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Preparation of TiO_2–Carbon Nanotube Composite Catalysts for Improvement of the Photocatalytic Activity of TiO_2

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TiO_2 nanoparticles were deposited on carbon nanotubes (CNTs) for improvement of their photocatalytic activity. CNTs could be uniformly covered with TiO_2 nanoparticles by the hydrolysis of titanium tetraisopropoxide in the presence of urea. Urea worked as linker molecules between the CNT surface and the TiO_2 nanoparticles. The resultant TiO_2–CNT composites showed a high catalytic activity for photodegradation of organic molecules.

Semiconducting materials such as TiO_2 are utilized as photocatalysts for the removal of organic contaminants in water or air and for hydrogen formation through water splitting. UV light irradiation causes the photoactivation of TiO_2 to generate electron–hole pairs. The electron–hole pairs in TiO_2 have a strong redox property to catalyze various reactions. However, the quantum yield of TiO_2 is not so high because of the rapid recombination of the electrons and holes generated by UV light irradiation. Thus, TiO_2 is frequently combined with carbon nanotubes (CNTs).[1–3] The electrons generated by photoirradiation of the TiO_2–CNT composites are transferred from TiO_2 to the CNTs, which retards the recombination of the electron–hole pairs. The TiO_2–CNT composites thus show a high photocatalytic activity. The TiO_2–CNT composites have been prepared by sol–gel methods from titanium alkoxides.[4–6] However, the deposition of TiO_2 onto CNT surfaces is a challenging task because of the chemical inertness of CNTs.[7,8] The introduction of functional groups such as –COOH and –OH groups onto CNTs enhances the interaction between the CNTs and TiO_2.[9,10] However, the density of the TiO_2 nanoparticles deposited on the CNT surfaces is not always high because of a low density of functional groups on the CNT surfaces and/or a weak interaction between TiO_2 and the functional groups. On the other hand, CNTs are modified with surfactant molecules such as sodium dodecyl sulfate or poly(ethyleneimine).[11–13] These surfactants led to the strong interaction between the CNTs and TiO_2 particles. However, it is difficult to remove surfactant molecules from CNTs without damaging the CNT surfaces. Unfortunately, the surfactant molecules left on the TiO_2–CNT composites sometimes spoil their catalytic activity. Thus, novel methods to uniformly cover the CNT surfaces with TiO_2 nanoparticles are required.

In the present study, we demonstrated that CNTs could be uniformly covered with TiO_2 nanoparticles by hydrolysis and condensation of titanium tetraisopropoxide ($Ti(O\textit{i}\text{-}Pr)_4$) in the presence of urea or glycine amide. Urea or glycine amide works as a linker molecule between the TiO_2 nanoparticles and CNT surface. The TiO_2–CNT composites showed a high catalytic activity for the photodegradation of organic molecules.

Multiwalled CNTs were refluxed in concentrated HNO_3 solution at 395 K to introduce oxygen-containing functional groups on their surfaces. $Ti(O\textit{i}\text{-}Pr)_4$ (0.5 mL) was diluted with 2-propanol (95 mL), and then 5 mL of 3.6 M HCl was added to the solution. CNTs (0.10 g) were ultrasonically dispersed in this solution at room temperature. The solution was heated at 323 K in air under magnetic stirring after the addition of urea (0.20 g). After filtration, the samples thus obtained were calcined at 603 K in air. Thermogravimetric analysis for TiO_2–CNT composites in air showed that CNTs in the composites were gradually gasified at temperatures higher than 650 K.

The photodegradation of acetic acid was performed over the TiO_2–CNT composites with a conventional batch-type reactor made from quartz. The catalysts were loaded into the reactor such that the amount of TiO_2 was the same (0.010 g) for all the reactions. The TiO_2–CNT composite was dispersed and stirred in an aqueous solution of acetic acid (0.20 mol L^{-1}) for 3 h at room temperature under oxygen atmosphere before photoirradiation to the reactor. The suspension was irradiated with an ultrahigh-pressure Hg lamp at room temperature. During the reactions, a part of the gas in the reactor was sampled and analyzed by gas chromatography.

CNTs were dispersed in a mixed solution of $Ti(O\textit{i}\text{-}Pr)_4$, 2-propanol, and aqueous HCl without any linker molecules to cover the CNTs with TiO_2. The TiO_2–CNT composite thus obtained was denoted as TiO_2–CNT(none). Figures 1a and 1b show TEM images of TiO_2–CNT(none). The loading of TiO_2 in the composites was evaluated by thermogravimetric analysis in air to be 45 wt %. CNTs were observed in the TEM images and the diameters of the CNTs ranged from 15 to 30 nm. Many particles were deposited on the outer surface of the CNTs. These particles in the TEM images were assignable to TiO_2 in the anatase phase, as confirmed from the corresponding X-ray diffraction pattern described below. Many TiO_2 particles were deposited on the outer surface of the CNTs in the TiO_2–CNT(none), but the exposed CNT surfaces could also be easily found in the TEM images. In addition, many TiO_2 particles, which were not in contact with the CNTs, were also observed. During the preparation of TiO_2–CNT(none), hydrolysis and condensation of $Ti(O\textit{i}\text{-}Pr)_4$ proceeded to form TiO_2 nanoparticles. The interaction between TiO_2 nanoparticles and the functional groups on CNT surfaces was not strong enough to enable the whole surface of the CNTs to be covered with TiO_2 particles.

The TiO_2–CNT composites were prepared by the hydrolysis of $Ti(O\textit{i}\text{-}Pr)_4$ in the presence of urea. The composites thus obtained were denoted as TiO_2–CNT(urea). The TEM images of TiO_2–CNT(urea) are shown in Figures 1c and 1d. The loading of TiO_2 in TiO_2–CNT(urea) was evaluated to be 58 wt %. The whole surfaces of the CNTs in TiO_2–CNT(urea) seemed to be uniformly covered with TiO_2 nanoparticles, and the exposed CNT surfaces were rarely seen in the TEM images. It is well

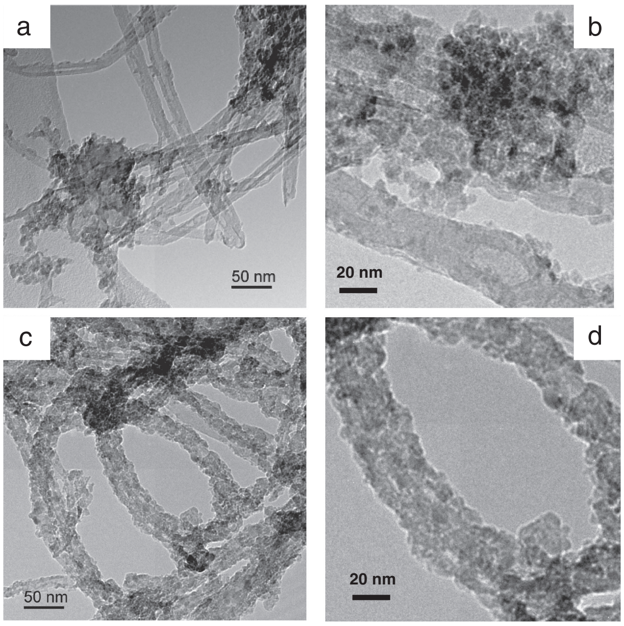

Figure 1. TEM images of TiO_2–CNT(none) (a, b) and TiO_2–CNT(urea) (c, d).

known that urea is hydrolyzed efficiently in water at temperatures higher than 353 K to form NH_3 and CO_2.[14,15] In the preparation of TiO_2–CNT(urea), the hydrolysis of Ti(O*i*-Pr)$_4$ was performed at 323 K. Thus, hydrolysis of urea hardly occurred during the hydrolysis of Ti(O*i*-Pr)$_4$. These results implied that the urea added during the hydrolysis of Ti(O*i*-Pr)$_4$ worked as linker molecules between the CNTs and TiO_2 nanoparticles.

Figure 2 shows XRD patterns of TiO_2–CNT(none) and TiO_2–CNT(urea). The XRD patterns for both the TiO_2–CNTs were very similar, and these diffraction lines were assignable to TiO_2 in the anatase phase. The crystallite size of TiO_2 in both the composites was evaluated from Scherrer's equation based on a line width at half-maximum for the corresponding XRD patterns. An average crystallite size of TiO_2 in the TiO_2–CNT(urea) (6.4 nm) was slightly larger than that of TiO_2 in TiO_2–CNT(none) (5.7 nm). Thus, the specific surface area of TiO_2–CNT(urea) ($140\,m^2\,g^{-1}$) was also smaller than that of TiO_2–CNT(none) ($178\,m^2\,g^{-1}$).

The outer surface of the CNTs could be uniformly covered with TiO_2 nanoparticles by the hydrolysis of Ti(O*i*-Pr)$_4$ in the presence of urea, as described earlier. Urea molecules would work as linker molecules between the TiO_2 nanoparticles and CNT surfaces. The FT-IR spectrum of the TiO_2 nanoparticles prepared by hydrolysis of Ti(O*i*-Pr)$_4$ in the presence of urea was thus measured. The spectrum was measured before the TiO_2 was calcined in air at 603 K. Figure 3 shows the FT-IR spectrum of TiO_2 thus obtained. Bands were observed at around 1650, 1565, and 1490 cm^{-1}. These bands are consistent with the bands for urea species adsorbed on Fe_2O_3–TiO_2 catalysts.[16] The adsorbed urea species were coordinated to the catalyst surface by N atoms of an amine group and the terminal O atoms of a carbonyl group, whereas the remaining amine group of the adsorbed urea did not interact with the catalysts. It is expected that the free amine group in urea adsorbed on TiO_2 should interact with the CNT surface, thus leading to the strong interaction between the TiO_2 particles and the CNTs. We have already reported the coverage of CNTs with thin silica layers by the hydrolysis of 3-aminopropyltriethoxysilane (APTES).[17] Amine groups in APTES have a strong interaction with graphene of CNT surface and/or functional groups on the CNT surface such as –COOH groups, leading to the uniform coverage of CNTs with silica layers. Thus, the surface of the CNTs is uniformly covered with TiO_2 nanoparticles formed by the hydrolysis of Ti(O*i*-Pr)$_4$ in the presence of urea as linker molecules.

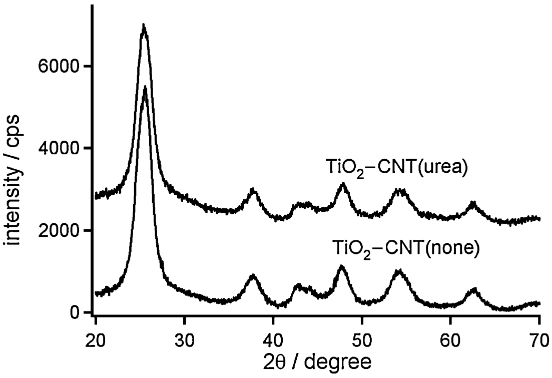

Figure 2. XRD patterns of TiO_2–CNT composites.

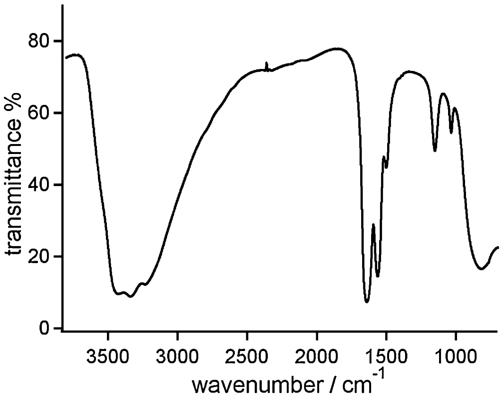

Figure 3. FT-IR spectrum of TiO_2 prepared in the presence of urea.

To further clarify the role of urea on the coverage of CNTs with TiO_2 nanoparticles, TiO_2–CNT composites were prepared by hydrolysis of Ti(O*i*-Pr)$_4$ in the presence of acetamide (CH_3CONH_2), oxamide ($(CONH_2)_2$), ethylenediamine ($NH_2CH_2CH_2NH_2$), or glycine amide ($NH_2CH_2CONH_2$). Figure 4 shows TEM images of these TiO_2–CNT composites. In the TEM images of the TiO_2–CNT composites prepared by addition of acetamide or oxamide, the exposed CNT surfaces were frequently observed although many TiO_2 particles were deposited on the CNT surfaces. The TEM images of these TiO_2–CNT composites are similar to those for the composites prepared without any linker molecules. This is because of the absence of amine groups in acetamide or oxamide for interaction with the CNT surface, although these molecules interact with the TiO_2 nanoparticles through –$CONH_2$. On the other hand, aggregated TiO_2 particles and the exposed CNT surface were frequently

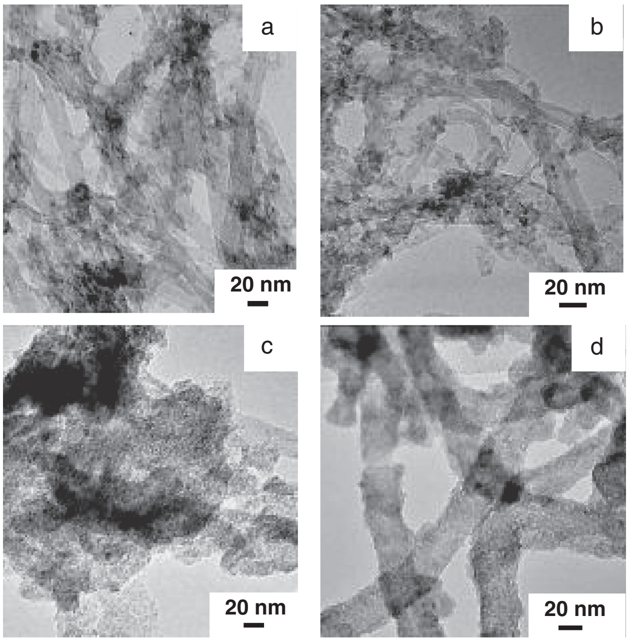

Figure 4. TEM images of TiO_2–CNT composites prepared by addition of acetamide (a), oxamide (b), ethylenediamine (c), and glycine amide (d).

found in the TEM image of TiO_2–CNT composites prepared by the addition of ethylenediamine. It is considered that ethylenediamine would not adsorb on TiO_2 nanoparticles but that it will adsorb on the CNTs. Thus, the CNT surfaces were not uniformly covered with TiO_2 nanoparticles. In contrast, TiO_2 nanoparticles were uniformly and densely deposited on the CNT surfaces by hydrolysis of $Ti(O\textit{i}\text{-}Pr)_4$ in the presence of glycine amide. These results strongly suggested that the $-CONH_2$ group in urea and glycine amide interacts with the TiO_2 nanoparticles and another $-NH_2$ group in these molecules is in contact with the CNT surfaces. Thus, CNTs were uniformly covered with TiO_2 nanoparticles by hydrolysis of $Ti(O\textit{i}\text{-}Pr)_4$ in the presence of urea and glycine amide.

Figure 5 shows a change in the amount of CO_2 formed during the photodegradation of acetic acid over TiO_2, a physical mixture of CNTs and TiO_2 particles, TiO_2–CNT(none), and TiO_2–CNT(urea). CO_2 was mainly formed in addition to a small amount of CH_4 in the reactions over all the catalysts. The addition of CNT in the photocatalysis system enhanced the catalytic activity of the TiO_2 photocatalysts. This is because of retardation of the recombination of a photogenerated electron–hole pair. TiO_2–CNT(urea) showed higher catalytic activity than a physical mixture of CNTs and TiO_2 particles and TiO_2–CNT(none). The strong interaction between TiO_2 nanoparticles and the CNTs in TiO_2–CNT(urea) efficiently prevents a rapid recombination of holes and electrons formed in the TiO_2, which improves the photocatalytic activity of TiO_2.

We demonstrated the uniform coverage of CNT surfaces with TiO_2 nanoparticles by the hydrolysis of $Ti(O\textit{i}\text{-}Pr)_4$ in the presence of urea or glycine amide as linker molecules. These linker molecules are easily removed by calcination of the catalysts in air, as compared to surfactant molecules such as sodium dodecyl sulfate, which have been frequently utilized for the coverage of CNTs with TiO_2. It is reported that the addition of urea during the preparation of TiO_2 does not spoil the photocatalytic activity of TiO_2 thus obtained.[18] Thus, our method is effective for the modification of CNT surfaces with metal oxides.

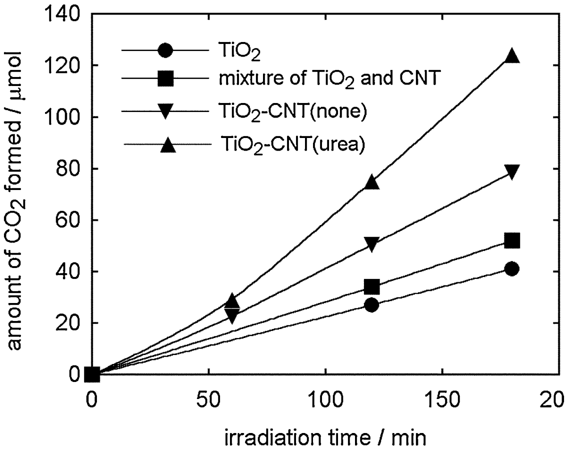

Figure 5. Observed change in the amount of CO_2 formed during the photodegradation of acetic acid over TiO_2, a physical mixture of TiO_2 and CNT (TiO_2 loading = 73 wt %), TiO_2(65 wt %)–CNT(none), and TiO_2(73 wt %)–CNT(urea).

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