Photocatalytic Oxidation of Water by Silica-Supported Tris(4,4'-dialkyl-2,2'-bipyridyl)ruthenium Polymeric Sensitizers and Colloidal Iridium Oxide

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A cationic polymer containing tris(4,4'-dialkyl-2,2'-bipyridyl)ruthenium groups linked by aliphatic spacers was studied as a photosensitizer for the catalytic oxidation of water in the presence of colloidal IrO₂. The polymer—colloidal IrO₂ system photocatalytically reduced persulfate, a sacrificial electron acceptor, and oxidized water to O₂ and H⁺ in solutions that were buffered at pH 6 by Na₂SiF₆ and NaHCO₃. The quantum efficiency for O₂ evolution and turnover number with respect to the Ru complex in the polymer reached 25% and 100, respectively. The polymer gradually aggregated in the Na₂SiF₆—NaHCO₃ buffer during the reaction, and this aggregation gradually decreased the photocatalytic activity of the system. Heterogeneous photocatalysts composed of this polymer and colloidal IrO₂ were also prepared using 70 nm diameter SiO₂ particles as supports. Photocatalysts made by the sequential loading of colloidal IrO₂ and the photosensitizer polymer onto SiO₂ particles at ca. pH 6 had much lower photocatalytic activity than did the unsupported system, presumably because there was little physical contact between the polymer and colloidal IrO₂ particles under these conditions. The most efficient heterogeneous photocatalyst was obtained by the adsorption of a mixture of the polymer and colloidal IrO₂ onto SiO₂ in Na₂SiF₆—NaHCO₃ solution. This composite had a high activity, comparable to that of the polymer—colloidal IrO₂ system. Transmission electron microscopy showed that the colloidal IrO₂ particles were covered with the polymer, which had aggregated in the solution. This result indicates that the polymer—IrO₂ aggregates retain their activity when immobilized on a support that might be used to organize overall water splitting systems.

Introduction

The goals of photocatalytic decomposition of water are to construct catalytic systems that split water into H₂ and O₂ under visible-light irradiation and to produce efficient photoconversion systems and devices for storing solar energy. Two basic approaches to these problems have emerged. One is to utilize wide band gap inorganic solar energy. Two basic approaches to these problems have been several reports of photocatalytic overall water splitting under UV irradiation. Another strategy is to use photosensitized systems that are responsive to visible light. In a previous paper, we reported light-driven electron and energy transfer reactions in lamellar polyanion/polycation thin film supported on SiO₂ particles. The energy/electron transfer cascade consisted of sequentially adsorbed polyanions, polycations, and charged porphyrin molecules, interleaved with anionic Zr(HPO₄)₂·H₂O and HTiNbO₅ sheets. The overall energy/electron transfer quantum yield of the photosensitized cascade that was irradiated with visible light exceeded 50%. The next logical step toward a water splitting system would be to couple these photoredox cascades to dark catalysts for hydrogen and oxygen evolution in appropriate layers. One of the biggest stumbling blocks to the development of such integrated photosystems is the absence of an effective and stable oxygen evolution catalyst.

Tris(2,2'-bipyridyl)ruthenium [Ru(bpy)₃] is a particularly interesting sensitizer for visible-light water splitting. Visible light is absorbed by [Ru(bpy)₃]²⁺, forming an energetic and long-lived metal-to-ligand...
charge transfer (MLCT) excited state. The complex in the MLCT state is oxidized to [Ru(bpy)3]3+$^-$ by sacrificial acceptors such as S2O82-. Without an appropriate catalyst, no O2 is formed and [Ru(bpy)3]3+$^-$ is destroyed by nucleophilic attack of water and/or hydroxide ions. In the presence of a catalyst, which is typically a transition metal oxide, the photosensitizer is recycled and O2 can be detected as a reaction product. The quantum yield for O2 evolution reaches ca. 60% under optimal conditions. RuO2 is an effective catalyst for O2 evolution under these conditions, but its turnover number is typically small because of anodic corrosion.

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The degree of polymerization was then calculated from the ratio between the average peak areas for the 1,5-bis(4-methyl-2,2′-bipyridyl-4-yl)pentane units and 2,2′-bipyridine units. The average degree of polymerization was determined by this method to be ca. 9. Anal. Calcd for C32H28F3I2O18Na4S3Te6Ru9 (found): C, 46.04% (46.33%); H, 3.70% (3.77%); 8.89% (8.88%).

The polymer was synthesized from the chloride salt by dissolving the product in a minimum amount of acetonitrile and adding tetraethylammonium chloride in acetonitrile and a few drops of 12 M HCl. The Cl– salt precipitates as a red film on the sides of the flask. Emission (λmax (nm), H2O): 620, excitation wavelength 460 nm. A 0.12 g portion of the solid polymeric chloride salt was dissolved in 50 mL of deionized water, and the solution (2.7 × 10$^{-3}$ M in Ru-complex) was used to prepare the composites used in the photolysis experiments.

The colloidal IrO2 solution was cooled to room temperature before being stirred with 10 mL of anion-exchange resin, Dowex 2×8-50 (chloride form), to remove excess chloride ions. After 30 min, the resin was removed by filtration, and the final solution was diluted to 100 mL. The diameter of the colloidal particles was estimated to be ca. 10–20 nm by transmission electron microscopy (TEM). The citrate-stabilized colloidal IrO2 solution was stable over a period of several months at this concentration.

**Preparation of AlCl32(OH)2(3H2O)2**2+. The aluminum Keggin ion, Al13O4(3H2O)2(3H2O)$^{2+}$, was prepared free of other Al species in soluble form by reaction of its sulfate salt with aqueous BaCl2.4 A 50 mL portion of an aqueous 0.25 M NaOH solution (12.5 mmol) was added dropwise to an aqueous

**Experimental Section**

**Materials.** Reagent grade AlCl3·6H2O, Na2SiF6, NaHCO3, Na2SO4, Na2SO4, and sodium hydrogen citrate sesquihydrate were obtained from commercial sources. [Ru(bpy)3]Cl2·6H2O and potassium hexachloroiridate, K3IrCl6, were used as received from Aldrich and Alfa, respectively. Spherical SiO2 particles (70 nm diameter), which were used as supports, were available from earlier studies.24 The SiO2 was heated in air at 550 °C for 5 h to remove any adsorbed organic compounds.

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solution of 1.2 g of AlCl3·6H2O (5 mmol) in 50 mL of deionized water, and the solution was heated to 85 °C in an oil bath with constant stirring. After 20 min, 80 mL of aqueous 0.12 M Na2SO4 (10 mmol) was added to the clear A(3+) solution. The solution was kept at room temperature for 1 day to yield crystals of the sulfate salt NaAl(SO4)(OH)(H2O)x·H2O. The crystals were separated by suction filtration, washed with deionized water, and dried. A 0.25 g portion of dry crystals was dispersed in 100 mL of deionized water, and a 10 mL portion of BaCl2·2H2O (1.15 mmol) was added to this suspension, which was stirred for 4 h and diluted to 250 mL (ca. 7 × 10⁻⁴ M Al2(SO4)3·2(H₂O)·xH₂O). The BaSO₄ produced in the reaction was removed by filtration and centrifugation.

**Supported Polymer/Catalyst Materials.** Two kinds of heterogeneous photocatalysts were made by loading the sensitizer polymer and colloidal IrO₂ onto spherical SiO₂ support particles. As a control experiment, underivatized SiO₂ was stirred in 10 mL of 7 M NaOH, and then centrifuged and re-suspended in 3 mL of deionized water. The amount of polymer adsorbed onto IrO₂/Keggin/SiO₂ was measured by the 460 nm absorbance of the supernatant rinse solution. The resulting loading was determined by measuring the 460 nm absorbance of the supernatant rinse solution. After 1 h, the colloidal IrO₂ samples were centrifuged and rinsed as described above.

**Photocatalytic Oxidation of Water.** Oxygen evolution was measured from photolysis of the monomeric tris(2,2'-bipyridyl)ruthenium complex ([Ru(bpy)₃]²⁺), in the presence of colloidal IrO₂, from the Ru-containing polymer in the presence of colloidal IrO₂, and from the heterogeneous photocatalysts A and B described above. All experiments were done using persulfate as a sacrificial electron acceptor in a Pyrex test tube reactor (36.5 mL total volume). The reactor was sealed with a silicone rubber septum and was enclosed in an outer Pyrex chamber with a rubber septum, with Ar flowing through the outer chamber in order to prevent atmospheric contamination of the inner reactor. The solutions were adjusted to pH 5.5–5.8 by using NaOH, KH₂PO₄, Na₂B₄O₇, or Na₂SiF₆– NaHCO₃ solutions. The total volume of the solution in the inner reactor was 5 mL, and the concentrations of Na₂S₂O₈ and Na₂SO₄ were 0.10 (50 mmol) and 0.28 g (1.2 mol). For O₂ evolution from the heterogeneous photocatalysts, 0.05–0.10 g of the catalysts (which contained 6.2 × 10⁻³ M colloidal IrO₂) were suspended in 5 mL of a solution composed of 5.0 × 10⁻² M Na₂SiF₆–NaHCO₃ (Na₂SiF₆ 2.2 × 10⁻² M; NaHCO₃, 2.8 × 10⁻² M), Na₂SO₄ (1.0 × 10⁻² M), and Na₂S₂O₄ (5.0 × 10⁻² M). The pH of the solution before reaction was 5.5–5.7. After being purged with Ar, the solutions were irradiated with constant stirring with a 300 W Xe lamp equipped with a 450 ± 20 nm interference filter. The gas accumulated in the dead volume of the reactor was withdrawn by a sample-lock syringe and was analyzed by gas chromatography using a thermal conductivity detector and Molecular Sieve 5Å packed columns (Supelco) held at ambient temperature. Air contamination, which could be detected as a nitrogen signal, was not observed. When the sacrificial acceptor was exhausted after photolysis, the reaction was resumed after 50 μmol of Na₂S₂O₄ was added to the reactor and the pH of the solution was restored to the initial value by the addition of NaHCO₃.

**Results and Discussion**

**Photochemical Oxygen Evolution from Ru Complex—Colloidal IrO₂ and Polymer—Colloidal IrO₂.** Figure 1 compares the time course of O₂ evolution from polymer—colloidal IrO₂ and [Ru(bpy)₃]²⁺—colloidal IrO₂ photosystems. The concentrations of the polymer, monomeric ([Ru(bpy)₃]²⁺), and colloidal IrO₂ were 1.2 × 10⁻⁵ (1.1 × 10⁻⁴ M on a monomer basis), 1.1 × 10⁻⁴, and 6.2 × 10⁻⁵ M, respectively. The pH of the solution before and after reaction is inset in the figure. The O₂ yield for the polymer—colloidal IrO₂ system in an unbuffered NaOH-containing solution was very low, and the pH fell rapidly during the reaction. In the unbuffered solution, the pH drops rapidly because the reaction produces H⁺, and at low pH, the thermodynamic driving force for O₂ evolution from [Ru(bpy)₃]³⁺ is reduced. O₂ evolution in [Ru(bpy)₃]²⁺—catalyst systems is known to proceed most efficiently in a narrow pH range around 5–6. When the polymer—colloidal IrO₂ system photosynthesis was carried out in a buffered solution (pH 5.8) with conventional phosphate buffer (KH₂PO₄, 7.2 × 10⁻⁴ M; Na₂B₄O₇, 2.9 × 10⁻³ M), the pH was almost constant during light irradiation but no oxygen was detected. This is consistent with our previous observations that phosphate accelerates the decomposition of Ru-complex sensitizers.¹⁷
[Ru(bpy)3]2+-colloidal IrO2 photocatalysts under visible-light irradiation (λ = 450 ± 20 nm): A, polymer–colloidal IrO2 system in a solution adjusted at pH 5.7 by NaOH; B, polymer–colloidal IrO2 photosystem in a Na2SiF6–NaHCO3 buffer containing solution; C, [Ru(bpy)3]2+-colloidal IrO2 photosystem in the Na2SiF6–NaHCO3 buffer-containing solution; solution, 5.0 mL; polymer, 1.4 × 10^{-5} M (1.1 × 10^{-4} M on a monomer basis); [Ru(bpy)3]2+, 1.1 × 10^{-4} M; colloidal IrO2, 6.2 × 10^{-8} M; Na2S2O8, 1.0 × 10^{-2} M; Na2SO4, 5.0 × 10^{-2} M; Na2SiF6–NaHCO3 buffer, 5.0 × 10^{-2} M (Na2SiF6, 2.2 × 10^{-2} M; NaHCO3, 2.8 × 10^{-2} M).

In a solution containing Na2SiF6 and NaHCO3 (Na2SiF6, 2.2 × 10^{-2} M; NaHCO3, 2.8 × 10^{-2} M), oxygen evolved from polymer–colloidal IrO2 solutions and the total turnover number exceeded 100. The initial quantum efficiency for O2 evolution was estimated to be 25% from the rate of O2 evolution (0.32 μmol min^{-1}) at the early stage of reaction (5–15 min) and the incident photon flux. The pH of the solution was almost constant during reaction as shown in Figure 1. This behavior is consistent with our previous observations of [Ru(bpy)3]2+-photolysis in the same buffer.17 Figure 2 correlates oxygen evolution activity with the concentration of the Ru-containing polymer. The rates were measured at the early stage of reaction (5–15 min). The turnover number reaches a maximum as the rate of O2 evolution reaches a plateau at a polymer concentration of 1.0–1.4 × 10^{-3} M. At low polymer concentration, the incident light is not efficiently absorbed and the oxygen evolution rate is near zero. Both the rate of oxygen evolution and the turnover number increase with increasing polymer concentration, suggesting that oxygen evolution only occurs when the polymer molecules are adsorbed on the colloidal. Similar behavior was found for the monomeric [Ru(bpy)3]2+-sensitizer.17 Beyond 1.0–1.4 × 10^{-5} M concentration, the background hydrolysis rate exceeds the rate of oxygen evolution and the turnover number decreases. This drop in turnover number is consistent with the idea that at high polymer concentration a larger fraction of the [Ru(bpy)3]2+-sensitizer is photo-oxidized but is not involved in oxygen evolution, because it does not have access to the IrO2 catalyst surface.

The Ru-containing polymer aggregated gradually during the reaction, as evidenced by the fact that it precipitated from a quiescent solution, and the Na2SiF6–NaHCO3 buffer was found to accelerate this process. When 5 mL of Na2SiF6–NaHCO3 solution (Na2SiF6, 2.2 × 10^{-2} M; NaHCO3, 2.8 × 10^{-2} M) containing 1.4 × 10^{-5} M polymer was stirred in the dark, the amount of aggregated polymer that precipitated increased with stirring time and reached ca. 70% of the polymer in the solution (4.9 × 10^{-8} mol) after 3 h of stirring. Further stirring did not increase the amount of aggregated polymer. Neither the Na2SiF6 solution nor the NaHCO3 solution precipitated the polymer, and a Na2SiF6–Na2B4O7 solution at pH 5.7 (Na2SiF6, 2.6 × 10^{-2} M; Na2B4O7, 0.11 M) aggregated the polymer as well as the Na2SiF6–NaHCO3 solution; therefore, the aggregation is attributed to a reaction between Na2SiF6 and the base. Silicic acid, H2SiO3, or colloidal silica formed by the hydrolysis of Na2SiF6 are likely candidates for the aggregation of the cationic polymer, because both should be polyanions at pH 5.5–5.8.18 The aggregation of the polymer in the Na2SiF6–NaHCO3 solution was not entirely irreversible. A rinse with 20 mL of 10^{-3} M HCl solution (pH 5.7) dissolved ca. 70% of the above aggregated polymer (3.2 × 10^{-8} mol) in the rinse solution.

The polymer–colloidal IrO2 system had a lower photocatalytic activity than the monomeric [Ru(bpy)3]2+-colloidal IrO2 system under the same conditions. As shown in Figure 1, 25 μmol of O2 was evolved from the latter system without any decrease in activity.17 This value corresponds to the stoichiometric amount of O2 that can be evolved from the sacrificial acceptor. Monomeric [Ru(bpy)3]2+ was not aggregated during the reaction, and no precipitate was found after stirring the solution in dark for 1 day. It is probable that the aggregation of the polymer causes the difference in activity between both systems. In the aggregated state, not all of the Ru subunits of the polymer are within electron transfer distance of the colloidal catalyst.

To examine the effects of aggregation of the polymer, [Ru(bpy)3]2+-colloidal IrO2 and polymer–colloidal IrO2...
solutions were irradiated with light after being allowed to stand for 1–5 h in dark before reaction. The aging period before reaction did not influence the activity of [Ru(bpy)₃]²⁺, while the activity of the polymer solution decreased substantially with time. Aging for 3 h reduced the rate of evolution and total turnover number to ca. 1/10th of their values under optimized conditions. Figure 3 shows TEM images of colloidal IrO₂ and aggregated polymer with colloidal IrO₂: A, colloidal IrO₂; B, polymer and colloidal IrO₂ aggregated in Na₂SiF₆–NaHCO₃ solution.

Figure 3. TEM images of colloidal IrO₂ and aggregated polymer with colloidal IrO₂: A, colloidal IrO₂; B, polymer and colloidal IrO₂ aggregated in Na₂SiF₆–NaHCO₃ solution.

polymer–colloidal IrO₂ photocatalysts, we prepared composites in which these components were immobilized on spherical silica particles. These silica particles serve as a model for more complex anionic supports, such as layered metal oxide semiconductors, which might be used to couple the oxygen evolution reaction to photocatalytic hydrogen evolution.⁷,⁸ To couple the polymer and IrO₂ to anionic silica, two approaches were tried. In one, cationic aluminum Keggin ions (Al₁₃O₄(OH)₂₄⁻·(H₂O)₁₂)⁷⁺ were first adsorbed to make the silica surface cationic. The IrO₂ colloid and sensitizer polymer were then sequentially adsorbed. In the other approach, the cationic polymer/IrO₂ composite was directly adsorbed on the anionic silica surface. The structure and catalytic activity of these composites were then compared.

**Oxygen Evolution from Polymer/IrO₂/Keggin/SiO₂**

The polymer/IrO₂/Keggin/SiO₂ samples prepared in dilute HCl solution had no photocatalytic activity for oxidation of water. The largest amount of adsorbed polymer on an IrO₂/Keggin/SiO₂ substrate (IrO₂, 3.1 × 10⁻⁷ mol; SiO₂, 0.10 g) was 5.8 × 10⁻⁸ mol (5.2 × 10⁻⁸ mol on a monomer basis). When 3.1 × 10⁻⁷ mol of colloidal IrO₂ was deposited onto 0.05–0.10 g of SiO₂, the maximum loading of the polymer increased in proportion to SiO₂ support, indicating that most of the polymer is not adsorbed on the colloidal IrO₂ particles but on the SiO₂ support itself. The water oxidation reaction becomes more efficient with increasing addition of the polymer to the solution. However, the polymer adsorbed onto IrO₂/Keggin/SiO₂ in an unbuffered solution does not oxidize water, presumably because little or none of it is in physical contact with IrO₂.

To increase the polymer loading on the IrO₂/Keggin/SiO₂ supports, the latter was stirred with a Na₂SiF₆–NaHCO₃ solution containing the polymer. In this case, IrO₂/Keggin/SiO₂ adsorbs the polymer aggregated by base hydrolysis of Na₂SiF₆. Figure 4 shows the time course of O₂ evolution from these samples. The amounts of SiO₂ support and deposited IrO₂ were 0.05 g and 3.1 × 10⁻⁷ mol, respectively. Total turnover numbers with respect to the monomeric Ru complex in the polymer are inset in the figure. The sample at 2.2 × 10⁻⁷ mol
(1.8 \times 10^{-6} \text{ mol monomer}), which was the maximum loading of the polymer under these conditions, had the highest activity among the polymer/IrO2/Keggin/SiO2 samples (IrO2, 5.0 \times 10^{-8} \text{ to } 1.1 \times 10^{-6} \text{ mol}; SiO2, 0.05 g). The amount of loaded polymer corresponded to ca. 70 times that in unbuffered dilute HCl solution and was larger than the total amount of the polymer in the polymer–colloidal IrO2 system (7.0 \times 10^{-8} \text{ mol} in 5 \text{ mL} (1.4 \times 10^{-5} \text{ M})). TEM images of the IrO2/Keggin/SiO2 and polymer/IrO2/Keggin/SiO2 samples under the optimal conditions are shown in Figure 5. A colloidal IrO2 particle of 20 nm diameter is attached to a 70 nm diameter SiO2 particle through Keggin ions on IrO2/Keggin/SiO2, and the TEM image of polymer/IrO2/Keggin/SiO2 shows that the substrate is covered with aggregated polymer. These results show that while the aggregated polymer is bound to the support, the activity is quite small compared to that of the unsupported polymer–colloidal IrO2 system.

Photocatalytic Oxidation of Water by Polymer–IrO2/SiO2. Polymer–IrO2/SiO2 samples (SiO2, 0.04 g) prepared in dilute HCl solution showed low oxygen evolution activity even under optimized conditions. The highest rate of O2 evolution and total turnover number were obtained with a maximum loading of the polymer (2.8 \times 10^{-8} \text{ mol}) and 8.1 \times 10^{-7} \text{ mol} of colloidal IrO2 but were only 0.01 \mu\text{mol min}^{-1} and 10, respectively.

On the other hand, the preparation of similar composites in a Na2SiF6–NaHCO3 solution resulted in efficient photocatalysts. Figure 6 compares the time course of O2 evolution from a polymer–IrO2/SiO2 sample prepared in Na2SiF6–NaHCO3 solution (polymer, 6.9 \times 10^{-8} \text{ mol} and IrO2, 3.1 \times 10^{-7} \text{ mol}) to that from a polymer–colloidal IrO2 sample (polymer, 6.9 \times 10^{-8} \text{ mol}; colloidal IrO2, 3.1 \times 10^{-7} \text{ mol}). The quantum efficiency for O2 evolution and total turnover number reached 20% and 80, respectively, which were somewhat lower than those of the polymer–colloidal IrO2 system. There was no noticeable difference in activity before and after the sample had been allowed to stand for 5 h prior to reaction, indicating that the silica support stabilizes the polymer/IrO2 composite against further aggregation. A TEM image of the polymer–IrO2/SiO2 sample is shown in Figure 7. The dark spots on the SiO2 particles covered with the aggregated polymer have the diameter that was expected for colloidal IrO2 particles, implying that the anionic SiO2 particles adsorb dispersed IrO2 particles covered by the cationic polymer. Figures 8 and 9 correlate the photocatalytic activity with the amounts of the adsorbed polymer and SiO2, respectively, and show that the highest activity is obtained by loading 6.9 \times 10^{-8} \text{ mol of the polymer and } 3.1 \times 10^{-7} \text{ mol of colloidal IrO2 onto } 0.04 \text{ g of SiO2. Although the preparation in Na2SiF6–NaHCO3 solution can increase the loading of the polymer on the SiO2 support, the adsorption of more polymer than } 6.9 \times 10^{-8} \text{ mol reduced the activity. This is possibly due to an inner filter of light that limits the amount of light reaching the support.}

Figure 5. TEM images of IrO2/Keggin/SiO2 and polymer/IrO2/Keggin/SiO2 samples: SiO2, 0.05 g; IrO2, 3.1 \times 10^{-7} \text{ mol; polymer, } 2.2 \times 10^{-7} \text{ mol.}

Figure 6. Time course of O2 evolution from polymer–IrO2/SiO2 system: A, polymer–IrO2/SiO2 sample (polymer, 6.9 \times 10^{-8} \text{ mol, and } 3.1 \times 10^{-7} \text{ mol; SiO2, 0.05 g); B, polymer–colloidal IrO2 sample (polymer, 1.4 \times 10^{-8} \text{ mol, and } 6.2 \times 10^{-8} \text{ mol).}}
absorption by the large amount of adsorbed polymer. As shown in Figure 9, a sample prepared without the SiO$_2$ support has low activity compared with polymer–IrO$_2$/SiO$_2$ or polymer–colloidal IrO$_2$ samples because of aggregation of the polymer during sample preparation. These results suggest that SiO$_2$ particles prevent the polymer-covered IrO$_2$ particles from aggregating and thereby prevent the loss of photocatalytic activity. In Figure 9, the addition of SiO$_2$ beyond 0.04 g reduces the activity. This is consistent with the idea that excess anionic SiO$_2$ support increases the polymer adsorption onto SiO$_2$ and therefore decreases polymer contact with IrO$_2$.

It is important to understand the characteristics of colloidal IrO$_2$ and the role of the Na$_2$SiF$_6$–NaHCO$_3$ buffer in making a comparison between heterogeneous photocatalysts. The activity of the polymer–IrO$_2$/SiO$_2$ system prepared in an unbuffered solution is very low even though the sample adsorbs a relatively large amount of the sensitizer polymer ($2.8 \times 10^{-8}$ mol). The polymer–colloidal IrO$_2$ system containing the same amounts of polymer and colloidal IrO$_2$ has activity that is several times higher. This implies that most of the polymer on the heterogeneous photocatalyst is adsorbed on SiO$_2$ and is not available for the reaction. On the other hand, the same preparation in Na$_2$SiF$_6$–NaHCO$_3$ buffer attaches colloidal IrO$_2$ particles covered with the aggregated polymer to the SiO$_2$ support, and this leads to a relatively high photocatalytic activity. In the case of the polymer/Ir$_2$O$_7$/Keggin/SiO$_2$ samples prepared in Na$_2$SiF$_6$–NaHCO$_3$ solution, the high loading of the aggregated polymer does not result in high efficiency. TEM images of the low activity polymer/Ir$_2$O$_7$/Keggin/SiO$_2$ samples and high activity polymer–Ir$_2$O$_7$/SiO$_2$ samples are quite similar (Figures 5 and 7, respectively), but the microscopic distribution of components is apparently quite different. These results can be reasonably explained by the idea that the cationic Keggin ions bind the IrO$_2$ particles to the silica surface, in the case of the polymer/Ir$_2$O$_7$/Keggin/SiO$_2$ samples, but that the photosensitizer polymer preferentially binds to SiO$_2$ rather than IrO$_2$.

Conclusions

A cationic polymer containing tris(4,4′-dialkyl-2,2′-bipyridyl)ruthenium groups linked by aliphatic spacers photocatalytically oxidizes water in the presence of colloidal IrO$_2$ in a pH 5.5–5.7 Na$_2$SiF$_6$–NaHCO$_3$ buffer. The quantum efficiency for O$_2$ evolution and O$_2$ yield of the polymer–colloidal IrO$_2$ system are smaller than those of the monomer tris(2,2′-bipyridyl)ruthenium complex–IrO$_2$ system because Na$_2$SiF$_6$–NaHCO$_3$ solution gradually aggregates the polymer.

With polymer/Ir$_2$O$_7$/Keggin/SiO$_2$ and polymer–Ir$_2$O$_7$/SiO$_2$ heterogeneous photocatalysts prepared in unbuffered solutions, the polymer is not significantly adsorbed onto IrO$_2$, and the photocatalytic activities are quite low. Preparation of these catalysts in the Na$_2$SiF$_6$–NaHCO$_3$ buffer substantially increases the loading by aggregation of the polymer, presumably through formation of anionic poly(silicate) or colloidal SiO$_2$ particles. The polymer/Ir$_2$O$_7$/Keggin/SiO$_2$ composites prepared under these conditions show low activity because the amount of sensitizer polymer available for the reaction is actually small despite the total adsorbed amount being large. When the polymer and colloidal IrO$_2$ are adsorbed onto SiO$_2$ in Na$_2$SiF$_6$–NaHCO$_3$ solution, the colloidal
IrO$_2$ particles are covered with a sufficient amount of the aggregated polymer to give a photocatalytic activity comparable to that of the polymer–colloidal IrO$_2$ system. To our knowledge, this is the first example of a heterogeneous water oxidation photosystem containing a polymeric sensitizer. Polyanions or anionic inorganic sheets such as Zr(HPO$_4$)$_2$$\cdot$H$_2$O or HTiNbO$_5$ could, in principle, be adsorbed onto the surface of the cationic polymer–IrO$_2$/SiO$_2$ or polymer–IrO$_2$/SiO$_2$ composites and might serve to couple these photocatalysts to electron acceptors other than persulfate. Future work will focus on linking electron/energy transfer cascades, grown layer-by-layer on these supports, to supported catalysts for oxygen evolution.

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