increase of methanol con-

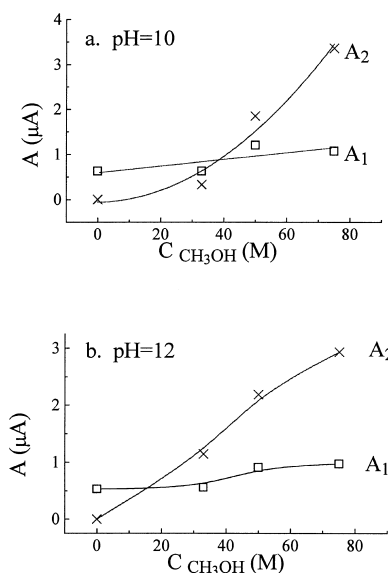


Fig. 6. The amplitudes of fast ( $A_1$ ) and slow ( $A_2$ ) components of transient responses of anodic photocurrent in different concentrations of  $\text{CH}_3\text{OH}$ , Q-ZnS/BCD  $10^{-3}$  M, (a) pH=10, (b) pH=12.

centration, however, the amplitude of fast component showed a less concentration dependent behavior. This results indicate that slow component of the transient anodic photocurrent response which was absent in the transient response of 100% H<sub>2</sub>O solution was correlative with the anodic reaction of  $\cdot\text{CH}_2\text{OH}$ , i.e. reaction (6). Presumably, the fast component may be associated with the anodic reaction of H<sub>2</sub>, i.e. reaction (5). From the analysis of the transient responses of anodic photocurrent, it is revealed that photooxidation of methanol by Q-ZnS/BCD (reaction (2)) was a slow process and photoreduction of H<sub>2</sub> evolution (reaction (4)) was a fast process.

In summary, PEC studies on photocatalysis of ZnS/BCD in aqueous methanol solution were reported in this paper, photocatalytic activity of ZnS/BCD for H<sub>2</sub> evolution was characterized by measuring the short circuit photocurrents collected at a Pt electrode. The photocatalytic mechanism was studied by examination of anodic and cathodic reactions in terms of the dependence of steady state anodic and cathodic photocurrents on solution pH. Analysis of the transient responses of anodic photocurrent in different concentration of aqueous methanol solution indicates that photoreduction of H<sub>2</sub> evolution was a fast process in several seconds and photooxidation of methanol was a slow process in more than one hundred seconds.

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