[Communication]

Photoelectrochemical Properties of the SnO₂ Nanoporous Film Sensitized by Cyanine Dye*

Zhang Li**　　Gao Enqin　　Yang Maizhi　　Qiao Xuebin

Hao Yanzhong　　Cai Shengmin

(College of Chemistry and Molecular Engineering, Peking University, Beijing　　100871)

Meng Fanshun　　Tian He

(Institute of Fine Chemicals, East China University of Science & Technology, Shanghai　　200237)

A new cyanine dye (abbr. PMC in the following) was synthesized and was used to sensitize SnO₂ nanostructured porous film studied in this article. The structure of PMC determined by NMR and element analytical technique is
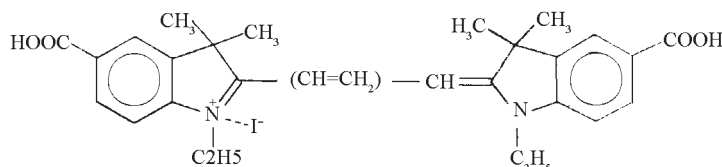
The photocurrent action spectra, the photocurrent-potential curves, the photocurrent transients and the UV-Vis absorption curves were measured with the unsensitized and sensitized elelctrodes. The positions of electron ground state and electron excited state of PMC were determined by cyclic voltammetry and UV-Vis spectroscopy. Subsequently, the mechanism of photo-induced current was studied preliminarily.

1　Experimentals

1. 1　Materials

The photoelectrochemical anodes were prepared on the conducting indium tin oxide coated glasses （8Ω/□, denoted hereafter as OTE）. All the chemical agents were A. R. grade

293

without further purification. The solutions were prepared with deionized water. All experiments were carried out at room temperature $(18 \pm 1℃)$.

1.2   Preparation of SnO₂ colloidal solution and working electrodes

SnO₂ colloidal solution was prepared as described in reference[1] . The morphology of SnO₂ particle was determined by AFM and TEM. SnO₂ particles are round in form and about 5 nm in diameter. OTE/SnO₂ electrode was prepared following the preparation process of OTE/TiO₂ electrode described in reference[2] . Preparation of OTE/ SnO₂/PMC electrode was carried out in the following way. The OTE/ SnO₂ electrode was immersed in 0.5 mmol·L^{-1} PMC alcohol solution for 24 h and then was dried in air.

1.3   Photoelectrochemical experiment

Two types of photoelectrochemical cells were used. Three-electrode cells with a quartz window were used when measuring photocurrent under potentiostatic or potentiodynamic scanning condition. Working electrodes were OTE/SnO₂ and OTE/SnO₂/PMC. Auxiliary electrode was Pt wire and reference electrode was saturated calomel electrode (SCE). All the potentials measured in this article were relative to SCE unless otherwise stated. Supporting electrolyte was 0.1 mol·L^{-1} NaSCN in a buffer solution of 0.2 mol·L^{-1} potassium biphthalate and 0.2 mol·L^{-1}NaOH solution was added to adjust the pH to 4.0.

Two-electrode sandwich cells were prepared by placing the counter electrode, a Pt plate, directly on top of OTE/SnO₂ or OTE/SnO₂/PMC and were used to measure IPCE (incident photon-to-current conversion efficiency) . The redox electrolyte, composed of 0.3 mol·L^{-1} LiI and 0.03 mol·L^{-1} I₂ in propylene carbonate solution, was introduced in between the two electrodes.

For the three-electrode system, the light source was a 200 W Xe lamp in combination with agrating monochromator. The illuminated area of working electrode was 0.5 cm². A high-pass filter (> 350 nm) was used to remove ultraviolet radiation in the light path. A potentiostat(Model 173 EG&G PARC) served to control the potential. An *X-Y* recorder(TYPE-3036, Sichuan Instrument Factory) was used for recording photocurrents which in this paper were all steady state values. The intensities of the monochromatic light were measured with a calibrated radiometer/photometer (Model 550-1, EG&G PARC) . The photocurrent spectra were normalized after subtracting the transmittance of the OTE.

The photocurrent-voltage curve was measured with the two-electrode system under illumination of a Xe lamp with a light intensity of 53 mW·cm^{-2}. The illuminated area of working electrode was 0.7 cm². The transmittance of OTE was 50% .

1.4   Physical property

Absorption spectra of the working electrodes referring to OTE were recorded on a UV-Vis spectrometer (Model Du-7 BECKMAN).
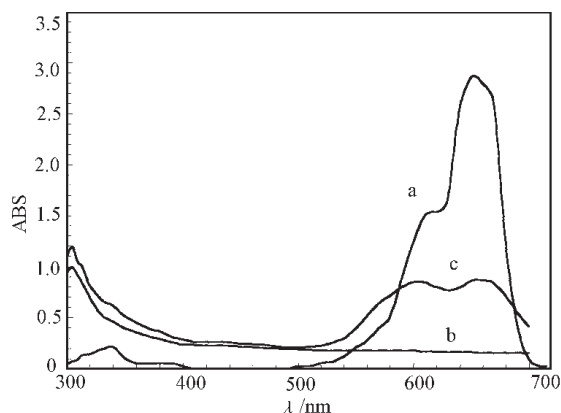
Fig. 1 Absorption spectra of cyanine dye (PMC) in absolute ethanol solution with ethanol asreference (a), OTE/SnO₂ (b) and OTE/SnO₂/PMC (c) with OTE as reference
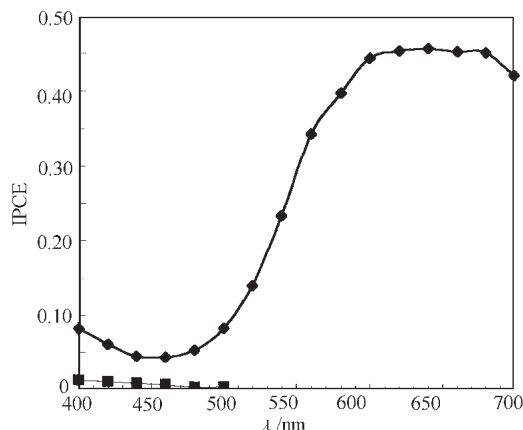
Fig. 2 Photocurrent action spectra of OTE/SnO₂ nanostructured porous films(a) and of OTE/SnO₂/PMC nanostructured porous films(b) The counter electrode was Pt sheet of 1cm². The electrolyte contained 0.3 mol·dm⁻³ LiI and 0.03 dm⁻³ I₂ solved in PC (1,2-propylene carbonate)

2   Results of the Experiment

2.1   The UV-Vis absorption spectra of PMC in ethanol

Fig. 1 shows that PMC in ethanol has a strong optical absorption band in the visible region, from 550 nm to 710 nm. In the UV region, from 300 nm to 400 nm, a weak absorption band is observed for PMC.

### 2.2   The absorption spectra of the working electrode

In order to verify whether PMC was absorbed on SnO₂ nano-particles, the absorption spectra of sensitized and unsensitized electrodes with OTE as the reference were measured (Fig. 1). The spectra shows that the unsensitized electrode has only a strong absorption peak in UV region. However, sensitized electrode has strong absorption bands in both UV and visible region. By comparing with the absorption spectrum of PMC solution as shown in Fig. 1(a), the broad absorption band from 550 nm to 700 nm corresponds to the absorption of the PMC. This indicates that the PMC dye has been absorbed onto the nano-porous OTE/SnO₂ electrode effectively.

2.3   Photoelectrochemical behaviors

Photocurrent spectra of OTE/SnO₂, OTE/SnO₂/PMC electrodes in the range of 400 − 700 nm were recorded with a two-electrode system(Fig. 2). The photocurrent of OTE/SnO₂ decreased to almost zero around 500 nm. The photocurrent generated by the light with wavelength higher than 400 nm may be related to the surface states or inner localized states of SnO₂ nanostructured film. The surface states or inner localized states of SnO₂ nanostructured film may absorb photon of energy smaller than its energy gap and make a contribution to produce photocurrent in this wavelength region. Having been sensitized by PMC, the photo response region was broadened to visible and near

infrared light region, especially in the wavelength region from 550 to 700nm. This strong photocurrent peak matches the light absorption band of the sensitized electrode. The IPCE[3] was calculated as the following:

$$IPCE = \frac{1241 \cdot \text{photocurrent density} \left(\mu A \cdot cm^{-2}\right) \cdot 100\%}{\lambda \left(nm\right) \cdot \text{photon flux} \left(\mu W \cdot cm^{-2}\right)}$$
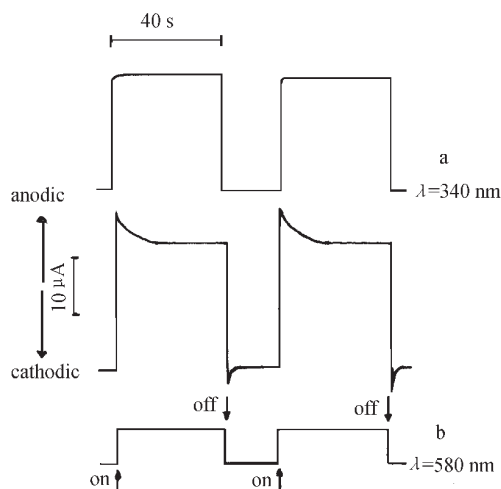
Fig. 3　**Photocurrent transients of OTE/SnO₂ illuminated at 340 nm (a) and OTE/SnO₂/PMC illuminated at 580nm (b)**
Electrolyte: 0.1 mol·L⁻¹ SCN⁻, pH = 4.0. Electrodepotential: 0.3 V(vs SCE)

The maximum of IPCE was 45.7% for sensitized electrode. It has been proved elsewhere that the OTE has no photo-response from 400 nm to 700 nm.

In order to study the stability and the photo-induced charge-transfer process of the photoanodeat constant potential, the photocurrent transients generated by monochromatic light were measuredin a three-electrode cell with SnO_2 nanostructured porous electrode as anode (Fig. 3). Fig. 3(a) shows the photocurrent transients of unsensitized OTE/SnO₂ electrode induced by the light of 340 nm. It indicates that when the OTE/SnO₂ electrode was illuminated by the photons with energy greater than the energy gap of SnO_2 (3.5 eV) [4,5], the holes could be produced in the valence band of SnO_2 and then reacted with the reductive agent at the interface of electrode/solution, consequently the photocurrent was generated. During illumination on the OTE/SnO₂ electrode, the intensity of photocurrent did not decayed. At the moment of turning off the light, the photocurrent decreased to its original value. Fig. 2 shows the photocurrent transients of the OTE/SnO₂/PMC electrode illuminated by the light of 580 nm whose energy was lower than the energy band gap (abbr. E_g) of SnO_2 but equal to its characteristic absorption wavelength. Illuminating the electrode with such light an anodic photocurrent was generated. The current decayed with time to a steady value. At the moment the light was shut down, a cathodic current transient occurred immediately and decayed to zero with time.

In the range of -0.4 to 1.0 V and under illumination with 580 nm light, the photocurrent of OTE/SnO₂/PMC electrode was measured as a function of potential(Fig. 4) . Fig. 4 shows the photocurrent increased when the potential increased. In the range of -0.4 to 0 V, the photocurrent increased slowly. When the potential was above 0 V, the photocurrent increased quickly with the potential increasing and at 0.39 V reached a saturate value. The photocurrent decreased slightly when the potential was above 1.0 V. The photon energy of 580 nm light was lower than the E_g of SnO_2, and situated in the optical absorption range of PMC. The photocurrent was therefore caused by the excitation of PMC. The potential was not increased any more to prevent the indium-tin oxide conductive layer from decomposing by high potential.

3   Results and Discussion

The energy level of the excited state of PMC was evaluated to be 0. 91 V （ *vs.* NHE） according to the optical absorption threshold and the result of cyclic voltammogram of PMC. The conduction band position of SnO_2 is 0. 23 V （ *vs.* NHE, extrapolated value at pH 4. 0 according to Refs. [4,5]）which is lower than the excited state energy level of PMC.   It is evident that the excited level of PMC matches the conducting band position of SnO_2 nanometer particles. The photoresponse range of nanometer electrode was enlarged to visible region by electron injection from excitedsen sitizers into the conduction band of SnO_2.

The performance of solar cell made from $OTE/SnO_2/PMC$ photoanode was measured and the short-circuit-photocurrent i_{sc} was 0. 50 mA·cm^{-2} , open-circuit voltage V_{oc} was 0. 42 V, and the light energy to electricity conversion efficiency was 0. 37% .

Fig. 3(b) indicates that photoelectrons injected into conduction band of SnO_2 could be caughtby oxidied sensitizer or oxidized product $(SCN)_2{}^-$ before flowing to the external circuit. It was the so-called recombination of photoelectrons, which resulted in the photocurrent decay with increasing irradiation time and the cathodic current transients in the moment of light shut off. As a result, the recombination of photoelectrons reduced the photo-to-current conversion efficiency. The study of the stability of PMC is still going on.
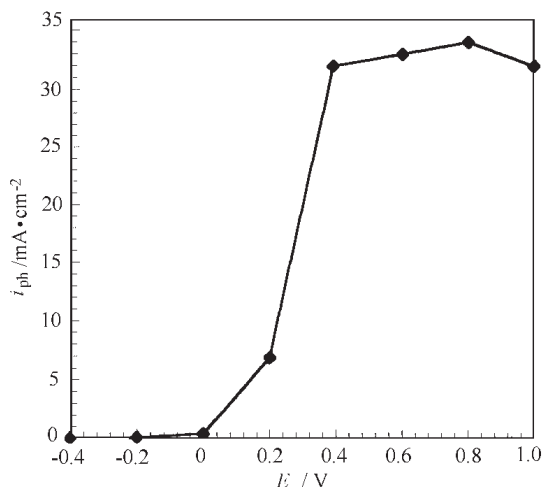

Fig. 4   Photocurrent-potential curve of $OTE/SnO_2/PMC$ electrode illuminated at 580 nm

The photo-to-current conversion efficiency of the sensitized semiconductor electrode related to the external potential applied on it. Variation of external potential could shift[6] the conduction band of SnO_2 nanocrystalline electrode and therefore the difference between the conduction band of SnO_2 and the excited state energy level of PMC was changed. Subsequently, the driving force of charge transferring from excited sensitizers to SnO_2 conduction band was changed. This was verified by the result of photocurrent *versus* potential shown in Fig. 4. The decrease of photocurrent in the potential range higher than 1. 0 V possibly was caused by the oxidization of PMC.

4   Conclusions

The new cyanide dye with carboxyl groups is a sort of hopeful dye for sensitizing nanostructured semiconductor porous electrode. PMC broadened the range of photoresponse of SnO_2 nanostructured electrode into visible and near infrared area. It has a good response in the range of

550 – 700 nm where photocurrent intensity and photo-to-current conversion efficiency increased significantly. The maximum IPCE of OTE／SnO$_2$／PMC is 45.7%.

References

1　Cheng Humin(程虎民), Ma Jiming(马季铭), Zhao Zhenguo(赵振国), *et al. Gaodeng Xuexiao Huaxue Xuebao*(高等学校化学学报), **1996, 17**: 833

2　Li Weihua(李卫华), Hao Yanzhong(郝彦忠), Qiao Xuebin(乔学斌), *et al. Wuli Huaxue Xuebao*(物理化学学报), **1998, 14**(9): 841

3　Nazeeruddin M K, Kay A, Rodicio I, *et al. J. Am. Chem. Soc.*, **1993, 115**: 6382

4　Hagfeldt A, Gratzel M. *Chem. Rev.*, **1995, 95:** 49

5　Memming R. *Electrochemica Acta*, **1980, 23:** 77

6　Hao Yanzhong(郝彦忠), Yang Maizhi(杨迈之), Cai Shengmin(蔡生民). *Wuli Huaxue Xuebao*(物理化学学报), **1998, 14**(4): 309

PMC 敏化 SnO$_2$ 纳米结构多孔膜电极的光电化学特性

张 莉　高恩勤　杨迈之　乔学斌　郝彦忠　蔡生民
(北京大学化学与分子工程学院,北京　100871)
孟凡顺　田 禾
(华东理工大学精细化工学院,上海　200237)

摘要　研究了五甲川菁（PMC）敏化 SnO$_2$ 纳米结构电极的光电化学行为. 结合循环伏安曲线及五甲川菁的光吸收阈值,初步确定了五甲川菁染料电子基态和激发态能级. 结果表明,五甲川菁染料电子激发态能级能与 SnO$_2$ 纳米粒子导带边位置相匹配,因而使用该染料敏化可以显著地提高 SnO$_2$ 纳米结构电极的光电流,使 SnO$_2$ 纳米结构电极吸收波长红移至可见光区和近红外区,光电转换效率(IPCE)得到明显改善,其值最高可达 45.7%.

关键词:　染料敏化,　SnO$_2$ 纳米结构多孔膜电极,　光电化学,　五甲川菁
学科代码: B030604