Research Article

Preparation of TiO$_2$-Fullerene Composites and Their Photocatalytic Activity under Visible Light

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Received 8 July 2011; Accepted 1 September 2011

Academic Editor: Shifu Chen

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The development of visible light-sensitive photocatalytic materials is being investigated. In this study, the anatase and rutile-C$_{60}$ composites were prepared by solution process. The characterization of the samples was conducted by using XRD, UV-vis, FT-IR, Raman, and TEM. The photocatalytic activity of the samples was evaluated by the decolorization of the methylene blue. From the results of the Raman, FT-IR, and XRD, the existence of the C$_{60}$ was confirmed in the samples. The C$_{60}$ was modified on the anatase or rutile particle as a cluster. The C$_{60}$ didn’t have the photocatalytic activity under UV and visible light. The anatase and rutile-C$_{60}$ composites exhibited lower photocatalytic activity than the anatase and rutile under UV light. The anatase-C$_{60}$ exhibited also lower activity than the anatase under visible light. On the other hand, the rutile-C$_{60}$ exhibited higher activity than the rutile under visible light. It is considered that the photogenerated electrons can transfer from the C$_{60}$ to the rutile under visible light irradiation.

1. Introduction

Since the photocatalytic activity of a TiO$_2$ was discovered in 1970s, it has been studied by many researchers because nontoxic, chemical stable, inexpensive, and widely available [1, 2]. When TiO$_2$ is irradiated by ultraviolet (UV) light, electron (e$^-$) and hole (h$^+$) pairs are generated and produce radical species such as OH radicals and O$_2^-$ by reaction with moisture in the atmosphere, which reduce and oxidize adsorbates on the surface. These radicals can decompose most organic compounds and bacteria [3–7]. Therefore, the photocatalyst has been applied on various industrial fields [8, 9]. However, since the band gap of TiO$_2$ is 3.0–3.2 eV, the TiO$_2$ photocatalyst is activated only by UV light irradiation (<400 nm) [10].

To exhibit the photocatalytic activity under visible light, metal (Cr, V, Fe, Mn, Co, and Ni) doping into Ti site and anion (N, S, and C) doping into O site have been studied [11–20]. These doped TiO$_2$ can be sensitive to visible light, but the oxidative power of holes decreases. Because the holes are generated in a localized narrow band originating from the dopant metal ions or anions in the forbidden band of TiO$_2$.

Recently, it has been reported that TiO$_2$ powders with grafted metal ions (Cu(II), Cr(III), Ce(III), and Fe(III)) were capable of serving as photocatalysts sensitive to visible light [21–25]. This system is called the interfacial charge transfer (IFCT) and has greatly an oxidative decomposition activity.

Among these materials, carbon-supported TiO$_2$ also exhibited the photocatalytic activity under visible light [26–30]. Fullerene (C$_{60}$) has the interesting properties which are the delocalized conjugated structures and electron-accepting ability. C$_{60}$ can efficiently promote a rapid photoinduced charge separation and slow charge recombination. Although the role of C$_{60}$, accepting the photogenerated electrons from TiO$_2$ particles, has been demonstrated, a few efforts are made to utilize the unique properties of C$_{60}$ to increase the efficiency of photocatalysis [31, 32]. However, the mechanism is not clear in detail.

In this study, TiO$_2$-C$_{60}$ composites were prepared and characterized, and the photocatalytic activity under UV and visible light was evaluated, comparing to the pure TiO$_2$. The mechanism of visible light-sensitive photocatalyst was investigated by using the photodeposition of platinum (Pt).
2. Experimental

2.1. Preparation of TiO$_2$-Fullerene Composites. Fullerene (C$_{60}$) solution was prepared by adding C$_{60}$ (1, 5, 10 mg) into toluene (30 mL) and mixing for 10 min. TiO$_2$ powder (anatase or rutile; 100 mg) was put in the solution, and it was mixed at 80°C for 24 hours. Then, the solution was evaporated and dried at 90°C, and the TiO$_2$-C$_{60}$ composite samples were obtained. The anatase powder and toluene were taken from Wako Pure Chemical Industries, Tokyo, Japan. The C$_{60}$ (carbon cluster; ST) was taken from Kanto Chemicals Co. Inc., Tokyo, Japan. The rutile powder (MT-150A) was taken from TAYCA Co., Tokyo, Japan. The samples with different C$_{60}$-additive amount are denoted in this report as “AXC or RXC.” A, R, X, and C indicate the anatase, rutile, C$_{60}$ additive amount, and C$_{60}$, respectively. For example, A1C means 1 mass % C$_{60}$ added anatase sample.

2.2. Synthesis of Photodeposited Samples. The prepared TiO$_2$-fullerene composite samples were dispersed in 3:7 (v/v) methanol/water solution (20 mL), and then the required amount (5 mass%) H$_2$PtCl$_6$ solution was added in. The mixture was irradiated by fluorescent light with cut filter (>420 nm) for 3 hours at room temperature. After irradiation, the sample was collected by centrifugation and washed several times with distilled water. The obtained paste was dried at 80°C.

2.3. Characterization of the Samples. The crystalline phases were identified by a high-power X-ray diffractometer (XRD, RINT-TR3B; Rigaku, Japan) using monochromated Cu Ka radiation (50 kV–200 mA). The samples were analyzed using a Raman spectroscopy (RAMANOR T64000; Jobin-Yvon S.A.S., France) with an Ar laser (514.5 nm) operated at 50 mW. UV-visible absorption properties of the samples were measured using a UV-visible scanning spectrophotometer (UV-vis, Lambda 35; PerkinElmer Inc., USA). Transmission electron microscopy (TEM) observation of the samples was performed using a transmission electron microscope (TEM, HF-2000, Hitachi, Japan) operating at 200 kV. IR measurements were performed using a Fourier transform-infrared spectroscopy (FT-IR, JIR-7000, JEOL, Japan).

2.4. Evaluation of Photocatalytic Activity. Photocatalytic activity of the samples was evaluated by decomposition of methylene blue (MB; C$_{16}$H$_{18}$ClN$_3$S). The samples were immersed in 0.02 mM MB aqueous solution for overnight to saturate the adsorption. After washing by ultrapure water, a cylinder (φ40 × 30 mm) was contacted on the SiO$_2$ glass (50 × 50 × 2t mm) by using silicone grease, and 0.01 mM MB aqueous solution was poured into the cylinder. And then, the samples (0.05 g) were put into the solution. Irradiating overhead UV light (1.0 mW/cm$^2$) or fluorescent light (10,000 lx), the absorption spectra of MB were measured by a UV-vis spectrophotometer.

3. Results and Discussion

3.1. Characterization of the TiO$_2$-C$_{60}$ Composite Samples. Anatase and rutile were white powders because they cannot absorb the wavelength in visible range. The obtained sample with C$_{60}$, however, had a color. With increasing C$_{60}$-additive amount, the color of the samples became gray. Figure 1 shows the UV-vis absorption spectra of the samples. The absorption spectra of MB were measured by a UV-vis spectrophotometer.
>400 nm, and the adsorption edge was about 700 nm. This is indicated that the sample with C\textsubscript{60} had absorption property in visible range. The spectrum shape of the sample with C\textsubscript{60} was similar to the C\textsubscript{60}, and the absorption increased with increasing C\textsubscript{60}-additive amount. Therefore, it is considered that the absorption in visible range is attributed to the C\textsubscript{60}.

Figure 2 shows the XRD patterns of the samples. The crystalline phases detected in the anatase composite samples were anatase, rutile, and C\textsubscript{60} (Figure 2(a)). Rutile was a little included in the anatase composite sample. This is attributed to the starting materials (chemical), and it was not formed during preparation process of the anatase-C\textsubscript{60} composite samples. The C\textsubscript{60} peaks of the A1C sample were not seen clearly, but the peaks appeared in the A5C and A10C samples. In the case of the rutile composite samples, the crystalline phases were rutile and C\textsubscript{60}, and anatase was...
Figure 4: Raman spectra of the TiO$_2$-C$_{60}$ composite samples. (a) The A1C, A5C, and A10C samples, (b) the R1C, R5C, and R10C samples.

Figure 5: High resolution TEM image of the R5C samples.

not included (Figure 2(b)). The C$_{60}$ peaks of the R1C sample were not seen clearly, but the peaks appeared in the R5C and R10C samples. This is the similar tendency in the anatase composite samples. In both cases, the values of the full width at half maximum (FWHM) in the anatase (101) peak ($2\theta$ = 25.32°) and rutile (110) peak ($2\theta$ = 27.44°) were almost the same, respectively. This is indicated that the crystallinity of the anatase or rutile composite samples have almost the same crystallinity, respectively.

Figure 3 shows the IR adsorption spectra of the samples measured in air at room temperature. In the infrared bands of C$_{60}$, there are the four most intense lines at 1429, 1183, 577, and 528 cm$^{-1}$ [33, 34]. The absorption bands at 1429 and 1183 cm$^{-1}$ were observed in A5C, A10C, R5C, and R10C samples, but those were not observed in A1C and R1C samples (Figures 3(a) and 3(b)). The adsorption bands at 577 and 528 cm$^{-1}$ were not seen in all samples because widely adsorption of TiO$_2$ was at 400–900 cm$^{-1}$. On the other hand, the adsorption band at 1618 cm$^{-1}$ was seen in all samples. This is attributed to the bending vibration of the H$_2$O molecule adsorbed on Ti$^{4+}$ site [35].

The Raman spectra of the samples are shown in Figure 4. The peak at 1642 cm$^{-1}$ appeared in all samples (Figures 4(a) and 4(b)). Cataldo [36] reported that the Raman spectrum of pure C$_{60}$ is characterized by several lines, the most intense which are the $A_g(1)$ and $A_g(2)$ modes lying, respectively, at 496 and at 1469 cm$^{-1}$. The $A_g(2)$ mode is also referred as the pentagonal pinch mode. It is considered that the peak observed at 1642 cm$^{-1}$ is $A_g(2)$ mode of C$_{60}$. The existence of the C$_{60}$ in A1C and R1C samples could not be detected by XRD and IR, but it could be confirmed by the Raman spectra. In A10C and R10C samples, the broad band at around 1600 cm$^{-1}$ appeared. It is guessed that the band is attributed to the carbon cluster.

Figure 5 shows the high resolution TEM image of the R5C sample. Considering the space of the lattice fringe, the particle was confirmed to rutile. Some small particles were observed at the edge of the rutile particle. In the case of the anatase-C$_{60}$ composite samples, the small particles were also observed at the edge of the anatase particles (not shown here). These particles were not the rutile and anatase particles. It is guessed that these small particles are the C$_{60}$ particles adhered to the rutile particles. In the TiO$_2$-C$_{60}$ composite samples, we consider that the C$_{60}$ particles are directly present on the surface of the TiO$_2$ particles.

3.2. Evaluation of the Photocatalytic Activity of the TiO$_2$-C$_{60}$ Composite Samples. Figure 6 shows the photocatalytic degradation of MB in the C$_{60}$. If the C$_{60}$ has photocatalytic
activity, MB is decolorized. Figure 6(a) shows the test under UV irradiation. When UV irradiation time increased, the variation of the MB concentration was little. This result indicates that the C₆₀ has little photocatalytic activity under UV light irradiation. The MB concentration slightly decreased with increasing visible light irradiation time (Figure 6(b)). However, the decrement of the MB concentration was a little. It is considered that the C₆₀ exhibited little the photocatalytic activity under UV and visible light.

Figure 7 shows the photocatalytic degradation of MB in the anatase, rutile, and anatase or rutile-C₆₀ composite samples under UV irradiation. When UV irradiation time
increased, the MB concentration of the anatase, A1C, A5C, and A10C samples decreased (Figure 7(a)). Among them, the MB concentration of the anatase decreased drastically. This result indicates that the photocatalytic activity of the A1C, A5C, and A10C samples is lower than that of the anatase. The activity of the A1C sample was higher than that of the A5C and A10C samples, and the A5C sample indicates a similar tendency to the A10C sample. With increasing the C\textsubscript{60} additive amount, the activity was lower in the anatase-C\textsubscript{60} composite samples. In the case of the rutile and rutile-C\textsubscript{60} composite samples, the decrement of the MB concentration in the rutile became the largest (Figure 7(b)). This is indicated that the photocatalytic activity of the rutile is higher than that of the rutile with the C\textsubscript{60} (R1C, R5C, and R10C samples). The activity of the R10C sample was higher than that of the R1C and R5C samples, and the R5C sample was higher than the R1C sample. The tendency was different from the anatase-C\textsubscript{60} composite samples. The anatase and rutile-C\textsubscript{60} composite samples exhibit lower photocatalytic activity under UV irradiation than anatase and rutile. It is guessed that the anatase and rutile surfaces are covered by the C\textsubscript{60}, and the number of absorbed photons in the anatase and rutile decreases.
Figure 8 shows the photocatalytic degradation of MB in the anatase, rutile, and anatase or rutile-C\textsubscript{60} composite samples under visible light irradiation. In Figures 8(a) and 8(b), the MB concentration of the anatase and rutile decreased with increasing visible light irradiation time. This result indicates that the anatase and rutile have the photocatalytic activity under visible light irradiation. This is because fluorescent light was used as a light source, so a little UV light was included in the light source. All samples exhibited the photocatalytic activity under visible light irradiation shown in Figure 8(a). But the activity of the A1C, A5C, and A10C samples was lower than the anatase. This is similar tendency to the case of UV irradiation (Figure 7(a)). On the other hand, the R1C, R5C, and R10C samples exhibited higher photocatalytic activity than the rutile (Figure 8(b)). This result indicates that the rutile-C\textsubscript{60} composite samples have greatly the photocatalytic activity under visible light.

The band structures of the anatase, rutile, and \textit{C}_60 are shown in Scheme 1. In the case of the \textit{C}_60, some researchers reported different band structures \cite{37, 38}. The conduction band (CB) positions of the \textit{C}_60 were higher energy than those of the anatase and rutile. Therefore, it is prospective that the photogenerated electrons transfer from the CB of the \textit{C}_60 to the CB of the anatase and rutile, and the anatase and rutile-C\textsubscript{60} composite samples have a higher photocatalytic activity than the anatase and rutile under visible light shown in Scheme 2. However, the anatase-\textit{C}_60 composite samples exhibited higher photocatalytic activity under visible light than the anatase (Figure 8(a)).

Figure 9 shows the TEM images of the A5C and R5C samples after conducting the photodeposition of Pt under visible light irradiation. In the case of A5C sample, the photodeposited Pt particles were not observed at the anatase particles but the \textit{C}_60 cluster. This is indicated that the photogenerated electrons cannot transfer from the \textit{C}_60 to the anatase (Scheme 3(a)). On the other hand, in the case of the R5C sample, the photodeposited Pt particles were observed at the rutile. This result indicates that the photogenerated electrons can transfer from the \textit{C}_60 to the rutile (Scheme 3(b)). Therefore, it is considered that the rutile-\textit{C}_60 composite samples exhibit the photocatalytic activity under visible light.

From the band structure shown in Scheme 1, it is possible that the photogenerated electrons transfer from the \textit{C}_60 to the anatase. In this study, however, it did not occur. It is guessed that the connecting state between the \textit{C}_60 and the anatase is one of the reasons why the photogenerated electrons cannot transfer from the \textit{C}_60 to the anatase. Further investigation is needed to clear the reasons.

Photocatalytic activity of the \textit{C}_60-rutile composite sample was superior to the \textit{C}_60-anatase sample under visible light (Figure 7). On the other hand, the \textit{C}_60-rutile sample exhibited lower activity than the \textit{C}_60-anatase sample under UV light (Figure 8). In this study, the number of photons absorbed to the samples was not uniformed in UV and visible lights shown in UV-visible absorption spectra (Figure 1). It is, therefore, difficult to compare the photocatalytic activities of the \textit{C}_60-anatase and \textit{C}_60-rutile samples under UV-visible light. However, the photocatalytic degradation rate of MB was greatly different between under UV and visible lights, and the rate under UV light was higher than that under visible light. It is guessed that the \textit{C}_60-anatase sample exhibits higher activity than the \textit{C}_60-rutile under UV-visible light.

### 4. Conclusions

In present study, the anatase and rutile-\textit{C}_60 composites were prepared, and the photocatalytic activity of the composites was investigated by the MB decolorization test. The \textit{C}_60 particles were directly adhered to the surface of the TiO\textsubscript{2} particles. When UV light was irradiated, the photocatalytic activity of the anatase and rutile-\textit{C}_60 composites became lower than the anatase and rutile particles without the \textit{C}_60. In the case of the visible light irradiation, the anatase-\textit{C}_60 composite exhibited also lower activity than the anatase. However, the rutile-\textit{C}_60
composite exhibited higher activity than the rutile. From the photodeposition of Pt on the composites under visible light, the photogenerated electron transfer from the C60 to the rutile occurred although the electron transfer did not occur in the anatase-C60 composite. Therefore, the rutile-C60 composite exhibits the photocatalytic activity under visible light. The rutile-C60 can be utilized for the new type of visible light sensitive photocatalyst.

Acknowledgments

The authors are grateful to Mr. Y. Komatsubata in Tokyo Institute of Technology for the HR-TEM observation. This work was supported, in part, by a “Grant-in-Aid for Cooperative Research Project of Nationwide Joint-Use Research Institutes on Advanced Materials Development and Integration of Novel Structured Metallic and Inorganic Materials” and “Inamori Foundation.”

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