

K. Yoshinaga
I. Toyofuku
K. Yamashita
H. Kanehara
K. Ohkubo

Photoinduced electron transfer catalysis of titania particles modified with a $\text{Ru}(2,2'\text{-bipyridyl})_3^{2+}$ -grafted polymer by visible light

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K. Yoshinaga (✉) · I. Toyofuku
Department of Applied Chemistry
Faculty of Engineering
Kyushu Institute of Technology, Sensui 1,
Tobata, Kitakyushu 804-8550, Japan
e-mail: khyosina@che.kyutech.ac.jp
Tel.: +81-93-8843316
Fax: +81-93-8843316

K. Yamashita
Polymer Chemistry Laboratory
The Institute of Physical and
Chemical Research (RIKEN), Hirosawa 2-1
Wako Saitama 351-0198, Japan

H. Kanehara · K. Ohkubo
Advanced Energy Utilization Division
Institute of Advanced Energy
Kyoto University, Gokashou, Uji
Kyoto 611-0011, Japan

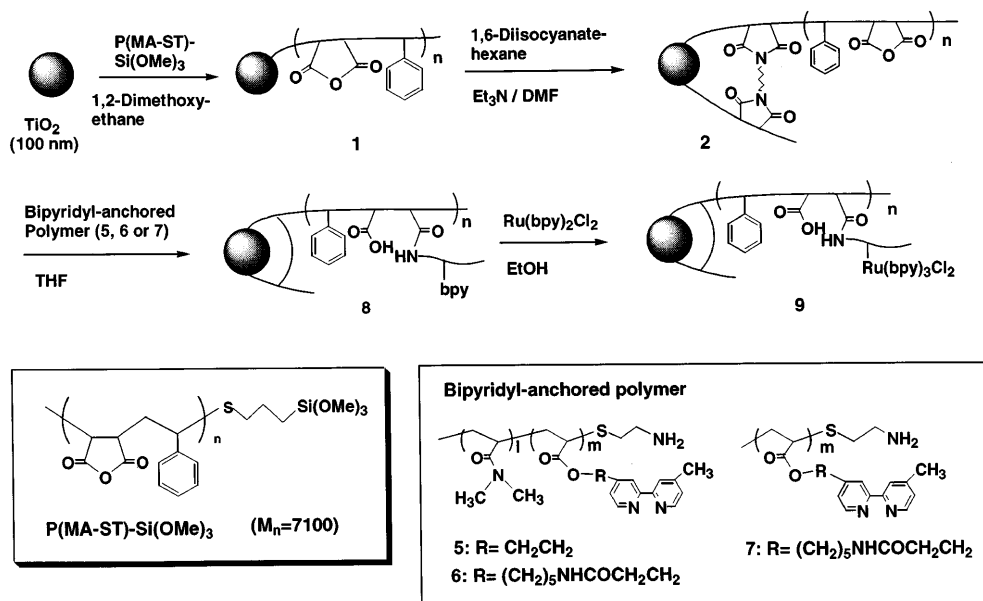
Abstract The preparation and photocatalysis of colloidal titania modified with $\text{Ru}(2,2'\text{-bipyridyl})_3^{2+}$ -grafted polyacrylate were investigated. Visible light irradiation of the $\text{Ru}(2,2'\text{-bipyridyl})_3^{2+}$ -tethered titania in pH 7.0 buffer solution gave electron transfer to methyl viologen to form the cation radical via electron migration from the $\text{Ru}(\text{II})$ complex to the titania surface.

Key words Hybrid titania · Photocatalysis · Visible light · $\text{Ru}(2,2'\text{-bipyridyl})_3\text{Cl}_2$ · Polymer modification

Introduction

The application of light-induced electron-transfer reactions in the development of photocatalytic reactions is of great interest. Most of the research in this field makes use of titanium oxide, an inexpensive, chemically stable and atoxic semiconductor which absorbs over all the UV region and causes charge separation [1–5]. If a visible part of the solar emission is absorbed, a method for solar energy conversion can be devised. In this respect photoelectrochemical reactions induced by visible light irradiation using organic dyes or metal complexes, for example, the ruthenium(II)-tris[2,2'-bipyridyl] complex $\text{Ru}(\text{bpy})_3\text{Cl}_2$ [6–9], are of interest. In this article, we

describe the preparation of colloidal titania particles modified with the polymer-grafting $\text{Ru}(\text{bpy})_3^{2+}$ complex, as shown in Scheme 1, and light-induced electron transfer from the sensitizer to *N,N'*-dimethyl-4,4'-bipyridinium dichloride (methyl viologen, MV^{2+}) via visible light irradiation. Regarding the polymer modification of colloidal particles, we have developed a new procedure using the reaction of surface hydroxyl groups with a polymeric silane coupling agent [10, 11]. Especially, the modification of colloidal silica by a poly(maleic anhydride-styrene)-silane, $\text{P}(\text{MA-ST})\text{-Si}(\text{OCH}_3)_3$, coupling agent led to the formation of stable and dispersible particles in organic solution and to the introduction of amino and carboxyl groups on the surface [11].



Scheme 1

Experimental

Materials

Monodisperse colloidal titania in aqueous suspension, containing 18 wt% TiO_2 of 100-nm diameter, was kindly supplied by Catalysts & Chemicals Co., Japan. The polymeric silane coupling agent $\text{P(MA-ST)-Si(OMe)}_3$ was synthesized by the method described previously [10]. Reagents of extrapure grade MV^{2+} and $\text{Ru(bpy)}_2\text{Cl}_2$ were used.

Preparation of composites 1 and 2

Precatalyst particles of composites 1 and 2 were prepared according to the method of the polymer-modified silica [10].

Synthesis of bpy-anchored polymers 5, 6 and 7

The amino-terminated, bpy-branched polymers 5–7 were synthesized by radical polymerization from an acrylate derivative, 2-(5'-methyl-bpy-5-yl)ethyl acrylate (3) or 6-[N-(3-(5'-methyl-bpy-5-yl)propionyl)]aminohexyl acrylate (4). A typical polymerization was carried out as follows. To a mixture of 4 (0.1 g) and 0.13 g *N,N*-dimethylacrylamide (DAAm) in tetrahydrofuran (THF) (1 cm^3) was added the ethanol solution (0.5 cm^3) containing 0.6 mg cysteamine hydrochloride and 2 mg 2,2'-azobis(isobutyronitrile). The solution was stirred at 65 °C in a nitrogen atmosphere for 24 h. Precipitation with diethyl ether and drying under a reduced pressure gave 0.15 g copolymer; the number-average molecular weight by polystyrene-calibrated gel permeation chromatography analysis was 2000.

Preparation of composites 8 and 9

Composite 8 was prepared by the reaction of composite 2 (0.25 g) with polymers 5, 6 or 7 (30 mg) under refluxing in dry THF (10 cm^3) for 24 h. The amount of polymer grafted on the titania

particles was determined by the weight decrease during the temperature elevation from 100 to 800 °C on thermal analysis. The coordination of the Ru(II)-bpy complex on composite 9 was carried out by the reaction of composite 8 (0.2 g) with $\text{Ru(bpy)}_2\text{Cl}_2$ (5 mg) under refluxing in 20 cm^3 ethanol in a nitrogen atmosphere. The amount of coordinated Ru-bpy complex on composite 9 was estimated from the difference between amounts of dosed $\text{Ru(bpy)}_2\text{Cl}_2$ and that remained in the filtrate after the coordination reaction. The concentration of the Ru complex was spectrophotometrically determined by the absorbance at 550 nm ($\epsilon = 5540$).

Photoreaction

Photocatalysis of composite 9 in the light-induced electron transfer was evaluated by spectrophotometric absorbance of the cation radical formed from MV^{2+} at 605 nm ($\epsilon = 10,700$) in pH 7.0 tris(hydroxymethyl)aminomethane(Tris)-HCl buffer solution (0.1 mol dm^{-3}). To 3.0 cm^3 Tris-HCl buffer solution containing 0.8 mmol dm^{-3} ethylenediaminetetraacetic acid (EDTA) and 0.4 mmol dm^{-3} MV^{2+} was added 0.3 mg titania composite in a 10-mm quartz cell, and then the solution was thoroughly purged with argon. The cell was irradiated with visible light ($\lambda > 400$ nm) through a UV-cut filter (Toshiba L-42) from a Xe lamp (500 W) at 25 °C for 3 h. A cocatalyst of EDTA was used as an electron source to reproduce Ru(II)-bpy from the Ru(III)-bpy complex formed by the light-induced electron donation. The quantum yield was determined using Reinecke salt according to the Wegner method [12].

Results and discussion

Since the radical polymerization of 3 did not give the homopolymer of higher molecular weight, we conducted the copolymerization of 3 and DAAm. In the present work, the copolymer composed of DAAm was used to give amphipathic properties to the composite particles. The results of the polymerization are shown in Table 1. Polymerization in the molar ratio of 3/DAAm = 3/1 afforded copolymer 5 composed of the monomer

Table 1 Preparation of bipyridyl-grafted polymers in the copolymerization, 1 mmol **3** or **4** was used and composite **8** the reaction of polymers **5**, **6** or **7** with 0.3 g composite **2** was carried out under refluxing for 24 h in 30 cm³ tetrahydrofuran in a nitrogen atmosphere

Monomer	Molar ratio of <i>N,N</i> -dimethylacrylamide/ 3 or 4	Polymer	Attached polymer on composite 8 ^b		
			<i>M_n</i>	<i>N,N</i> -dimethylacrylamide/ 3 or 4 ^a	(mg/g)
3	3/1	5	1700	8/1	45.4
4	5/1	6-1	2000	7.6/1	26.2
4	1/1	6-2	1300	1.2/1	25.0
4	—	7	1250	—	16.5

^a The molar ratio of *N,N*-dimethylacrylamide/**3** or **4** in the copolymer

^b Estimated from the weight decrease during temperature elevation from 100 to 800 °C on thermal analysis

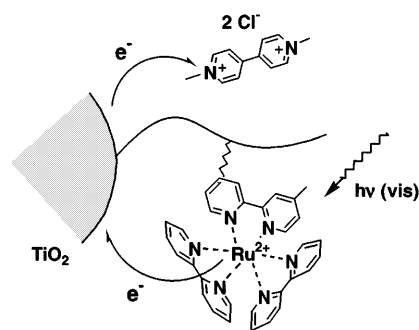
fraction ratio of 8/1, and an increase in the monomer molar ratio in the reactant scarcely affected the fraction of **3** in the copolymerization. The result therefore suggests that the bulkiness of the bpy group in **3** probably suppresses the monomer fraction in the copolymer. The reaction of composite **2** with copolymer **5** in THF under refluxing gave composite **8**, which attached 45.4 mg/g copolymer **5**. Further, the reaction of composite **8** with Ru(bpy)₃Cl₂ in ethanol resulted in anchoring of Ru(bpy)₃²⁺ of only 1.47 × 10⁻⁵ mol/g, or 0.59 Ru(II) atoms/nm² (Table 2). Thus, in order to increase the Ru(II) coordination on composite **9**, we conducted the synthesis of a copolymer with a higher fraction of grafted bpy by using **4** and DAAM, compared to copolymer **5**. As shown in Table 1, increasing the **4**/DAAM molar ratio from 1/5 to 1/1 in reactants resulted in the elevation of the monomer ratio from 1/7.6 in copolymer **6-1** to 1/1.2 in copolymer **6-2**, while the molecular weight of the copolymer decreased with the monomer ratio. Moreover, copolymer **6-2** led to a higher tethering of the Ru(II)-bpy complex of 1.19 × 10⁻⁵ mol/g, or 0.48 Ru(II) atoms/nm², in composite **9**, compared with copolymer **6-1** (Table 2). On the other hand, homopolymer **7**, prepared from **4**, afforded the highest tethering of the Ru(II)-bpy complex of 2.83 × 10⁻⁵ mol/g, or 1.14 Ru(II) atoms/nm², on composite **9**, in spite of a decreased amount of attached polymer on composite **8**.

In the preliminary experiments using a nonmodified titania suspension, the formation of the cation radical from MV²⁺ by the irradiation of unmodified titania through the UV-cut filter was not observed, so the electron transfer to MV²⁺ induced by the visible light irradiation of the colloidal titania was negligible. The results of the light-induced electron transfer on composite **9** are also shown in Table 2. The maximum yield of MV^{•+}, 6.1%, was observed in the reaction using composite **9(6-2)**. Composite **9(5)**, with a short spacer between the polymer chain and the branched bpy group, gave extremely low activity for the photoinduced electron transfer. Also, composite **9(6-1)** with a low bpy fraction in the grafted copolymer showed a lower

Table 2 Preparation of composite **9** and photocatalytic activity. The numbers in parentheses correspond to the copolymers in Table 1

Composites	Coordinated Ru(II) on composite 9		Yield of methyl viologen radical (%)
	(×10 ⁻⁵ mol/g)	(atoms/nm ²)	
9(5)	1.47	0.59	1.9
9(6-1)	0.44	0.18	2.5
9(6-2)	1.19	0.48	6.1
9(7)	2.83	1.14	4.0
Silica (6-2)	2.95	1.18	0.0

catalytic activity than that with a high bpy fraction. Therefore, these results suggest that the flexibility of the bpy group on the grafted polymer is probably important for the conformation of the Ru(bpy)₃²⁺ complex which is effective for the light-induced electron excitation of composite **9(6-2)**. The quantum yields of the photoreaction by the composite, which gave the maximum yield of MV^{•+}, were very low (less than 0.001); however, optimization of the photoreaction might give a higher quantum yield. On the other hand, it is noticeable that the polymer-modified silica particles, which were prepared by the same procedure as that of composite **9(6-2)**, did not give radical formation due to light-induced electron transfer under the same conditions (Table 1). In the present photoreaction, therefore, it is suggested that the photoexcited electron of Ru(bpy)₃Cl₂ tethered by the



Scheme 2

copolymer on titania is transferred to MV^{2+} via the titania surface (Scheme 2). The transfer of the photoexcited electron from anchored $Ru(bpy)_3Cl_2$ to titania was supported by the following observations. The light irradiation of the suspension of composite **9(7)** in 3 cm^3 Tris-HCl buffer without MV^{2+} and EDTA for 3 h led to an absorbance decrease from 0.655 to 0.608 at 450 nm, at which $Ru(bpy)_3Cl_2$ exhibited the maximum absorbance. Also, the absorbance (0.859) of the mixture

of unmodified titania (0.3 mg) and $Ru(bpy)_3Cl_2$ in the Tris-HCl buffer (3 cm^3) at 450 nm was unchanged before and after light irradiation.

In conclusion, we have demonstrated that light-induced electron transfer to MV^{2+} as an electron acceptor can be achieved by the visible light irradiation of colloidal titania modified with $Ru(bpy)_3^{2+}$ -grafted polymer. The high quantum yield of electron transfer might have practical implications for solar energy utilization.

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