Macromol. Symp. ***186****, 177–158 (2002)*

Water Phase Sensitization of TiO_2 Particles Film by Adsorbed Polypyridine Ru Complexes

Masao Kaneko, Tadashi Moroi, Hidenobu Shiroishi*

Faculty of Science, Ibaraki University, Mito, 310-8512, Japan

Summary: Sensitization of porous TiO_2 film was achieved in water phase by monomeric as well as polymeric polypyridine Ru complexes, i.e., $Ru(bpy)_3^{2+}$, polymer-pendant $Ru(bpy)_3^{2+}$, dicarboxybipyridine Ru complex ($Ru(dcbpy)_3^{4-}$), and bipyrimidine Ru complex, to generate photocurrent. It was found that the photocurrent induced by $Ru(bpy)_3^{2+}$ is saturated with the increase of the complex concentration in water showing that adsorption of the complex onto the TiO_2 is important for the sensitization. The water insoluble poly-$Ru(bpy)_3^{2+}$ could be used as a film on the TiO_2 although the efficiency was not very good under the conditions employed. The anionic $Ru(dcbpy)_3^{4-}$ gave the best results probably because of its electrostatic adsorption onto the positively charged TiO_2.

INTRODUCTION

Artificial photosynthetic system is attracting a great deal to create energy resources from solar energy and water (Ref.1,2). Sensitization of nanosized TiO_2 films by adsorbed Ru(4,4'-dicarboxy-2,2'-bipyridine)$_2$(NCS)$_2$ gave a photoelectrochemical cell of nearly 10% conversion efficiency under AM1.5 illumination (100mWcm^{-2}) in the presence of I^-/I_3^- redox couple in an organic medium (Ref.3), which evoked great attention to convert solar energy. One of the remarkable features of this dye-sensitized solar cell is sensitization of the highly porous TiO_2 film (roughness factor is almost 1000) by condensed dye molecules.

We have been investigating construction of an artificial photosynthetic system that we proposed in 1976 (Ref.4), which consists of water oxidation catalyst, proton reduction catalyst, photoexcitation center (sensitizer), and mediator molecules connecting each unit electronically, and reporting successful achievement of each unit, i.e., water oxidation catalyst (Ref.5), proton reduction catalyst (Ref.6), electron transfer at photoexcited state metal complexes (Ref.7), and charge transport between redox molecules (Ref.7,8) by utilizing polymer matrixes involving functional metal complexes. We are now under intensive investigation to couple these units by photoinduced charge separation system, which should be established to approach the final goal of an artificial photosynthesis. In order to construct a photochemical charge

CCC 1022-1360/00/$ 17.50+.50/0

separation system, utilization of the avobe mentioned dye-sensitized TiO_2 nanoporous film in water phase instead of an organic medium is one of the promising candidates. However, the sensitization of the TiO_2 film has been possible only in an organic medium, and the efficiency decreases drastically in water phase. Alhotugh some trials have been reported (Refs.9-11) to apply this in water phase, there are still many problems to be investigated. Desorption of the dye from the TiO_2 is one of the sincerest problems when used in water phase. The rate of the electron transfer from the excited state dye to the TiO_2 phase is dependent on the electronic coupling between the sensitizer and the TiO_2 orbitals, so that adsorption of the dys onto the TiO_2 is a crucial conditon to be fulfilled.

The strategy to adopt in the present work is to affect the condensed (adsorbed) metal complex dye on the TiO_2 film as follows:

1) To use water-insoluble polymer-pendant $Ru(bpy)_3^{2+}$ sensitizer to attach the sensitizer on the TiO_2 film in water.

2) To investigate the nature of the ligand of the metal complex sensitizer to change the adsorptivity on the TiO_2.

3) To change the concentration of the water-soluble $Ru(bpy)_3^{2+}$ sensitizer to shift the adsorption equlibrium onto the TiO_2.

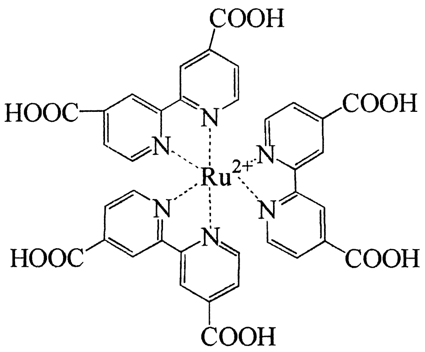
The results are reported and discussed mainly relevant to the nature of the sensitizer.

EXPERIMENTAL

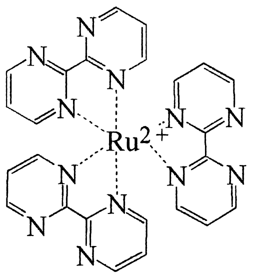
Materials

Sensitizers:

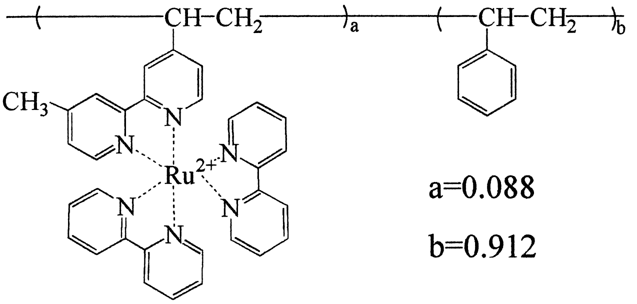
Tris(2,2'-bipyridine)rutheinum(II)dichloride (abbreviated to $Ru(bpy)_3^{2+}$) was synthesized by the reaction of $RuCl_3$ with 2,2'-bipyridine and purified as reported earlier (Ref. 12). Tris(4,4'-dicarboxy-2,2'-bipyridine)ruthienum(II) ($Ru(dcbpy)_3^{2+}$,**1**) and tris(bipyrimidine)ruthenium(II) ($Ru(bpym)_3^{2+}$,**2**)were prepared the same as the $Ru(bpy)_3^{2+}$. Polymer-pendant $Ru(bpy)_3^{2+}$, $Ru[P(St\text{-}Vbpy)](bpy)_2^{2+}$ abbreviated to Poly-$Ru(bpy)_3^{2+}$(**3**), was prepared by the reaction of copoly(styrene-4-methyl-4'-vinyl-2,2'-bipyridine) with cis-$Ru(bpy)_2Cl_2$ in xylene/n-butylalcohol=1/4(v/v) mixture under reflux (118°C)(Ref.13). The composition of the polymer is shown as **3**.



1, Ru(dcbpy)$_3^{2+}$



2, Ru(bpym)$_3$2$^+$



3, Poly-Ru(bpy)$_3^{2+}$ (Ru[PSt-Vbpy)](bpy)$_3^{2+}$)

Nanocrystalline TiO_2 film:

12 g TiO_2 powders (P-25, Japan Aerosil Co,Ltd.) were mixed well with 4ml pure water and 0.4ml acetylacetone to obtain a sticky paste. After adding 16ml pure water they are mixed again well, and then TritonX-100 (detergent) was added. This mixture was spread on a fluorine-doped SnO_2 conductive glass (conductivity, 0.1 S/Ω), and then it was calcinated at 450℃ for 1 h. This coating procedure was repeated to obtain an intended thickness film, usually of 10 μm thickness. Cu wire was attached to this TiO_2-coated NESA glass by silver paste (abbreviated to NESA/TiO_2).

Photoelectrochemical measurement:

An aqueous solution containing 0.5 - 2.5 mM (M=moldm^{-3}) sensitizer and 0.1 M ethylenediaminetetraacetic acid (EDTA) donor was used with the NESA/TiO_2 working, spiral platinum counter, and Ag-AgCl reference electrodes. For the poly-Ru(bpy)$_3^{2+}$

sensitizer, a DMF solution of 3 was cast onto the NESA/TiO_2 and it was dried. For the 1, the dye was preadsorbed from its aqueous solution (pH 3.5) onto the NESA/TiO_2. The working NESA/TiO_2 electrode was placed near the cell glass wall so as to minimize a filter effect of the sensitizer solution, and it was irradiated from the NESA side. A 500W xenon lamp was used as a light source with a UV cutoff filter Y-43 in combination with some neutral density filter(s) to adjust the light intensity (usually 66.4mWcm^{-2}). The photoelectrochemical response was measured with a potentiostat, function generator, and a X-Y recorder.

RESULTS AND DISCUSSION

The cyclic voltammograms at the NESA/TiO_2 electrode soaked in an aqueous solution (pH 4.6) containing 1 mM $Ru(bpy)_3^{2+}$ and 0.1 M EDTA are shown in Fig. 1 in the dark as well as under illumination. The voltammogram under illuminaton shows a stable anodic photocurrent.

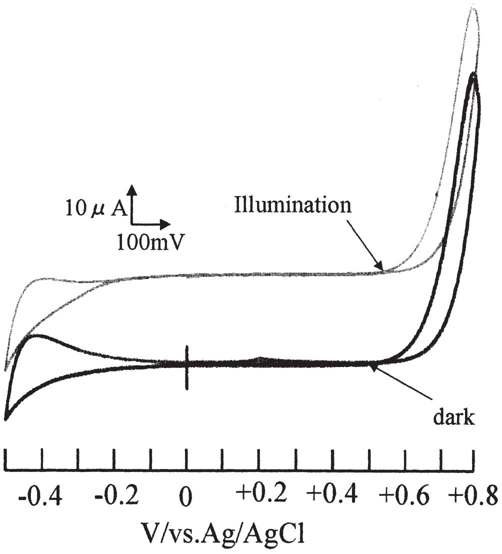


Fig.1 Cyclic voltammograms at ITO/TiO_2 electrode in a pH4.6 aqueous solution containing $Ru(bpy)_3^{2+}$ (1mM) as a photosensitizer, and EDTA(0.1M) as an electron donor.

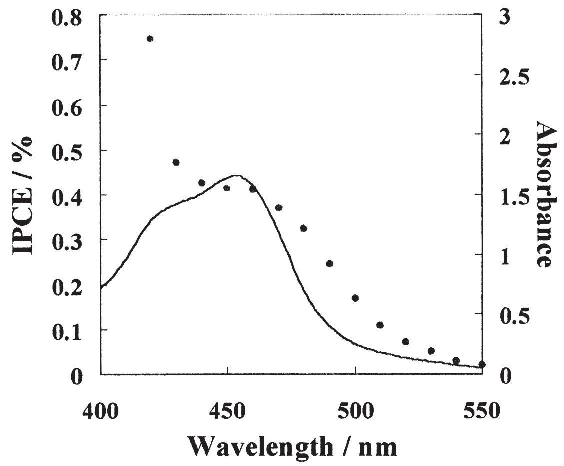


Fig.2 Absorption spectrum of $Ru(bpy)_3^{2+}$ solution and photocurrent action spectrum at ITO/TiO_2 electrode in an aqueous solution containing $Ru(bpy)_3^{2+}$ and EDTA.

The action spectrum for the photocurrent by the $Ru(bpy)_3^{2+}$ sensitizer is shown in Fig. 2 with the absorption specrum of the sensitier in an aqueous solution, where IPCE is the incident photon to current conversion efficiency (η %).In the wavelength region below 440nm, photocurrent increased because of a possible direct excitation of the TiO_2 layer in spite of a UV cutoff filter used (bandgap for the TiO_2 is around 3 eV, effective wavelength < 400nm). However, the action spectrum around 450nm shows evidently that the excitation of the complex induces the photocurrent.

Important point for the sensitization by the $Ru(bpy)_3^{2+}$ is its concentration dependent photocurrent. The photocurrent dependence on the complex concentration is shown in Fig. 3. The photocurrent at first increased with the concentration and then saturated beyond 1.5 mM. This saturation behavior is indicative of a chemical adsorption, i.e., single molecular adsorption of the complex onto the TiO_2 particles. This point will be discussed later from the pH dependence of the photocurent.

The effects of various sensitizers on photocurrent are shown in Table 1. In this table the complexes, $Ru(bpy)_3^{2+}$ and $Ru(bpym)_3^{2+}$, are present in the aqueous phase, Ru[P(St-Vbpy)]$(bpy)_2^{2+}$(Poly-$Ru(bpy)_3^{2+}$) is preadsorbed from its DMF solution onto the TiO_2 layer, and $Ru(dcbpy)_3^{4-}$ is either present in the solution or preadsorbed onto the TiO_2

from its aqueous solution (pH 3).A simple comparison between the sensitizers should not be done, because there are many factors to affect the photoelecrochemical event,

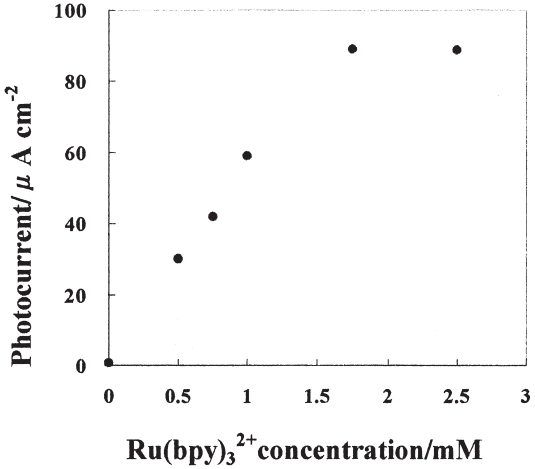


Fig.3 Relationship between photocurrent and $Ru(bpy)_3^{2+}$ concentration at applied potential of 0V vs. Ag/AgCl. [EDTA]=0.1M, pH5.5.

Table 1 Comparison of photocurrent with ITO/TiO_2 electrode using various sensitizers. Light source, 500W Xe lamp

sensitizer	pH	concentration	EDTA	photocurrent / μ Acm^{-2}
-	4.5	-	0.1M	1.0
$Ru(bpy)_3^{2+}$	4.5	0.25mM	0.1M	8.1
$Ru(bpy)_3^{2+}$	4.5	1mM	0.1M	21.5
$Ru[P(St\text{-}Vbpy)](bpy)_2^{2+}$	4.5	$2.4\times10^{-8}molcm^{-2}$ a)	0.1M	10.1
$Ru(bpym)_3^{2+}$	4.5	0.25mM	0.1M	1.6
$Ru(dcbpy)_3^{4-}$	4.5	0.25mM	35mM	26.7
$Ru(dcbpy)_3^{4-}$	3.5	$6.0\times10^{-9}molcm^{-2}$ b)	0.1M	122.2

a) Prepared by casting of Poly-$Ru(bpy)_3^{2+}$/DMF solution
b) Prepared by adsorption with dipping into $Ru(dcbpy)_3^{4-}$ aqueous solution (pH3.0)

but the preadsorption of the $Ru(dcbpy)_3^{4+}$ onto the TiO_2 gave a high photocurrent most probably indicating that adsorptivity of the sensitizer onto the TiO_2 is an important factor for the sensitizetion. The water-insoluble polymer complex was expected to show a high efficiency because of its stable attachment on the TiO_2. Although the conditions are not optimized, the result for the polymer complex is not very good probably because of some resistivity by a multi-layered coating, but the merit of the polymer sensitizer is its high stability on the TiO_2.

To obtain more information about sensitization, pH dependence of the photocurrent was investigated, and the results are shown in Fig. 4 for the $Ru(bpy)_3^{2+}$ as well as for the Poly-$Ru(bpy)_3^{2+}$ sensitizers. The photocurrent sensitized by $Ru(bpy)_3^{2+}$ exhibited an optimum point at pH 6. The protonation and dissociation of the Ti-OH groups on the TiO_2 (P-25) surface are represented by the eq.(1).

$$\mathrm{Ti\text{-}OH_2^+} \overset{pK_{a1}\,(4.98)}{\rightleftharpoons} \mathrm{Ti\text{-}OH} \overset{pK_{a2}\,(7.80)}{\rightleftharpoons} \mathrm{Ti\text{-}O^-} \qquad (1)$$

If a simple adsorption of the sensitizer is the major factor for the sensitization, higher pH should favor the proces since the electrostatic repulsion between the positively charged sensitizer and $Ti\text{-}OH_2^+$ supresses adsorption, while electrostatic attraction between the sensitizer and $Ti\text{-}O^-$ favors the adsorption. However, the optimum conditions at pH 6 show that other factor(s) should be taken into account.

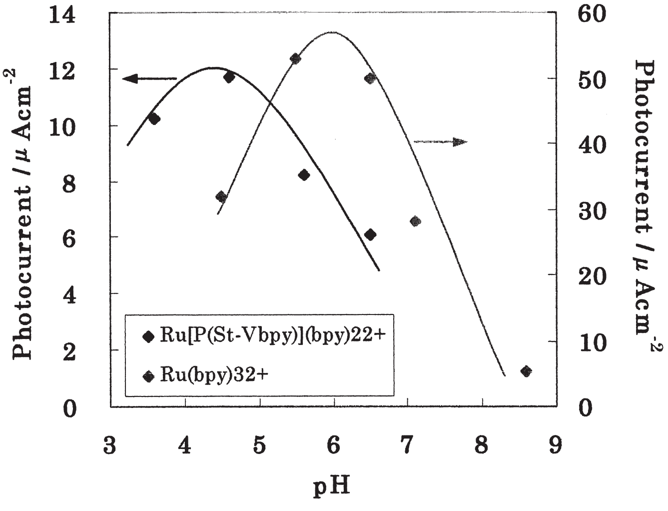


Fig.4 Relationship between photocurrent and pH at applied potential of 0V vs. Ag/AgCl. [EDTA]=0.1M, $[Ru[P(St\text{-}Vbpy)](bpy)_2^{2+}]=2.4\times10^{-8}$ molcm^{-2}(adsorbed), $[Ru(bpy)_3^{2+}]$=1mM in solution.

As for such factor, the conduction band energy level of the TiO_2 (bandedge -0.42 eV vs.SHE at pH 7) must be important. The energy level of the conduction band becomes more negative with increasing pH, so that higher pH unfavors electron injection from the photoexcited sesitizer (-0.83 V vs.SHE) to the conduction band. For the poly-Ru(bpy)$_3^{2+}$, the electrostatic factor for the adsorption would be less effective, so that the optimum conditons are at lower pH, altough the peak at 4.5 still suggests some suppressive effect of the repulsive interaction between the cationic sensitizer and the Ti-OH$_2^+$.

Although it is not the aim of the present work to study the characteristics of a photoelectrochemical cell, the best system in Table 1, i.e., sensitization by preadsorbed Ru(dcbpy)$_3^{4-}$, was applied to a photoelectrochemical cell which uses redox couple electrolyte instead of EDTA with the configuration;

NESA/TiO$_2$/Ru(dcbpy)$_3^{4-}$/redox couple aq.soln./Pt counter electrode.

In this cell the redox couple aqueous solution is adsorbed in the nanoporous TiO$_2$ layer, and no spacer is used between the NESA/TiO$_2$/Ru(dcbpy)$_3^{2+}$ working and Pt counter electrodes. The photon-to-electricity conversion characteristics of the cell using I$^-$/I$_3^-$ or hydroquinone/quinone (HQ/Q) redox couple are shown in Table 2.

Table 2 Characteristics of the photoelectrochemical cell.

Run	Redox couple	**Dye /molcm^{-2}**	**J_{sc}/μAcm^{-2}**	**V_{oc}/V**	**ff**	**η/%**
1	I^-/I_3^-	1.4×10^{-8}	52.6	0.20	0.33	0.005
2	H_2Q/Q	3.6×10^{-8}	31.6	0.15	0.15	0.001

To conclude, these results show that this sensitized system can be applicable in future to a water phase photochemical conversion system to create high energy compound from solar energy and water, which is an urgent and important research subject all over the world.

ACKNOWLEDGEMENT

The authors acknowledge the Grant-in-Aid No. 10650862 from the Ministry of Education, Science, Sports and Culture.

1.G.J.Meyer ed., Molecular Level Artificial Photosynthetic Materials, Progress in Inorganic Chemistry, vol.**44**, John Wiley &Sons,Inc., New York (1997).

2. M.Kaneko and I.Okura ed., Photocatalysis -Science and Technology-, Springer Verlag, in press (2001).

3. B.O'Regan and M.Graetzel, Nature, 353, 737 (1991).

4. M.Kaneko, Symposium on Unsolved Problems in Polymer Chemistry, p.21, Soc.Polym.Sci.Jpn, Tokyo (1976).

5. M.Yagi and M.Kaneko, Chem.Rev., **101**, 21 (2001).

6. T.Abe and M.Kaneko, Reduction Catalysis by Metal Complexes Confined in a Polymer Matrix, Progress in Polymer Science, Elsevier Science, Oxford, submitted.

7. M.Kaneko, Charge Transport in Solid Polymer Matrixes with Redox Centers, Progress in Polymer Science, Elsevier Science, Oxford, in press (2001).

8. J.Zhang, F.Zhao, and M.Kaneko, J.Porphyrins & Phthalocyanines, **4**, 65 (2000).

9. J.Desilvestro, M.Graetzel, L.Kavan, and J.Moser, J.Am.Chem.Soc., **107**, 2988 (1985).

10. N.Vlachopoulos, P.Liska, J.Augustynski, and M.Graetzel, J.Am.Chem.Soc., **110**, 1216 (1988).

11. L.Kavan and M.Graetzel, Electrochim.Acta, **9**, 1327 (1989).

12. M.Kaneko and A.Yamada, Photochem.Photobiol., **33**, 793 (1981).

13. M.Kaneko, A.Yamada, E.Tsuhicda, and Y.Kurimura, J.Polym.Sci.Polym.Let.Ed., **20**, 593 (1982).