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Influence of the mixed ratio on the photocurrent of the TiO_2/SnO_2 composite photoelectrodes sensitized by mercurochrome

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Abstract

The mercurochrome-sensitized TiO_2/SnO_2 composite photoelectrodes with different mixed ratio have been prepared. When the mixed ratio of TiO_2 to SnO_2 was equal to 1:1, the maximal photocurrent was obtained at 0.1 V applied potential (versus saturated calomel electrode (SCE)). In the sensitized composite electrodes, the energy barriers formed between TiO_2 and SnO_2 particles have double functions: (1) they could reduce the recombination of the photo-induced electrons and the holes in the oxidized mercurochrome, or in the electrolyte (I_3^-), (2) they could also block the transport of the photo-induced electrons to the outer circuit. Spectro-electrochemical (SEC) measurements of the TiO_2, SnO_2 and TiO_2/SnO_2 composite electrode also provided the evidence for the existence of the barriers in the composite electrode. The energy barrier is about 80 mV calculated from the difference in the bleaching width of the SnO_2 and TiO_2/SnO_2 composite electrode.

Keywords: Composite electrode; Photocurrent; Spectro-electrochemistry; Energy barrier

1. Introduction

Recently, many researchers have interest in the Grätzel-type photoelectrochemical cell [1,2] and efforts have been devoted to improving its efficiency [3–5]. The cell was considered as a possible alternative to present day p–n junction photovoltaic devices. It consists of three components: dye-sensitized wide-band gap oxide semiconductor photoelectrode, electrolyte and counter electrode [6]. Under illumination, the photo-induced electrons in the conduction band of the semiconductor, which were injected from the excited state of the dye, could transport to the outer circuit, and then the anodic photocurrent was generated. At the same time, the oxidized dye was regenerated by I^-, and at the counter electrode, I_3^- was reduced to I^- by the photo-induced electrons. The reaction of the photo-induced electrons in the conduction band of the semiconductor involves three steps: back-reacting with the oxidized dye, reducing I_3^- to I^- and transporting to the outer circuit. In order to suppress the first two steps, two kinds of semiconductors with different gaps have been used, for example, SnO_2/TiO_2 [7–9], TiO_2/Nb_2O_5 [10] and ZnO/SnO_2 [11,12]. As a result, energy barriers formed at the interface of the different semiconductors layers, which reduced the recombination of the photo-induced electrons and the holes.

In this paper, the mixed suspension of TiO_2 and SnO_2 was used to prepare the SnO_2/TiO_2 composite electrodes. Mercurochrome, whose molecular structure was present in Scheme 1, was used as sensitizer. The photocurrent responses of the mercurochrome-sensitized SnO_2/TiO_2 composite electrodes have been studied. At a specific mixed ratio, the sensitized electrode generated a maximal photocurrent. Spectro-electrochemistry of the SnO_2/TiO_2 composite electrodes was used to explain the formation of the energy barriers between SnO_2 and TiO_2. The model of the photo-induced electrons transport in the sensitized composite electrodes was established according to the experimental data.

2. Experiment section

2.1. Preparation of the mercurochrome-sensitized SnO_2/TiO_2 composite electrodes

TiO_2 (P25) was purchased from Degussa Corp, which is a mixture of anatase and rutile TiO_2. SnO_2 powders were synthesized according to the reference [13]. Briefly, the pH value of 0.5 mol/l solution of $SnCl_4{\cdot}5H_2O$ (Beijing Chemical Co.) was adjusted to 1.0 by potassium hydroxide (Beijing

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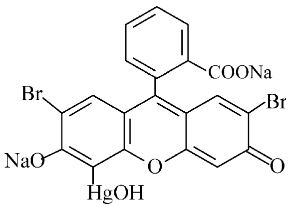


Scheme 1. The molecular structure of the mercurochrome molecule.

Chemical Co.). The solution was put into sealed hyperbaric vessel cushioned with polytetra-flurethylene, and was kept at 180 °C for 2 h. After cooled naturally to room temperature, the powders were obtained by centrifugation. Before used to prepare electrode, the powers were sintered at 500 °C for 2 h. The sizes of TiO_2 and SnO_2 particles were 30 and 11 nm, respectively, calculated by XRD.

In this paper, we have prepared five groups of oxide semiconductor electrodes, in which the mixed mass ratios of TiO_2 to SnO_2 were 1:0 (one-component TiO_2), 2:1, 1:1, 1:2, 0:1 (one-component SnO_2), respectively. The suspension was obtained by adding TiO_2 and SnO_2 powder to ethanol (Beijing Chemical Co.) and stirred for 2–3 h. The total solid concentration of the suspension was 20 wt.%. A layer of adhesive tape (about 50 μm) was stuck to the four edges of the conducting glass (ITO, 200 Ω/□) and an area of 2.3 cm × 0.8 cm was enclosed. The thickness of the film was controlled by the tape. The electrode was prepared by a new, simple method—compression [14]. The suspension was spread on the conducting glass by glass rod and dried in air for 30 min. A pressure of 1.25 t/cm^2 was used to press the deposited suspension layer which was placed between two planar steel plates. Between the upper steel plate and the SnO_2/TiO_2 film, a slice of glass was placed to prevent adhesion. Then the electrode was sintered at 450 °C for 10 min. After naturally cooled to room temperature, the electrode was immersed in a 0.5 mM ethanolic solution of mercurochrome (Acros) for 12 h, and the mercurochrome-sensitized SnO_2/TiO_2 composite electrode was obtained.

2.2. Characterization

XRD patterns were obtained with a Rigaku D/max γA X-ray diffractometer, Cu $K\alpha = 0.15418$ nm. Thickness of the oxide semiconductor film was measured using a surface profile measuring system (DEKTAK). The electrochemical and photoelectrochemical measurements were performed in a three-electrode single-compartment cell. Potential control was provided by an EG&G Princeton Applied Research Scanning potentiostat/galvanostat. The reference electrode was the saturated calomel electrode (SCE), and a Pt slice served as the counter electrode. For the measurements of the photocurrent, the mercurochrome-sensitized SnO_2/TiO_2 composite electrode served as the working electrode. A solution of 0.3 M LiI (Acros)/0.03 M I_2 (Beijing Chemical Co.) in acetonitrile (Shanghai Chemical Co.) was used as electrolyte. The light source was 400 W Xe lamp. The 522 nm monochromatic light obtained with an optical filter was used as incident light. Its intensity was estimated with a radiometer (Photo-electronic Instrument Factory attached to Beijing Normal University). In the spectro-electrochemical (SEC) measurement, a homemade cell was incorporated into the sample compartment of the cary100 UV-Vis spectrophotometer (Varian Corp). The SnO_2/TiO_2 composite electrode served as the working electrode. The electrolyte was 0.1 M $HClO_4$ (Tianjin Dongfang Chemical Co.). Before experiment, the electrolyte was bubbled for 20 min with high-pure N_2. The cyclic voltammograms of mercurochrome were

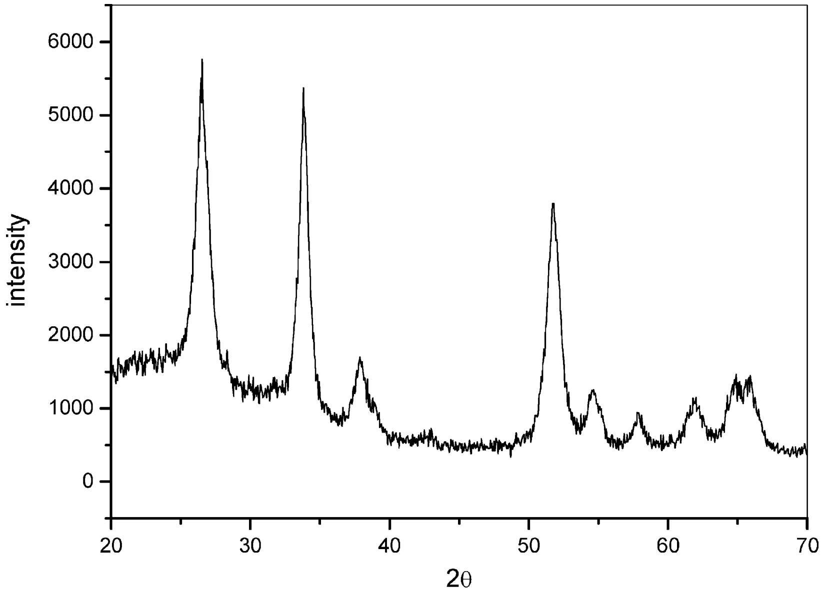


Fig. 1. XRD patterns of SnO_2 particles after sintered at 500 °C for 2 h.

recorded at a Pt slice electrode in the H_2O solvent containing 0.1 M Na_2SO_4, which is redox passive in our scan region.

3. Results and discussion

3.1. *The photocurrent responses of the different mercurochrome-sensitized TiO_2/SnO_2 composite electrodes (MSC-electrodes)*

Fig. 1 indicated that the obtained particles were tetragonal SnO_2. The strong diffraction peaks originated from (1 1 0), (1 0 1), (2 1 1) crystal planes, respectively (JCPDS, 21-1250). Fig. 2 shows the UV-Vis absorption spectra of the mercurochrome in ethanol and the mercurochrome-sensitized TiO_2/SnO_2 composite electrode. The absorption peak at 517 nm was attributed to the absorption of the monomer. The shoulder peak at 484 nm was the absorption of the H-aggregates [2,15]. The scatter of the mercurochrome-sensitized composite electrode was strong.

The HOMO level of mercurochrome was about 0.96 V (versus NHE) determined from the half-wave potential ($E_{1/2}$) of the cyclic voltammogram. The HOMO-LUMO transition energy (E_g) is 2.28 eV assessed from the

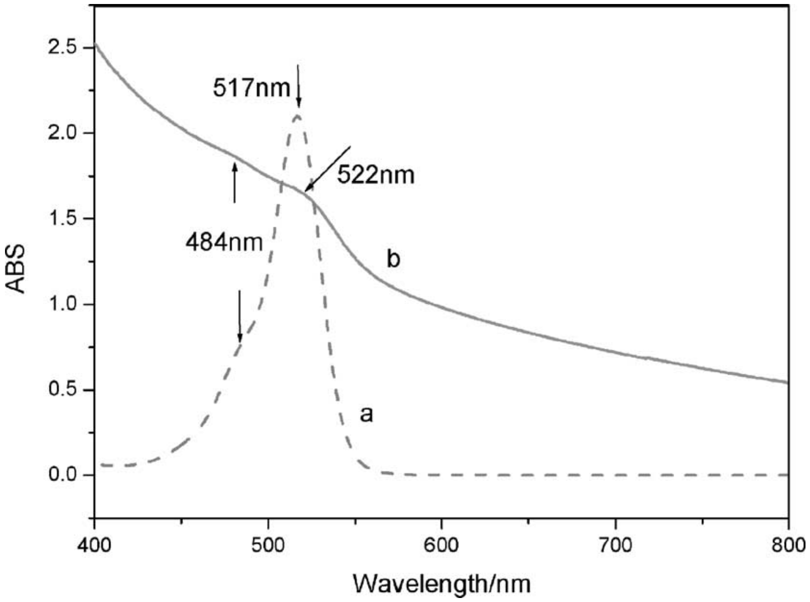


Fig. 2. The UV-Vis absorption spectra of (a) the mercurochrome in ethanol (0.1 mmol) and (b) the mercurochrome-sensitized TiO_2/SnO_2 composite electrode.

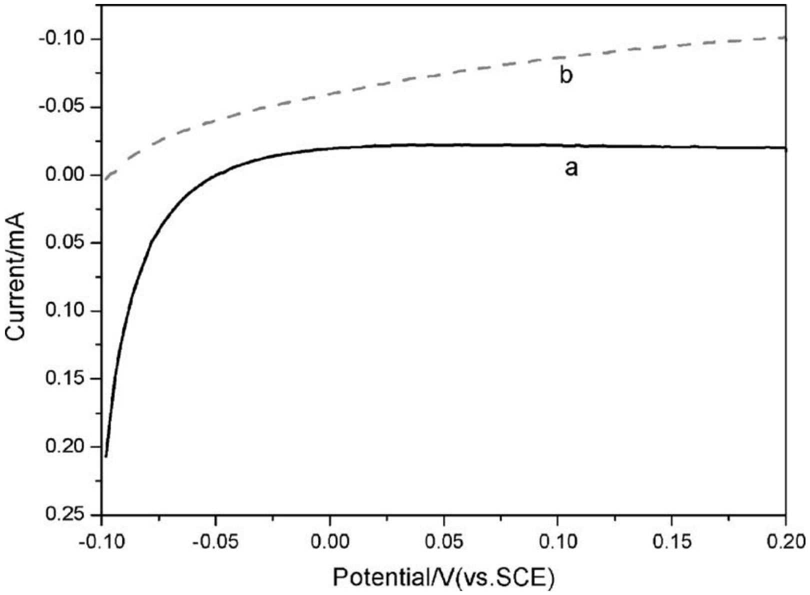


Fig. 3. The linear scan curve of the MSC-electrode consisting of 50% TiO_2 content and 50% SnO_2 content at (a) dark and (b) at 522 nm monochromatic light.

absorption onset of mercurochrome (545 nm). So, the LUMO level is about −1.32 V [16]. The conduction band potentials of TiO_2 and SnO_2 are −0.2 and 0.5 V [17] (versus NHE) at pH = 1, respectively. Levy et al. [18] investigated the photogenerated charge transfer in a double-layer TiO_2/SnO_2 heterostructured film prepared from a colloidal suspension of TiO_2 deposited on a transparent layer of F-doped SnO_2 on glass. According to their diagram, the energy bands of TiO_2 and SnO_2 would bend downward and bend upward, respectively. This will generate energy barriers between TiO_2 and SnO_2. Fig. 3 shows the linear scan curves of the MSC-electrode consisting of 50% TiO_2 content and 50% SnO_2 content (TiO_2:SnO_2 = 1:1) at dark and at 522 nm monochromatic light. From the figure, we could found that the photocurrent increased when the applied potential became positive. When the potential exceeded 0.1 V (versus SCE), the photocurrent was almost steady.

Table 1

The preparation conditions and the IPCE of the five MSC-electrodes at 0.1 V (vs. SCE) potential

Electrode no.	TiO_2:SnO_2[a] (mass ratio)	I_{ph}[b] (μA/cm^2)	IPCE (%)
MSC-E1	1:0[c]	53.6	10.7
MSC-E2	2:1	43.5	8.7
MSC-E3	1:1	70.2	14.0
MSC-E4	1:2	62.9	12.6
MSC-E5	0:1[d]	58.7	11.7

The incident light was 522 nm monochromatic light and its intensity was 12 W/m^2. The thickness of the oxide semiconductor film was about 7.5 μm. The effective area of every electrode was 1.04 cm^2.

[a] The mass ratio of TiO_2 to SnO_2.

[b] The average value of two same MSC-electrodes.

[c] The one-component TiO_2 electrode.

[d] The one-component SnO_2 electrode.

The preparation conditions and the IPCE of the five MSC-electrodes at 0.1 V (versus SCE) potential are showed in Table 1. These electrodes were denoted MSC-E1, MSC-E2, MSC-E3, MSC-E4, MSC-E5 (see the Table 1), respectively. Fig. 4 shows the transient photocurrent responses of the five MSC-electrodes. Among the five MSC-electrodes, MSC-E3 with TiO_2:SnO_2 = 1:1 had the maximal photocurrent. When the mixed ratio of TiO_2 to SnO_2 was 2:1 (MSC-E2), the photocurrent was minimal, which was even less than that of one-component TiO_2 (MSC-E1). The amount of the dye adsorbed by TiO_2 and SnO_2 may be different, because of their different surface properties. The surface of SnO_2 is more acidic, whose isoelectric point is at pH 4–5 as compared to pH 6.2 for TiO_2 (anatase) [19,20]. The amount of the dye adsorbed by MSC-E1 or by MSC-E2 should be the most. But neither the MSC-E1, nor the MSC-E5 showed the maximal photocurrent. So, it was the energy barriers, not the difference in the amount of the dye that played an important role on the photocurrent of the mercurochrome-sensitized composite electrodes. In the MSC-electrodes, the following processes may occur when the mercurochrome (Mer) molecules were excited (Mer + hv → Mer*):

(1) The photo-induced electrons were injected to TiO_2 from Mer*, and then transported to the outer circuit: Mer* + TiO_2 → Mer(h) + TiO_2 (e).
(2) The photo-induced electrons were injected to SnO_2 from Mer*, and then transported to the outer circuit: Mer* + SnO_2 → Mer (h) + SnO_2 (e).
(3) The photo-induced electrons in the conduction band of TiO_2, which were injected from Mer*, transferred to the conduction band of SnO_2 assisted by the energy

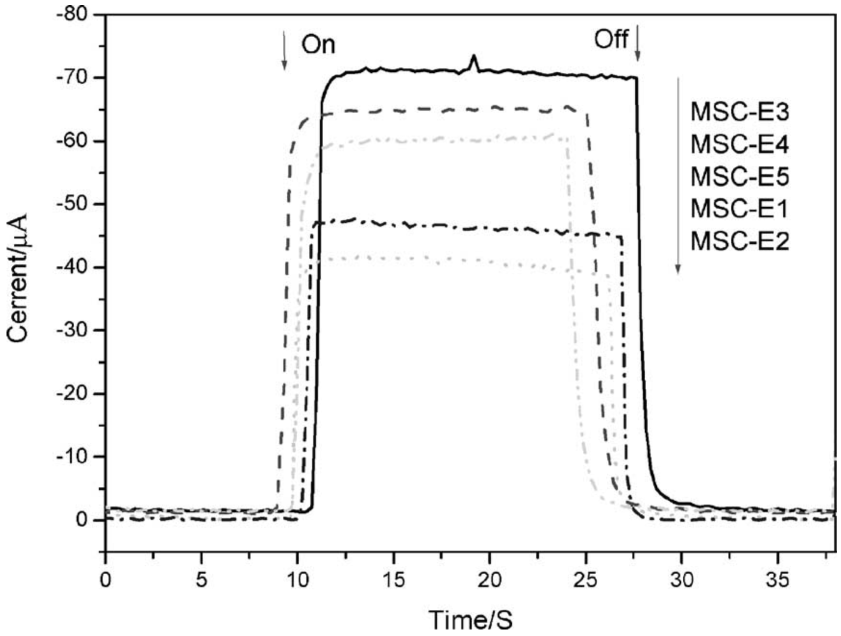
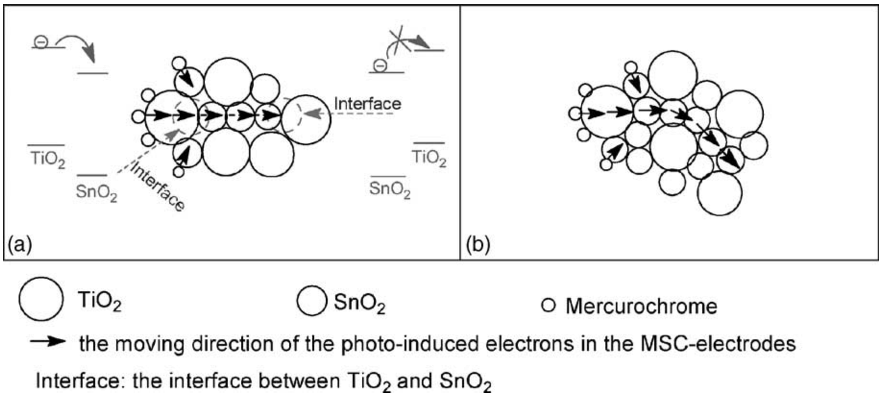


Fig. 4. The transient photocurrent responses of the five MSC-electrodes.



Scheme 2. The possible model of photo-induced electrons transport in the MSC-electrodes with different mixed ratio: (a) the high mixed ratio of TiO_2 to SnO_2; (b) the low mixed ratio of TiO_2 to SnO_2.

barriers, and then transported to the outer circuit: TiO_2 (e) + SnO_2 → TiO_2 + SnO_2 (e).

(4) The photo-induced electrons in the lower conduction band of SnO_2, which were injected from Mer* or from TiO_2, cannot migrate to the higher conduction band of TiO_2. This process increased the recombination of the photo-induced electrons and holes.

So, in the MSC-electrodes, the energy barriers have double functions. On the one hand, they could reduce the recombination between the photo-induced electrons and the holes (process (3)). On the other hand, they could also block the transport of the photo-induced electrons (process (4)), which increased the recombination. In terms of microscope, the mixture of TiO_2 and SnO_2 will generate a large number of energy barriers. At different mixed ratio, the energy barriers may show different functions. Scheme 2 shows the possible model of the photo-induced electrons transport in the MSC-electrodes with different mixed ratio of TiO_2 to SnO_2. At a high mixed ratio (TiO_2:SnO_2), the MSC-electrode was mainly composed of the interconnected TiO_2 particles, and the SnO_2 particles were isolated one another by TiO_2 particles. The transport of the photo-induced electrons in the conduction band of SnO_2, which were injected from the conduction band of TiO_2 or from the excited mercurochrome, was blocked when they met the TiO_2 particles. This meant that the energy barriers between TiO_2 and SnO_2 would increase the recombination between the photo-induced electrons and the holes. When the mixed ratio was low, the MSC-electrodes comprised mainly of the interconnected SnO_2 particles. The photo-induced electrons in the conduction band of SnO_2, despite that they were injected from the excited mercurochrome or from the conduction band of the TiO_2 particles, were all able to transport to the outer circuit. The energy barriers between TiO_2 and SnO_2 could suppress the recombination of the photo-induced

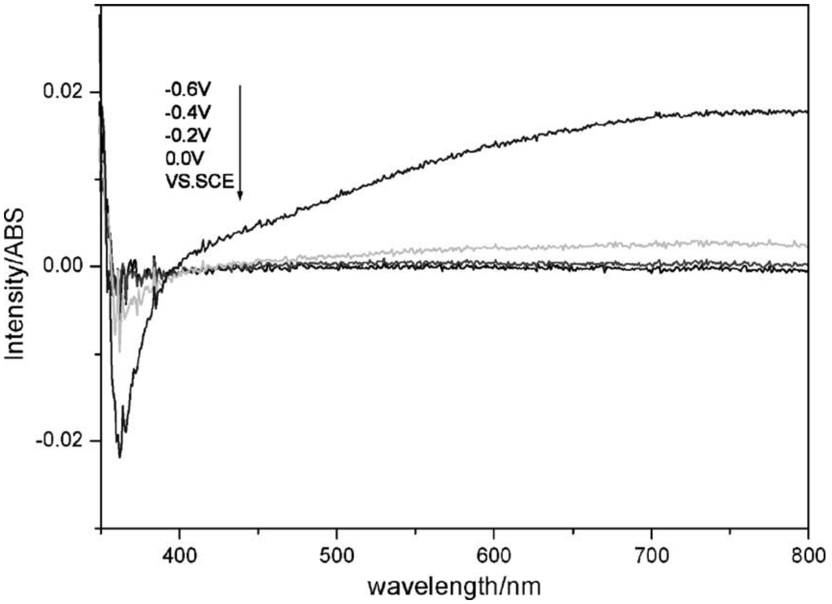


Fig. 5. The absorption changes of the C-E1 at 0, −0.2, −0.4 and −0.6 V (vs. SCE), respectively.

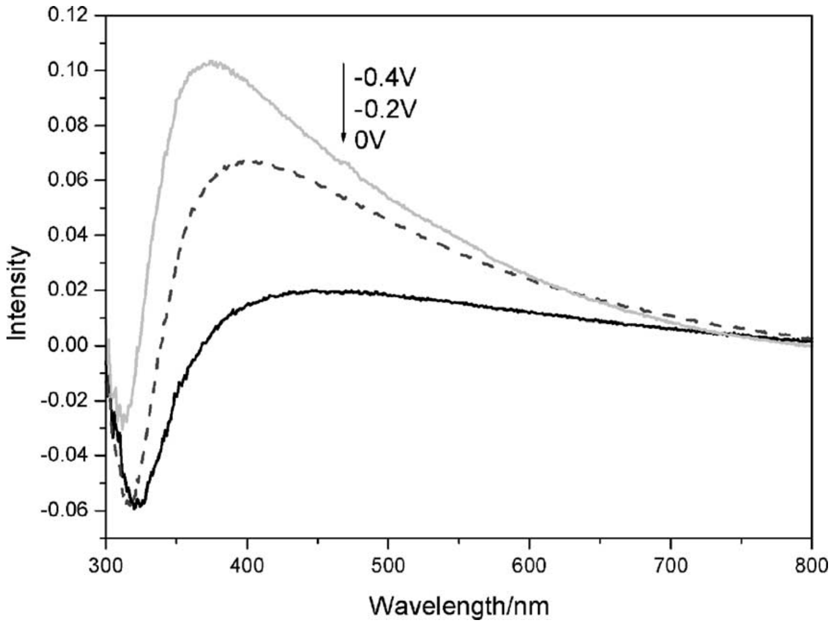


Fig. 6. The absorption changes of the C-E5 at 0, −0.2 and −0.4 (vs. SCE), respectively.

electrons in the conduction of the TiO_2 particles with the holes. Hence, the appropriate mixed ratio in the MSC-electrodes was so vital that the energy barriers did not increase the charge recombination.

3.2. Spectro-electrochemical measurements of the different TiO_2/SnO_2 composite electrodes (C-electrodes)

Corresponding to the mercurochrome-sensitized TiO_2/SnO_2 composite electrodes, the TiO_2/SnO_2 composite electrodes were denoted C-E1, C-E2, C-E3, C-E4, and C-E5. The spectro-electrochemical measurement of C-E1, C-E5 and C-E3 were performed. SEC measurement was used to probe the band structure of the transparent nanocrystalline semiconductor films such as TiO_2 and ZnO in different solvent [21,22].

For every electrode, the absorption change at a certain applied potential was obtained by subtracting the absorption at no potential from the absorption at applied potential. This was realized by Origin Software. Figs. 5 and 6 show the absorption changes of the TiO_2 electrode (C-E1) and

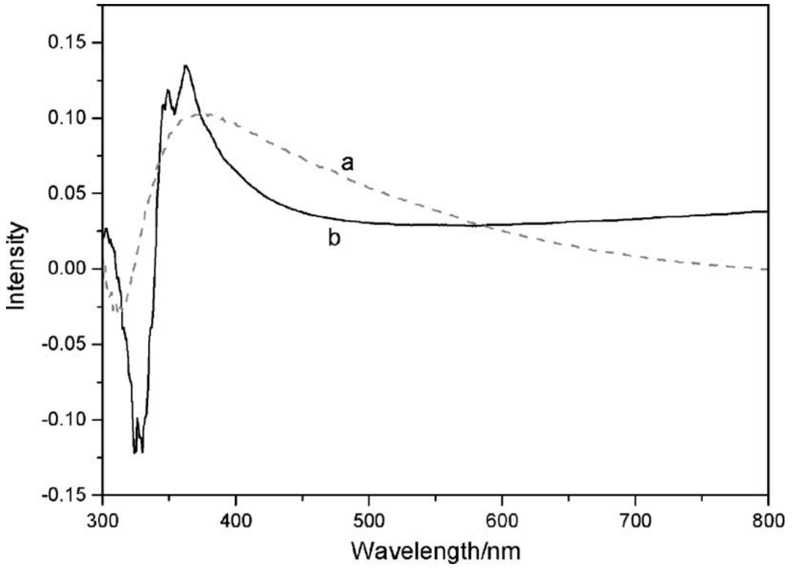
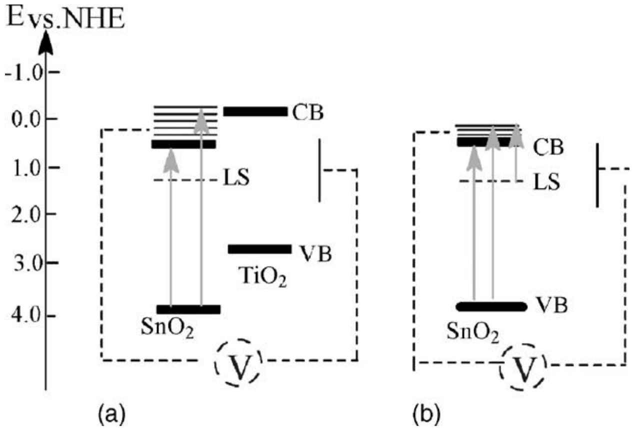


Fig. 7. The absorption changes of the C-E5 (a) and (b) C-E3 at −0.4 V bias (vs. SCE).

SnO_2 electrode (C-E5) at various potential, respectively. Fig. 7 shows the absorption changes of the (a) C-E5 and (b) C-E3 at −0.4 V bias (versus SCE). When a bias more negative than the flat potential of the semiconductor is applied to the semiconductor film, the concentration of the electrons in conduction band increases, which results in free carrier absorption, intraband absorption and absorption by localized states [23,24]. When the −0.4 V potential was applied to the C-E1 (one-component TiO_2), because the potential of the conduction band of TiO_2 equals to about −0.4 V (versus SCE), the electron concentration in conduction band of TiO_2 changed a little, so the absorption increase above 400 nm and the spectral bleach in the band gap region below 400 nm were not obvious. (The obvious spectral signals were obtained at a more negative potential, for example, at −0.6 V). While for the C-E5 and C-E3, the −0.4 V potential was more negative than the potential of the conduction band of SnO_2, the applied potential induced an obvious absorption increase at longer wavelength and bleach at shorter wavelength. But, there had obvious differences between curve (a) and curve (b). The curve (b) (C-E3) showed the characters of SnO_2; obvious absorption increase above 337 nm and bleach at 328 nm were observed. Based on the position of the bleaching peak (at 328 nm), we could calculate the band gap of SnO_2 which was 3.78 eV, which correlated well with the [17]. At the bleaching region, the intensity of the bleaching signal of C-E3 was four times as much as that of the C-E5, and the bleaching peak of C-E3 was wider than that of the C-E5. When the same potential was applied to the C-E3 and the C-E5, more electrons could accumulate in the conduction band of SnO_2 in the C-E3 because of the energy barrier formed by TiO_2, which blocked the electrons to react with the electrolyte (see Scheme 3 [10]). Based on the difference in the bleaching width, we calculated approximately 80 mV difference between the highest occupied orbit of the C-E3 and C-E5. Between 337 and 800 nm, the absorption change of the C-E3 did not always exceed that of the C-E5, which may indicate that the interfusion of TiO_2 affected the localized states of SnO_2. The localized state of Sn^{3+} has been characterized by Liu et al. [13].



Scheme 3. The explanation of the absorption changes in (a) C-E3 and (b) C-E5; in (a), more electrons could accumulate in the conduction band of SnO_2 because of the energy barriers formed by TiO_2, which suppress the electrons to react with the electrolyte. This induced strong bleaching peak at 337 nm and absorption increase above 580 nm. The decreased absorption of (a) between 370 and 580 nm indicated that the interfusion of TiO_2 may affect the localized state (Sn^{3+}) of SnO_2. VB: valence band, CB: conduction band, LS: localized state.

4. Conclusions

The photocurrent responses of the mercurochrome-sensitized TiO_2/SnO_2 composite electrodes have been studied. The optimal mixed ratio for the generation of the photocurrent was 1:1, which formed effective energy barrier between TiO_2 and SnO_2 particles. The possible process of photo-induced electron transport was established. Spectro-electrochemical measurements of the TiO_2/SnO_2 composite electrode provided new evidence for the existence of the energy barriers between TiO_2 and SnO_2. The energy barriers suppressed the recombination of the photo-induced electrons in the conduction band of the TiO_2 and the holes. So, the IPCE of the MSC-E3 increased.

Acknowledgements

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