Nanostructures and physicochemical properties of Pt nanoparticle-loaded titania nanotubes synthesized by photoreduction method

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Titania nanotubes (TNTs) were synthesized by a low-temperature chemical processing method and then hybridized with Pt nanoparticles (NPs) by a UV-light-induced photoreduction method using H_2PtCl_6 . Optical band gap energy was slightly increased by the Pt NPs loading. Methylene blue (MB) removal test revealed that the both pure and Pt-loaded TNTs eliminated the MB under dark and UV-light irradiation conditions, showing the molecular adsorption property was kept even after the Pt loading. Ultraviolet (UV) light induced photocatalytic degradation of MB mainly underwent at the surface of TNT while Pt NPs accumulated photoinduced electron sufficiently. Pt-loaded TNTs exhibited higher performance of photocatalytic than non-Pt-loaded TNTs at the early stage of photodegradation of MB. It indicated that the Pt NPs worked well as co-catalysts with the TNTs. These results suggest that the present nanocomposite is suitable for elimination of molecules through the combination of two functions as molecular adsorption and photocatalytic reaction.

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Titania nanotubes (TNTs)^(1,2) are highly promising nanostructured materials because of the synergistic combination of their unique one-dimensional (1D) nanostructure and the fundamental physicochemical characteristics of TiO_2 , which is a well-known semiconductor oxide having excellent photochemical properties.⁽³⁾ Because titania nanotubes have a very high surface area ($\sim 300 \text{ m}^2/\text{g}$) owing to their unique 1D nano-tubular and layered-compound-like structures, they have high molecular adsorption capability, a property that is negligibly small for common TiO_2 nanoparticles (NPs), as well as photocatalytic properties.⁽⁴⁾ These facts imply that TNTs may be possible candidates as high-performance environmental purification materials.

In addition, hybridizing nanostructured photocatalysts with metal NPs such as those of noble metals is a beneficial way to enhance photocatalytic properties owing to the co-catalytic effect of the metal NPs. There are various hybridizing methods for the deposition of metal NPs onto semiconductor oxides such as TiO_2 . One of the simplest methods is photoreduction,⁽⁵⁻⁷⁾ where excited electrons generated by incident light irradiation reduce metal cations on the semiconductor surface to metallic NPs, resulting in the formation of NP-loaded TiO_2 . The photoreduction method is a useful route to metal/semiconductor nanocomposites such as Cu/TiO_2 ,^(5,6) Ag/TiO_2 ,⁽⁶⁾ Pt/TiO_2 ,⁽⁶⁾ and Cu/ZnO .⁽⁷⁾

In this study, we focused on hybridizing titania nanotubes with platinum (Pt) NPs (TNT/Pt NPs) by photoreduction to improve the photocatalytic function of TNTs. As mentioned above, TNT has high molecular adsorption capability which might contribute to enhance catalytic reaction. Further, it has been reported that TNTs exhibit longer lifetimes of photo-induced charges because of their 1D characteristics,⁽⁸⁾ which contributes to better photo-

catalytic performance. Therefore, it is expected that noble metal NPs loaded onto TNTs might provide further enhanced photocatalytic properties owing to co-catalytic effects.

In fact, loading of Pt NPs on TNT has attracted attentions due to the expectation of enhancing heterogeneous catalytic activity, and various synthesis methods for NPs loading such as impregnation and following thermal, photo or chemical reduction have been reported.⁽⁹⁻¹⁴⁾ Nishijima et al.⁽⁹⁾ reported site-selective loading of Pt to TNTs by thermal (H_2) and photo (UV) reduction methods, and found that the Pt-loading inside of TNT showed the highest photocatalytic activity for oxidation of acetaldehyde gas due to remaining of active sites on the outer-surface of TNTs from the Pt covering. Heterogeneous catalysis for gases such as CO_2 hydrogenation⁽¹⁰⁾ or CO oxidation⁽¹¹⁾ using TNT supported Pt NPs were also investigated; it was reported that Pt-loaded TNTs reduced conversion temperature of these reactions, while the catalytic activity was often degraded due to the agglomeration and coarsening of Pt NPs during catalytic operation.⁽¹¹⁾ Zhao et al.⁽¹²⁾ synthesized Au and Pt NPs loaded TNTs by photoreduction route and reported the enhanced photocatalytic activity in methyl orange aqueous solution. Khan et al.⁽¹³⁾ prepared Pt-loaded TNTs by thermal reduction of Pt^{4+} ion-exchanged TNTs and reported the decrease of band gap energy and resultant visible light responsible high photocatalytic activity.

These reports concluded that the enhancement of catalytic and photocatalytic properties could be achieved due to the loading of nanosized Pt particles, showing the advantage of this kind of nanocomposite catalysts. However, to the best of our knowledge, there have been no detailed reports on the molecular adsorption properties of Pt-loaded TNTs prepared via the photoreduction method in aqueous solutions. In this study, synthesis of Pt NPs loaded TNTs and their molecular adsorption and photocatalytic properties have been investigated.

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Fig. 1. (Color online) TEM image of Pt nanoparticle-loaded TNTs prepared by UV light reduction that shows tubular structures with diameters above 10 and 2–3 nm-sized particles on the TNT surfaces.

TNTs were synthesized by a low-temperature chemical processing method^{3),4)} and then hybridized with Pt NPs via UV light-induced photoreduction.⁵⁾ The physicochemical properties of these TNT/NPs were investigated. A methylene blue (MB) removal test was performed to confirm their environmental purification performance. In the test, the adsorption and photocatalytic degradation of MB molecules occurred on the Pt-loaded TiO_2 nanotubes.

First, pure TNTs were synthesized from commercial anatase TiO_2 powder (99.9%, Kojundo Chemical Laboratory Co. Ltd., Tokyo, Japan). The anatase TiO_2 powder was added to a 10 M NaOH solution in fluoropolymer bottles and refluxed at 110°C for 22 h, after which time the product was washed with distilled water (DW) several times and neutralized with 0.1 M HCl. The Brunauer–Emmett–Teller (BET) surface area of the synthesized TNTs was 279 m^2/g , which is a sufficiently high value for TNTs. The obtained powder was filtered, rinsed with ethanol, and dried at 70°C for 24 h. Next, the TNTs were mixed with a solution of 30 mM H_2PtCl_6 (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and polyvinylpyrrolidone (PVP, 40-500G, Sigma-Aldrich, Ltd., Tokyo, Japan) in ethylene glycol (EG, Wako Pure Chemical Industries, Ltd.) solvent.¹⁵⁾ The reduction reaction was performed by irradiating the suspension with UV light (Toscore100, Japan Technology System Co., Tokyo, Japan, Hg–Xe lamp, 365 nm, 200 mW/cm^2 at the surface of reaction solution) for 3 h. Finally, dark brownish powders were obtained after filtering and drying. Pt concentration in the sample was evaluated by X-ray fluorescence spectrometer, and was calculated to be 0.10 wt %. The MB removal test was performed by adding 20 mg of TNT powders into 10 mg/L of an MB solution (200 ml) and stirring both in the dark and under UV light irradiation (Toscore100, Hg–Xe lamp, 365 nm, 200 mW/cm^2). For the comparison, the variations of MB solution without any catalyst under the UV irradiation and with TiO_2 nanoparticles (P-25, Degussa, Germany) are also carried out. In order to separate the effect of MB adsorption on the photocatalytic reaction, UV irradiation for the samples to which MB was sufficiently adsorbed under the dark condition was also performed; in this experiment, pure and Pt-loaded TNTs were kept in 20 mg/L of MB solution under the dark condition for 45 h, and then UV light was irradiated.

Figure 1 shows the transmission electron microscope (TEM) image of the Pt-loaded TNTs. Tubular titania with a diameter of approximately 10 nm was maintained after the photoreduction

Fig. 2. (Color online) UV–visible light optical transmission spectra of anatase, pure and Pt-loaded TNTs measured by the diffuse reflectance mode.

reaction. In addition, fine particles of approximately 2–3 nm in size were found to be attached to the TNT surface, which confirmed the formation of the TNT/NPs nanocomposite. Neither change of color nor precipitation of particulates was confirmed when the reaction vessel was kept under the dark condition without any light irradiation for 24 h at room temperature. This fact implies that the irradiation of UV light to TNTs triggers the photo-induced excitation and followed reduction reaction of Pt^{4+} ions to form Pt nanoparticles.

X-ray diffraction patterns of the products (not shown) consisted only of TNT reflections, and neither crystalline Pt nor other impurity phases were detected. The amount of NPs found on the TNT surface was very small; the precipitated amount of 0.10 wt % might be lower than the detection limit for crystalline Pt by XRD. In addition, the NPs had a spherical shape and a rather dark contrast, which are typical morphological characteristics of precipitated noble metal NPs. Therefore, the observed NPs by TEM are regarded as metallic Pt that precipitated as a result of the UV-light-induced reduction reaction.

Optical transmission spectra were measured by the UV–visible light spectrometer and shown in **Fig. 2**. Blue shift of TNT samples was clearly confirmed, however, no significant difference in absorption edge between pristine and Pt-loaded TNTs except lower transmission value for the Pt-loaded sample above 380 nm. Optical band gap energy was calculated by assuming direct transition model to be 3.38 and 3.43 eV for pure and Pt-loaded TNTs, respectively. The increase in the value for TNTs from that of anatase (3.04 eV) is regarded due to the quantum effect in TNT.⁴⁾ Further increase in the band gap energy of approximately 0.05 eV was found when Pt NPs were loaded to TNT, which is inconsistent with the report by Khan et al.¹³⁾ They reported the significant decrease in band gap of TNT from 3.1 to 2.48 eV when Pt was loaded by thermal reduction of Pt^{4+} ion-exchanged TNT, and claimed that this phenomenon was caused by the negative shift of Fermi level of TiO_2 owing to electron accumulation from embedded Pt NPs to the conduction band in TiO_2 .¹³⁾ The shift of Fermi level by Au NPs loading to TiO_2 particles was certainly confirmed,¹⁶⁾ however, this should be caused by light irradiation and resultant photo-induced electron accumulation.^{16),17)} On the other hand, it was reported that Pt often exist as oxidized form in Pt-loaded TNTs depending on the preparation method,^{10),17),18)} implying the formation of mid-gap bands and resultant reduction of the effective band gap energy.¹⁷⁾

Fig. 3. (Color online) MB degradation experiments in the dark and under UV light irradiation with a 30 mM concentration of Pt NP/TNTs prepared by the UV light reduction reaction. Blank data for MB solution in the dark condition and the comparison of TiO₂ NPs (P-25) are also plotted.

In the present case, the band gap energy was slightly increased by the Pt loading; it is generally known that a Schottky barrier was formed between n-type semiconductor-metal interface such as TiO₂ and Pt,^{19),20)} owing to the difference of work function of two materials and resultant electron accumulation from semiconductor to metal, and hence the bands of semiconductor bent upward at the surface to form charge depletion region (also called as space charge region) under the surface in nanometer scale. The wall thickness of TNT is sufficiently thin, below 2 nm. Therefore, it is speculated that the formation of depletion region may play an important role in the slight increase of the band gap energy of TNTs loaded with metal nanoparticles. More detailed investigation using electrochemical and/or photoelectrochemical analyses is, however, necessary to understand exact electric structure for the metal nanoparticles loaded TNTs in the future.

The variation in MB concentration for pure TNTs, Pt-loaded TNTs and TiO₂ NPs (P-25) as a function of the soaking time (up to 420 min) is shown in Fig. 3. Under dark conditions, the MB concentration for the pure TNTs decreased rapidly, indicating that the TNTs effectively adsorbed the MB molecules, which was dominant characteristic for the TNTs by comparing with that for TiO₂ NPs (P-25) in the dark condition. The decrease in the MB concentration for the TNT/Pt NPs in the dark was lower than that of the pure TNT, implying that the molecular adsorption activity of the TNTs was degraded by NP loading. Recently Wang, et al.²¹⁾ reported the synthesis of Pt nanoparticles loaded TiO₂ nanowires (NWs) and their catalytic properties using MB removal test. They reported that the Pt loading greatly decreased the adsorption amount of MB to TiO₂ NWs (from 58% to 7% for pure NWs and 2 at% Pt loaded TiO₂ NWs, respectively) due to the occupation of adsorption site by precipitated NPs.²¹⁾ In the present system, however, larger adsorption amount was still kept even after the Pt NPs loading; adsorption isotherm experiments using MB for the pure and Pt-loaded TNTs under the dark condition exhibited that the saturated amount of MB adsorption for the pure and Pt-loaded TNTs was 96.0 µg of MB/mg of catalyst and 67.8 µg/mg, respectively, even though the surface area of Pt-loaded TNT, 375 m²/g, was larger than that of non-loaded one (279 m²/g). Nevertheless, it is considered that the fundamental characteristic of titania nanotube having molecular adsorption property owing to its high surface area and unique layered compound-like structure is the essential also for the present Pt-loaded titania nanotubes.

Fig. 4. Variation of the MB concentration difference ($C_{UV} - C_{dark}$) of pure and Pt-loaded TNTs showing the contribution of the photocatalytic reaction, where C_{UV} and C_{dark} are measured MB concentration (Fig. 3) under the UV and dark conditions, respectively.

Under UV light irradiation conditions, on the other hand, both the pure and Pt-loaded TNTs exhibited a higher degradation in MB concentration than that in the dark. The MB concentration without any catalyst was slightly decreased by UV irradiation (see Fig. 3) because of photodegradation such as demethylation of the molecule. Nevertheless, MB decrease for the pure and Pt-loaded TNTs is considered due to their high photocatalytic properties. These results clearly indicate that the pure and Pt-loaded TNTs have molecular adsorption and photocatalytic properties at the same time. In fact, the MB removal for NPs (P-25) under the UV irradiation was the highest above 180 min. However, it is advantageous that the TNTs could remove molecules under the both dark and UV irradiation conditions.

To clarify the contribution of the molecular adsorption and photocatalytic properties to MB degradation, the difference in the MB concentration ($C_{UV} - C_{dark}$) between the UV (C_{UV}) and dark (C_{dark}) conditions was calculated from Fig. 3. The values are plotted in Fig. 4. In the case of pure TNTs, the MB degradation by photocatalytic means seems to occur in the early stages of UV irradiation (less than 60 min) and to be suppressed at a longer irradiation time (above 60 min). This behavior was probably due to the competitive phenomenon of MB adsorption and photocatalytic degradation kinetics, because of the TNTs large molecular adsorption capability. For the Pt-loaded TNTs, on the other hand, the photocatalytic contribution increased with increased soaking time. This result indicates that Pt loading sustains the photocatalytic reaction.

However, in this experiment, both molecular adsorption and subsequent photocatalytic degradation continuously and competitively progressed under the UV irradiation condition. Therefore, to compare the photocatalytic activity more clearly, MB was sufficiently adsorbed to pure and Pt-loaded TNTs under the dark condition for 45 h, and then UV light was irradiated. The results are shown in Fig. 5 as the degradation rate, $[(C_0 - C)/C_0] \cdot 100$ (%), of MB solution on the irradiation time,¹²⁾ where C_0 and C are initial and observed concentration of MB solution at any time, respectively. It was found that the difference of photodegradation rates between these two systems was slight. However, in detail, the Pt-loaded TNT exhibited quick response of the photodegradation at the early stage compared to the pure TNT. This is reasonably considered due to the efficient photogenerated electron separation in the Pt-loaded TNTs owing to the presence

Fig. 5. (Color online) Variation of the MB degradation rate of pure and Pt-loaded TNTs on the UV light irradiation time, to which the MB was sufficiently adsorbed in advance.

of metallic Pt on the surface and resultant formation of Schottky barrier that would suppress charge recombination.^{12),20)}

Photocatalytic degradation of organic molecules in TiO₂ surface is argued by the reduction and oxidation reaction by various radicals such as O₂^{•−}, OH[•] or R[•] from O₂, H₂O or R–H, which are generated by the photogenerated electrons and holes at the surface. For the methylene blue degradation, Housas et al.²²⁾ analyzed and proposed detailed reaction pathway. Briefly, the initial step is adsorption of MB molecule on TiO₂ surface due to coulombic interaction between surface O[−] (derived from surface hydroxyl, –OH) and the C–S⁺=C functional group in MB molecule, because the MB is cationic molecule. Subsequently, the cleavage of the bonds of the C–S⁺=C functional group undergoes by the attack of OH[•] radicals; R–S⁺=R + OH[•] → R–S(=O)–R + H⁺, which induces the opening of the central aromatic ring containing both heteroatoms (S and N). Then the sulfoxide group undergoes alternative attacks by the OH[•] radicals together with the dissociation of benzene rings, and finally mineralizes to form SO₄^{2−}. Similar to the sulfur oxidation to SO₄^{2−}, complete mineralization of carbon and nitrogen to produce CO₂, NH₄⁺ and NO₃[−] undergoes simultaneously through the oxidation process. Photoinduced electron is consumed for the reduction of protons, H⁺ + e[−] → H[•], which is used for protonation of MB and its intermediates to form C–H and N–H bonds.

According to this degradation sequence of MB, it is considered that the Pt NPs plays a major role in realizing charge separation to hold electrons for reduction reaction while the TNT acts individual reaction site by providing photogenerated holes for oxidation. In addition, high adsorption capability and long lifetime of photogenerated holes and radicals of the TNT⁸⁾ are considered to be beneficial for initiating and continuing the degradation of the molecules. This is thus regarded as one of the reason of the result found from Fig. 5 that the photodegradation rate difference between pure and Pt-loaded TNTs is minor. The MB degradation rate of Pt-loaded TNT seemed to be suppressed at a longer UV irradiation time. It is considered to be due to the catalyst poisoning effect of loaded Pt NPs, in which the Pt might be covered by the intermediate species such as CO and carbonyl (R–HC=O), and hence photocatalytic reduction reaction on the Pt surface may be suppressed.

In summary, Pt nanoparticles of approximately 3 nm in diameter were successfully hybridized to titania nanotubes by a UV-induced reduction. The TNT/Pt NPs nanocomposites ex-

hibited molecular adsorption and photocatalytic properties under the UV light irradiation condition. Higher molecular adsorption property was kept even after the loading of Pt NPs to TNTs. The photocatalytic degradation of methylene blue was considered to be promoted by the simultaneous oxidation at the TNT surfaces triggered by the photoinduced holes. The photocatalytic degradation performance was accelerated at the early stage of UV irradiation by Pt loading because of the co-catalytic properties of the NPs, despite the very low loading levels obtained for the Pt NPs. This result suggests that the present hybrid nanocomposite is suitable for elimination of molecules through the combination of two types of environmental cleaning functions of molecular adsorption and photocatalytic reaction.

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