



Short communication

Water phase sensitization of nanoporous TiO₂ film

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1. Introduction

There has recently been much research on solar-to-electrical energy conversion with dye-sensitized nanoporous TiO₂ photoelectrochemical cells [1–5]. Grätzel and co-workers have reported a photoelectrochemical solar cell showing excellent energy conversion efficiency (around 10%) based on a nanoporous TiO₂ semiconductor electrode sensitized with *cis*-bis(isothiocyanato)bis(4,4'-dicarboxyl-2,2'-bipyridine)ruthenium(II) (Ru(dcbpy)₂(NCS)₂) [1]. However, the system shows high conversion efficiency only in an organic medium, and only poor characteristics are obtained when using an aqueous medium. One reason for the poor performance is attributable to detachment of the dye in aqueous electrolyte solution. We have been investigating sensitization of a nanoporous TiO₂ film in water medium in order to utilize it for water cleavage [6]. In this work, we have succeeded in sensitizing nanoporous TiO₂ thin films in the aqueous phase in the presence of the Sn^{2+/4+} redox couple, and the fundamental behavior is reported.

2. Experimental

A nanoporous TiO₂ film was prepared by coating TiO₂ (P-25, Nippon Aerosil Co. Ltd.) paste on a transparent indium tin oxide (ITO) electrode by spin coating (at 2000 rpm) three or four times and calcining in air at 450 °C for 30 min [7]. The final film thickness was 10 μm. A coating of the TiO₂ film with dye (bis(2,2'-bipyridine)(4,4'-dicarboxyl-2,2'-bipyridine)-ruthenium(II) (Ru(bpy)₂(dcbpy) (Figure 1) was achieved by soaking the TiO₂ film in an aqueous solution of 2 × 10⁻⁴ M Ru(bpy)₂(dcbpy). The amount of absorbed dye was determined by measuring its absorption spectrum at 458 nm (ε = 1.5 × 10⁵) before and after adsorption. The photoelectrochemical cell comprised ITO|TiO₂|Ru(bpy)₂(dcbpy) as working electrode (effective area 0.8 cm²), a platinum wire as counter and a Ag|AgCl electrode as reference. These electrodes were soaked in an aqueous solution containing the metal ion

redox couple, and the photoelectrochemical measurement was carried out under argon with a potentiostat/galvanostat (Hokuto Denko, HA-310) and X-Y recorder (Rikadenki, RW-21). A Xenon lamp was used as a light source with cut off filters (Y-43 and IRA-25) to irradiate only visible light.

3. Results

Figure 2 shows photocurrent changes induced by switching the irradiation on and off by using the ITO|TiO₂|Ru(bpy)₂(dcbpy) electrode in a Sn^{2+/4+} aqueous solution at 0 V vs. Ag|AgCl. A high photocurrent of about 3 mA cm⁻² was obtained. The photocurrent gradually decreased to reach a steady state after about 30 min. and a steady state photocurrent of about 400 μA cm⁻² was obtained. Desorption of the Ru complex was negligible during the measurement. Figure 3 shows the cyclic voltammogram of the ITO|TiO₂|Ru(bpy)₂(dcbpy) electrode in a Sn^{2+/4+} aqueous solution

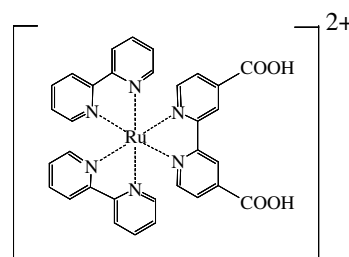


Fig. 1. The structure of Ru(bpy)₂(dcbpy).

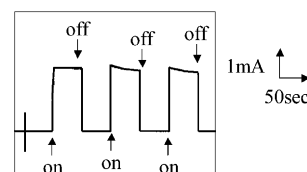


Fig. 2. Current change induced by on and off the irradiation by using ITO|TiO₂|Ru(bpy)₂(dcbpy) electrode in a Sn^{2+/4+} aqueous solution. by using three electrode system. Bias potential 0 V vs. Ag|AgCl.

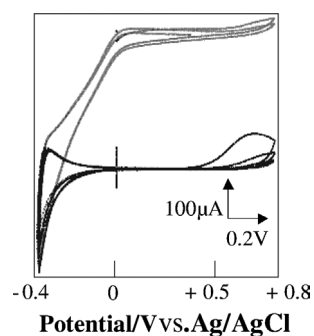


Fig. 3. Cyclic voltammogram of ITO|TiO₂|Ru(bpy)₂(dcbpy) electrode in a Sn^{2+/4+} aqueous solution using the three electrode system.

Table 1. Results of the photocurrent using various sensitizer and redox couple aqueous solutions

Sensitizer	Redox couple	Conc.	pH	Photocurrent /μA cm ⁻²
	I ⁻ /I ₃ ⁻	1/0.1 M	1.9	12.5
	Fe ^{2+/3+}	4/0.4 mM	1.8	18.8
		4/4 mM	1.5	10.0
Ru(dcbpy) ₃	Cu ⁺²⁺	0.1/0.01 M	1	244.0
		0.1/0.1 M	1	56.3
	Sn ^{2+/4+}	0.1/0.01 M	1.1	37.5 ^a
		0.1/0.1 M	0.9	325.0 ^a
Ru(bpy) ₂ (dcbpy)	Cu ⁺²⁺	0.1/0.01 M	1	68.8
		0.1/0.1 M	1	–
	Sn ^{2+/4+}	0.1/0.01 M	1.1	125.0 ^a
		1/0.1 M	0.9	406.0 ^a

^a Photocurrent after reaching a steady state in about 1 h.

after the photocurrent reached a steady state. Table 1 shows the values of the photocurrents using various redox couples and sensitizers. I⁻/I₃⁻ was the best redox couple in Grätzel's cell, but in the present system, only a small photocurrent was obtained. The photocurrent decreased to about 1/10 of the initial value for most cases, and the highest photocurrent was obtained when using the Sn^{2+/4+} redox couple. The degree and stability

of the present photocurrent is remarkable for an aqueous medium.

In order to examine the reason for the decrease in the photocurrent, a cyclic voltammogram was measured in aqueous solution containing 0.1 M KNO₃ using the ITO|TiO₂|Ru(bpy)₂(dcbpy) electrode. First, the cyclic voltammogram was measured in a 0.1 M KNO₃ aqueous solution, and then, after this electrode was exposed to irradiation for 30 min in a Sn^{2+/4+} aqueous solution, a second cyclic voltammogram was measured in aqueous solution containing 0.1 M KNO₃, where an anodic peak was observed at -0.2 V. This peak was not observed before irradiation in a Sn^{2+/4+} aqueous solution. It is suggested that Sn⁰ was adsorbed on the TiO₂ surface during the irradiation so that the Sn-modified TiO₂ provided an effective surface for photoelectrochemical response. Further work is in progress.

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