

Visible-Light-Responsive Photocatalytic Flow Reactor Composed of Titania Film Photosensitized by Metal Complex-Clay Hybrid

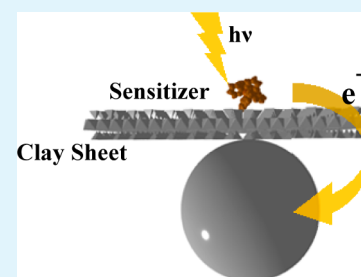
Takehito Goto[†] and Makoto Ogawa^{*,†,‡}

[†]Graduate School of Creative Science and Engineering, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan

[‡]Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555 Moo 1 Tumbol Payupnai, Amphoe Wangchan, Rayong 21210, Thailand

Supporting Information

ABSTRACT: Synthetic saponite containing a photosensitizing metal complex, tris(2,2'-bipyridine)ruthenium(II), in the interlayer space was complexed with anatase nanoparticles to obtain transparent hybrid film photocatalyst. The catalyst film was mounted in a flow reactor device to catalyze such photocatalytic reactions as the decomposition of aqueous acetic acid and *N*-alkylation of benzylamine with ethanol.

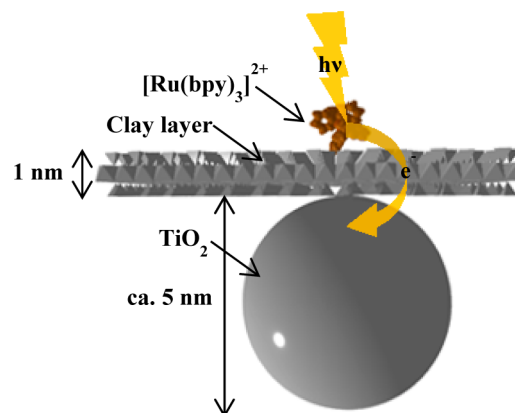


KEYWORDS: flow reactor, smectite, TiO₂, visible-light-responsive photocatalyst

The photosensitization of such wide band gap semiconductors as zinc oxide and titanium dioxide is a way for the visible-light-responsive photocatalysts and for the dye-sensitized solar cells.^{1–3} Dyes have been designed in order to obtain efficient charge injection from the photoexcited state to the semiconductors, which is one of the important prerequisites for the improved efficiency.^{4–6} By designing molecular structures, absorption characteristics in a wide range of visible light for the use of solar irradiation have been tuned³ and the adsorbed states of the photosensitizing dyes on semiconductor surfaces have been examined.⁷ The stability of the photosensitizing dye is also a topic of interest for dye-sensitized solar cells^{8,9} and photocatalysts,^{1,2,10,11} therefore, searching dyes and ways of dye-immobilization for higher stabilities and better efficiency has been conducted.^{4–6,10–14}

Ruthenium(II) poly(pyridyl) complexes have been used to extend the photoresponse of TiO₂ into the visible region.^{12–15} In our previous communication,¹⁶ we have shown improved stability of tris(2,2'-bipyridine)ruthenium(II) complex (hereafter abbreviated as [Ru(bpy)₃]²⁺) in [Ru(bpy)₃]²⁺-clay@TiO₂ hybrid if compared with that of an analogous ruthenium poly(pyridine) complex (tris(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) dichloride, abbreviated as Ru470) attached on the surface of a commercially available TiO₂ (AEROXIDE TiO₂ P25, Nippon Aerosil Co., Ltd.). This was achieved probably by the [Ru(bpy)₃]²⁺ being separated from the semiconductor surface by clay nanosheet (thickness of 1 nm), while at the same time, photoexcited metal complex can still communicate with the semiconductor because of the hybrid structure schematically shown in Scheme 1. Nanometer-sized clay (Synthetic saponite, Sumecton SA, Kunimine Ind. Co., Ltd., cation exchange capacity (CEC) of 71 mequiv (100 g of

Scheme 1. Schematic Drawing of the Proposed Structure of [Ru(bpy)₃]²⁺-Clay@TiO₂



clay)⁻¹) was used as the host material for cationic photosensitizing metal complex ([Ru(bpy)₃]²⁺), and the [Ru(bpy)₃]²⁺-clay intercalation compound was coated with titania nanoparticles by a hydrothermal reaction of titanium tetraisopropoxide to obtain hybrid composed of anatase and clay.¹⁶ There are several studies to efficiently attach sensitizing dyes on the semiconductor surfaces,^{4–6,17,18} whereas the present methodology is a very simple alternative to complex photosensitizing cationic species with semiconductor.

In the present study, hybrid catalyst was prepared by an easier way, where [Ru(bpy)₃]²⁺-SSA intercalation compound,

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which was prepared by simple ion exchange reaction and the amount of loaded $[\text{Ru}(\text{bpy})_3]^{2+}$ was 7.1 mequiv/g clay, is mixed with an aqueous colloidal suspension of anatase (particle size of ca. 5 nm, concentration of 0.21 g/L, Nissan Chemical Ind. Co., Ltd.), to obtain transparent homogeneous film of $[\text{Ru}(\text{bpy})_3]^{2+}$ -SSA@TiO₂. The application of the film as the photocatalysts was examined using a flow reactor device. The photochemical reaction in the flow reactor equipped with photocatalysts have following advantages if compared with those using conventional batch reactors; the separation of powdered catalysts is not required after the reaction, light absorption and scattering by the dispersed powder photocatalysts can be avoided to achieve homogeneous illumination.^{19,20}

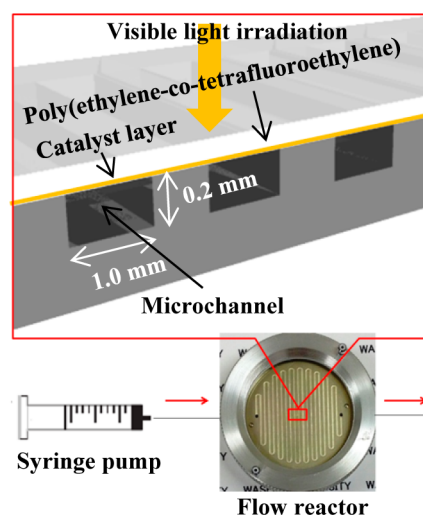
The intercalation of $[\text{Ru}(\text{bpy})_3]^{2+}$ into smectites has been reported so far.^{21–23} One of the advantages of the present system is the film forming ability of smectite by simple casting without use of any additives.²⁴ The $[\text{Ru}(\text{bpy})_3]^{2+}$ loading was determined in order to obtain high-quality film with efficient light absorption. The higher $[\text{Ru}(\text{bpy})_3]^{2+}$ loading may lead to more efficient light absorption with the lower quality film because of the lower suspension viscosity and stability.

By simply casting the aqueous suspension of $[\text{Ru}(\text{bpy})_3]^{2+}$ -SSA and colloidal TiO₂ on poly(ethylene-co-tetrafluoroethylene) (abbreviated as PETFE) substrate, a film with the thickness of ca. 1.5 μm was obtained. (The photograph, visible absorption spectrum, and XRD pattern of the film are given as Figures S1 and S2 in the Supporting Information.) The $[\text{Ru}(\text{bpy})_3]^{2+}$ -SSA@TiO₂ film was stuck to the PETFE substrate even after immersing in water with sonication as confirmed by naked eye observations, SEM observations, and visible absorption spectra. Therefore, the film was used as photocatalyst. It should be noted here that film was not obtained without SSA. Moreover, the ratio of SSA and TiO₂ is a very important parameter to obtain better performance as photocatalyst film. The SSA:TiO₂ mass ratio of 2:9 was initially determined from the designed structure where SSA particle was surrounded with a monolayer of anatase nanoparticle (radius of ca. 5 nm), and the ratio was proven to be appropriate by the preliminary experiments, so that the SSA:TiO₂ mass ratio of 2:9 was used in the present study. When larger amount of SSA was used (SSA:TiO₂ mass ratio of 4:9), the photocatalytic reaction was less efficient. When lower amount of SSA was used (SSA:TiO₂ mass ratio of 1:9), film quality was low and may be peeled off from the substrate during the reaction. (The photograph of the films is given as Figure S1 in the Supporting Information.) Thus, it was thought that the catalyst layer was composed of molecularly hybridized complex-clay intercalate with titania nanoparticle.

The present flow reactor (KeyChemLumino, YMC Co., Ltd.) has a bent straight channel with the width and the depth of 1.0 and 0.2 mm, respectively, and the total path length of 560 mm. The $[\text{Ru}(\text{bpy})_3]^{2+}$ -SSA@TiO₂ photocatalyst deposited on PETFE was mounted on the channel as shown in Scheme 2 and the irradiation was done through the quartz window.

As the first application, the decomposition of acetic acid was examined by visible-light irradiation. The reaction was monitored by monitoring the acetic acid concentration, which was determined by high-performance liquid chromatography. Aqueous acetic acid solution (120 ppm, pH 3.7) was irradiated by visible light (light source is San-Ei Electronic XES-502S solar simulator and the light intensity is 100 mW/cm²) at the flow rate of 100 μL/min, which corresponds to the residence time of the solution in the flow reactor device of 1.1 min. The experiment was conducted 10 times to examine the

Scheme 2. Schematic Drawing of the Flow Reactor Used in the Present Study



reproducibility of the reaction and the stability of the catalysts layer in the flow reactor. The concentrations of the final acetic acid solution ranged within 104 ± 4 ppm and the decomposition efficiency was observed when the reaction was conducted several times using the same device. When the flow rate was 10.0 μL/min (residence time of 11 min), the decomposition proceeded more efficiently (ca. 25% of acetic acid was decomposed). When lower concentration (12 ppm) of acetic acid solution was employed, complete decomposition was achieved when the irradiation was repeated three times at the flow rate of 10.0 μL/min (total residence time of 33 min). The changes in the concentration of acetic acid during the irradiation is shown in Figure 1. Thus, the present photocatalytic

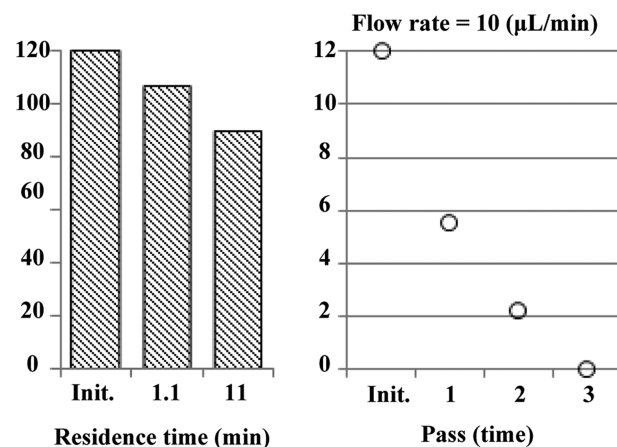


Figure 1. Quantitative data for the photocatalytic decomposition of acetic acid (left, the initial concentration of acetic acid is 120 ppm; right, the initial concentration of acetic acid is 12 ppm).

flow reactor was successfully applied for the decomposition of acetic acid in water. It should be noted here that the blank tests were conducted in the dark, without the photocatalyst under irradiation, and with the metal complex clay without TiO₂ under irradiation. All the blank tests gave no reactions. The photoexcited electron transfer to TiO₂ from the metal complex through silicate layer is thought to be concerned for the photosensitized catalytic reaction.

As another application of the present photocatalyst flow reactor, *N*-alkylation of benzylamine with ethanol was examined. It was reported that flow reactor with deposited titania layer as photocatalyst was used for the *N*-alkylation of benzylamine by UV irradiation.^{19,20} In the present study, an ethanol solution of benzylamine (1000 $\mu\text{mol/L}$) was irradiated by visible light (with solar simulator at the light intensity of 100 mW/cm^2) and the products were evaluated by gas chromatography with FID detector. Figure 2 shows the changes in the

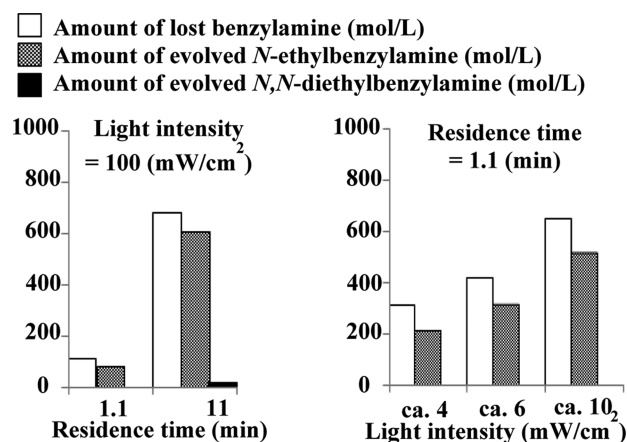


Figure 2. Quantitative data for the photocatalytic *N*-alkylation of benzylamine.

concentrations of benzylamine and *N*-ethylbenzylamine by the irradiation. When the flow rate was 100 $\mu\text{L/min}$ (residence time of 1.1 min), the concentration of benzylamine decreased to be ca. 890 $\mu\text{mol/L}$ (11% of the original benzylamine was lost). To compensate the loss of benzylamine, *N*-ethylbenzylamine formed in the solution. The amount of *N*-ethylbenzylamine was ca. 80 $\mu\text{mol/L}$ (which corresponds to the yield of 72% based on the loss of benzylamine; 80/110). The reaction was reproducible; the concentration of the final benzylamine and *N*-ethylbenzylamine ranged within 890 ± 4 and 80 ± 3 $\mu\text{mol/L}$, respectively, and the reaction efficiency was not changed for the repeated irradiation using the same reactor.

When the flow rate was 10 mL/min (residence time: 11 min), the concentration of benzylamine decreased to be ca. 320 $\mu\text{mol/L}$ (68% of the initial benzylamine was lost) and the concentration of the formed *N*-ethylbenzylamine was ca. 610 $\mu\text{mol/L}$. (The yield of *N*-ethylbenzylamine toward the lost benzylamine was 89%). The reaction was also reproducible; the concentration of the final benzylamine and *N*-ethylbenzylamine ranged within 320 ± 50 $\mu\text{mol/L}$ and 610 ± 70 $\mu\text{mol/L}$, respectively, after the reactions were repeated several times.

Depending on the irradiation conditions, the yields as well as products selectivity varied. It should be noted here that the *N*-alkylation of benzylamine with ethanol occurred under weaker light irradiation (natural sun light on a building roof; the light intensity of ca. 4–10 mW/cm^2). Thus, the application of the present photocatalytic flow reactor to other reactions is promising.

In conclusion, the photosensitizing metal complex intercalated in the interlayer space of smectite clay was complexed with finite particles of TiO_2 to obtain visible-light-responsive photocatalyst. The roles of the smectite clay in the present success are many; immobilizing and stabilizing the $[\text{Ru}(\text{bpy})_3]^{2+}$, complexing $[\text{Ru}(\text{bpy})_3]^{2+}$ with titania nanoparticles,

and forming transparent film of titania nanoparticle on the substrate. Thanks to the film forming ability of smectite²² and possible effect on the improved stability of the guest species achieved by the complexation with the smectite clay,^{16,25–28} the photocatalyst film was fabricated in a flow reactor to construct visible-light-responsive photocatalytic flow reactor for possible repeated uses.

■ ASSOCIATED CONTENT

Supporting Information

The photograph, XRD pattern, and the UV–visible absorption spectrum of the catalyst film. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03128.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: waseda.ogawa@gmail.com.

Notes

The authors declare no competing financial interest.

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