Effect of Mixed Valence States of Platinum Ion Dopants on the Photocatalytic Activity of Titanium Dioxide under Visible Light Irradiation

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Supporting Information

ABSTRACT: Titanium dioxide doped with the Pt ion (Pt−TiO₂) was synthesized by a sol−gel method using only water as the solvent and conducting dialysis. The photocatalytic activity for the degradation of 4-chlorophenol (4-CP) on Pt−TiO₂ was not affected by the Brunauer−Emmett−Teller specific surface area under visible light (VL) irradiation. X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure measurements revealed that only the Pt(IV) ion existed in the TiO₂ bulk and both Pt(II) and Pt(IV) were present near the Pt−TiO₂ surface. Pt(IV) is most likely substituted in the Ti(IV) site of the TiO₂ lattice because of their similar ionic sizes. Quantitative analysis of Pt(II) was performed in the XPS measurements, indicating that the amount of Pt(II) on the surface increased with an increase in the doping amount from 0.2 to 1.0 atom %. We synthesized 0.5 atom % Pt−TiO₂ with various Pt(II)/Pt(IV) ratios by changing the Ti(OC₃H₇)₄ concentration used in the sol−gel synthesis. The 4-CP conversion on Pt−TiO₂ increased linearly with an increase in the Pt(II)/Pt(IV) ratios. A similar relationship was obtained with Pt−TiO₂, which was prepared by a conventional sol−gel method in ethanol−water mixed solvent. Therefore, the Pt(II)/Pt(IV) ratio is a key factor affecting the photocatalytic activity of Pt−TiO₂ under VL irradiation. Our results indicate that controlling the mixed valence states of the doped metal ions is a new strategy to developing highly active metal-ion-doped TiO₂ under VL irradiation.

INTRODUCTION

Titanium dioxide (TiO₂) has been widely studied for photocatalytic degradation of organic environmental pollutants because it is inexpensive and chemically stable and has strong oxidation power. Photogenerated holes with oxidative power because it is inexpensive and chemically stable and has strong photocatalytic degradation of organic environmental pollutants because it is inexpensive and chemically stable and has strong oxidation power. Photogenerated holes with oxidative power because it is inexpensive and chemically stable and has strong photocatalytic degradation of organic environmental pollutants because it is inexpensive and chemically stable and has strong oxidation power.
standing a key factor affecting the photocatalytic activity is required. Many studies have reported that the oxidation states of metal-ion dopants, the presence of fractional content of the rutile phase, oxygen vacancies, crystallinity, or Brunauer–Emmett–Teller (BET) specific surface area influence the photocatalytic activity of VL-responsive M-TiO2. However, the most influential factor for the photocatalytic activity of M-TiO2 is not fully understood.

Previously, we have prepared porous M-TiO2 doped with seven different metal ions by the sol–gel method using only water as the solvent and conducting dialysis to purify the obtained TiO2 sol before drying and reported that Pt–TiO2 sintered at 200 °C showed the highest photocatalytic activity for the degradation of 4-CP. Kinetic studies of the degradation of 4-CP on Pt–TiO2 revealed that 4-CP was degraded to CO2 via the formation of hydroquinone and benzoquinone as the intermediates. During dialysis, protons adsorbed on the surface of TiO2 nanoparticles are gradually removed and then the particles tend to undergo aggregation with the formation of pores, leading to the BET specific surface area larger than 200 m2 g−1. Such an aqueous sol–gel method with no addition of alcohol is more suitable for industrialization.

In this work, we prepared Pt–TiO2 with different BET specific surface areas or with various ratios of Pt(II)/Pt(IV) and clarified the relationship between the ratio and the photocatalytic activity of Pt–TiO2. There are few studies elucidating the effect of multiple valence states of single metal ions doped in TiO2. Our results will provide a new strategy to developing highly active M-TiO2 working under solar light.

**RESULTS AND DISCUSSION**

**Effect of Doping of Pt Ions.** Figure 1 shows the time course of 4-CP conversion on 0.5 atom % Pt–TiO2, Pt–TiO2 synthesized without dialysis (Pt–TiO2(ND)), and TiO2 under VL or UV irradiation.

![Figure 1. Time course of the 4-CP conversion on Pt–TiO2, Pt–TiO2(ND), and TiO2 under VL or UV irradiation.](image)

The 4-CP conversion is defined as the concentration of 4-CP degraded divided by the initial 4-CP concentration. Complete degradation of 4-CP, that is, 100% conversion, was obtained on Pt–TiO2 under UV irradiation for 60 min or under VL irradiation for 120 min. It is worth noting that the photocatalytic activity of Pt–TiO2 is much higher than that of TiO2 under UV radiation, suggesting that the doped Pt ions hardly act as a recombination center of the photogenerated holes and electrons. Figure 1 also indicates that the 4-CP conversion is almost the same on Pt–TiO2 and Pt–TiO2(ND) under VL irradiation, whereas that on Pt–TiO2 is higher than that on Pt–TiO2(ND) under UV irradiation. Both Pt–TiO2 and Pt–TiO2(ND) were anatase (Figure S1), and the crystallite size was estimated to be 4.5 or 4.3 nm, respectively, which was evaluated by the Scherrer equation. As shown in Table 1, the BET specific surface area of Pt–TiO2 is 250 m2 g−1, which is higher than that of Pt–TiO2(ND) by a factor of 1.5. It is generally believed that a higher photocatalytic activity is obtained for the catalysts with a higher specific surface area because the photocatalytic reaction proceeds on the surface. Thus, the higher activity of Pt–TiO2 than that of Pt–TiO2(ND) under UV irradiation, as shown in Figure 1, is explainable. However, Figure 1 also indicates that the photocatalytic activity of Pt–TiO2 is not affected by the BET specific surface area under VL irradiation. The reason will be discussed later.

Figure 2 shows the effect of Pt doping amount in the range of 0.2–1.0 atom % on 4-CP conversion after VL irradiation for 90 min, indicating that the photocatalytic activity increases with an increase in the doping amount. No appreciable change in morphology was observed between TiO2 and Pt–TiO2 (Figure S2). Even for 1.0 atom % Pt–TiO2, no diffraction peak attributable to the Pt metal or PtO2 was detected by X-ray diffraction (XRD) measurements (Figure 3). Thus, the doped Pt ions are present homogenously inside or between TiO2 lattices. Figure 4 shows the diffuse reflectance spectra of TiO2 and 0.2–1.0 atom % Pt–TiO2 indicating an enhancement of absorption in the visible light region by Pt doping. From the Tauc plots shown in the inset of Figure 4, the band-gap energy...
of TiO₂ was evaluated to be 3.08 eV. With an increase in the doping amount, the band-gap energy of Pt−TiO₂ decreases from 2.98 to 2.82 eV (Table 1), indicating that the higher photocatalytic activity observed at a higher doping amount is attributable to an increase in the VL absorption ability.

Valence States of the Doped Pt Ions. Figure 5 shows the X-ray photoelectron spectroscopy (XPS) spectrum of 0.5 atom % Pt−TiO₂, and its deconvoluted bands indicate the presence of Pt(II) and Pt(IV) states on the surface. The Pt LIII edge X-ray absorption near-edge structure (XANES) spectra of 0.2−1.0 atom % Pt−TiO₂ and 0.5 atom % Pt−TiO₂(ND) are presented in Figure 6 with the reference spectra of PtCl₂ and PtO₂. The sharp absorption band at the Pt LIII edge, which is called white line, corresponds to the electron transition from 2P½ to 5d½. In general, when the oxidation state of Pt is lower, the density of the unoccupied d states is lower, resulting in the decrease in the white line intensity. The Pt ion exists as Pt(IV) in the bulk because the XANES spectra of all Pt−TiO₂ samples resembled the spectrum of PtO₂. Choi et al. have reported that a metal ion having an ionic radius similar to that of Ti(IV) (0.745 Å) is doped by being substituted in the Ti(IV) site, whereas a larger metal ion is most likely located in the interstitial positions of the TiO₂ lattice. The ionic radii of Pt(II) and Pt(IV) are 0.94 and 0.765 Å, respectively, and thus Pt(II) is significantly larger than Ti(IV). This is coincident with our findings that Pt(II) was detected only by XPS, which mainly reflects the chemical environment on the surface, and no Pt(II) was detected by XANES, which can provide information on the bulk. Kim et al. have reported that Pt(II) and Pt(IV) in Pt−TiO₂ synthesized in the ethanol−water mixed solvent by the sol−gel method act as trap sites of the photogenerated holes and electrons, respectively, resulting in the suppression of their recombination. As described above, because the photocatalytic activity of Pt−TiO₂ was not affected by the BET specific surface area in spite of the surface reaction, we attempted to quantify Pt(II) on the surface of Pt−TiO₂.

Quantitative Analysis of Pt(II) near the Surface of TiO₂. The PtCl₂ powders were mixed with TiO₂ at various ratios in an agate mortar and ground thoroughly for 10 min using a pestle for the XPS measurement. Figure 7 shows a linear relationship between moles of Pt(II) (4.21 × 10⁻⁷ − 1.68 × 10⁻⁶ mol) and the peak area due to Pt(II) after the deconvolution of the XPS spectra. The details of the measurement method are provided in the Supporting Information. Using this linearity, the moles of Pt(II) in 0.2−1.0 atom % Pt−TiO₂ were estimated from the XPS spectra. As listed in Table 2, the moles of Pt(II) increased from 0.68 × 10⁻⁷ mol in 0.2 atom % Pt−TiO₂ to 10.65 × 10⁻⁷ mol in 1.0 atom % Pt−TiO₂. These values indicate that the Pt(II) ion near the surface is only 3.88−12.1% (the details of the calculation are described in the Supporting Information) of the total Pt amounts in 0.2−1.0 atom % Pt−TiO₂. Table 2 also lists the ratios of the peak area of Pt(II) to that of Pt(IV) (Pt(II)/Pt(IV)), which were calculated by deconvoluted bands in the XPS spectra, suggesting that the Pt(II)/Pt(IV) ratios increase with an increase in the doping amounts and are almost the same.
same for 0.5 atom % Pt−TiO2 and Pt−TiO2(ND), whose photocatalytic activities are almost the same, as shown in Figure 1. Higher photocatalytic activity was obtained on Pt−TiO2 with a higher doping amount, as mentioned above. Therefore, it is expected that the photocatalytic activity as well as the Pt(II)/Pt(IV) ratios increases by increasing the doping amount more than 1.0 atom %. However, an increase in the Pt doping amounts is found to be expensive and thus we tried to find a way to increase the Pt(II)/Pt(IV) ratio of 0.5 atom % Pt−TiO2 by changing the synthetic conditions.

**Effect of Pt(II)/Pt(IV) on Photocatalytic Activity.** We have found that the Pt(II)/Pt(IV) ratio in 0.5 atom % Pt−TiO2 can be controlled by changing the volume of Ti(OC3H7)4 titanium tetraisopropoxide (TTIP) used for TiO2 synthesis (Table 3). Figure 8 shows that Pt(II) estimated from the XPS spectra of 0.5 atom % Pt−TiO2 increases from 1.08 × 10−7 to 1.46 × 10−6 mol by adding 0.75−20 mL of TTIP to 180 mL of aqueous HNO3 solution using the sol−gel method. Concerning the formation of Pt(II), it is likely that some H2PtCl6 are reduced by C3H7OH, which is produced via the hydrolysis of TTIP. An increase in the TTIP volume used in the synthesis results in a high concentration of C3H7OH, leading to acceleration of the reduction of Pt(IV) to Pt(II). The Pt(II)/Pt(IV) ratio was estimated from the peak area of the deconvoluted bands in the XPS spectra, and its dependence on the moles of TTIP is plotted in Figure 8, indicating a similar dependence on the amounts of Pt(II) determined quantitatively.

The photocatalytic degradation of 4-CP was performed on 0.5 atom % Pt−TiO2 with various Pt(II)/Pt(IV) ratios. Figure 9 indicates that the 4-CP conversion increases linearly with an increase in the Pt(II)/Pt(IV) ratio regardless of the VL irradiation times of 30, 60, and 90 min. This finding suggests that the Pt(II)/Pt(IV) ratio is an important factor affecting the photocatalytic activity of Pt−TiO2.

To examine the validity of this finding, Pt−TiO2(ref) was synthesized by conducting hydrolysis of TTIP in HNO3 aqueous solution containing ethanol. In our method using only water as the solvent, white precipitates (Ti(OH)4) are formed and stirring vigorously for a few days is necessary to disperse them into a homogenous sol. For saving time, many

![Figure 7](image_url)  
**Figure 7.** Dependence of the peak area of Pt(II) obtained by peak deconvolution of XPS spectra on the moles of Pt(II) mixed with TiO2.

![Figure 8](image_url)  
**Figure 8.** Dependence of the moles of Pt(II) or the Pt(II)/Pt(IV) ratio in 0.5 atom % Pt−TiO2 on the moles of TTIP used for sol−gel synthesis.

![Figure 9](image_url)  
**Figure 9.** Effect of the Pt(II)/Pt(IV) ratio of Pt−TiO2 (solid triangle) and Pt−TiO2(ref) (open circle) on the 4-CP conversion after VL irradiation for 30, 60, and 90 min.

### Table 2. Amounts and the Peak Area of Pt(II) and the Pt(II)/Pt(IV) Ratio of Pt−TiO2 and Pt−TiO2(ND)

| doping amount (atom %) | [Pt(II)] (10−7 mol) | area of Pt(II) (102) | peak area of Pt(II)/peak area of Pt(IV) |
|------------------------|---------------------|----------------------|----------------------------------------|
| 0.2                    | 0.68                | 7.65                 | 2.0                                    |
| 0.5                    | 5.13                | 29.96                | 14.0                                   |
| without dialysis       | 4.49                | 26.75                | 14.7                                   |
| 1.0                    | 10.65               | 57.69                | 31.5                                   |

### Table 3. BET Specific Surface Area, Crystallite Size, Band-Gap Energy, and Pt(II)/Pt(IV) Ratio of 0.5 Atom % Pt−TiO2

| TTIP (10−2 mol) | BET specific area (m² g⁻¹) | crystallite size (nm)² | band gap (eV) | peak area of Pt(II)/peak area of Pt(IV) |
|-----------------|----------------------------|------------------------|---------------|----------------------------------------|
| 0.239           | 282                        | 3.9                    | 2.94          | 2.7                                    |
| 0.479           | 297                        | 4.1                    | 2.89          | 4.8                                    |
| 0.958           | 259                        | 3.9                    | 2.90          | 5.7                                    |
| 1.596           | 276                        | 4.0                    | 2.86          | 10.0                                   |
| 3.192           | 263                        | 4.1                    | 2.88          | 10.4                                   |
| 4.788           | 250                        | 4.5                    | 2.89          | 14.0                                   |
| 6.385           | 256                        | 4.6                    | 2.93          | 21.2                                   |

²Crystallite size was evaluated from the XRD peak of anatase (101).
research groups have synthesized metal-ion-doped TiO₂ in an aqueous solution containing ethanol and metal-ion precursors. Previously, we compared the photocatalytic activity of Pt–TiO₂ to that of Pt–TiO₂(ref) that was prepared by the standard method reported by Kim et al. and reported that the photocatalytic activity of our Pt–TiO₂ was much higher than that of Pt–TiO₂(ref) under both UV and VL irradiation. However, in this study, we observed that the Pt(II)/Pt(IV) ratios in 0.5 atom % Pt–TiO₂ and Pt–TiO₂(ref) were 14.0 and 10.3, respectively. The Pt–TiO₂(ref) powders with Pt(II)/Pt(IV) ratios of 4.2, 9.7, 10.3, and 13.8 were prepared by changing the TTIP concentration. As shown in Figure 9 with open circles, the 4-CP conversion on Pt–TiO₂(ref) increases linearly with an increase in the Pt(II)/Pt(IV) ratio and is nearly equal to that on Pt–TiO₂ when being compared at the same Pt(II)/Pt(IV) ratio. Figure 10 indicates that the 4-CP conversion on Pt–TiO₂ increases linearly with an increase in the Pt(II)/Pt(IV) ratio under UV irradiation for 15 or 30 min. Therefore, regardless of the synthetic method and the light source, similar linearity was obtained between the 4-CP conversion and the Pt(II)/Pt(IV) ratio, indicating that the Pt(II)/Pt(IV) ratio is a key factor affecting the photocatalytic activity of Pt–TiO₂.

On the basis of the above results, a schematic representation of the reaction mechanism of Pt–TiO₂ is shown in Scheme 1. The XPS and XANES measurements revealed that Pt(II) and Pt(IV) existed near the TiO₂ surface and only Pt(IV) existed in the TiO₂ bulk. It is likely that the photogenerated electrons are trapped at Pt(IV) in the bulk and the photogenerated holes can escape from the recombination with the photogenerated electrons and reach the Pt(II) site on the surface, where 4-CP is oxidized. Because Pt(IV) is present from the surface to the bulk, the trapped electrons migrate by hopping toward the surface and react with oxygen. Spatial separation of photogenerated carriers through the coexistence of Pt(II) and Pt(IV) and the presence of more Pt(II) near the surface might be the reason why the Pt(II)/Pt(IV) ratio affects the photocatalytic activity under VL irradiation. At a higher Pt(II)/Pt(IV) ratio on the surface, the distribution of Pt(II) is more biased and more photogenerated holes can exist near the surface for the degradation of 4-CP. We have examined the effect of illumination on the Pt(II)/Pt(IV) ratio of Pt–TiO₂. After the photocatalytic degradation of 4-CP on 0.5 atom % Pt–TiO₂ (Pt(II)/Pt(IV) ratio = 14.0) was performed for 150 min, where 100% of 4-CP was degraded, and for 450 min, the Pt–TiO₂ powders were collected by filtration and then dried. No significant change in their XPS spectra was observed (Figure S6), and Pt(II)/Pt(IV) ratios were evaluated to be 13.5 and 14.1, respectively. This finding indicates that the ratio of Pt(II)/Pt(IV) remains almost constant after being used for the photocatalytic experiments.

The photocatalytic activity under VL irradiation was not dependent on the BET specific surface area, whereas under UV irradiation, Pt–TiO₂ (specific surface area: 250 m² g⁻¹) exhibited a higher activity than that of Pt–TiO₂(ND) (167 m² g⁻¹). Such a difference might be due to the number of photogenerated holes and electrons. Under VL irradiation whose energy is less than the band-gap energy, electrons are excited from the VB of TiO₂ to the energy levels below the CB, which are formed by the doped Pt ion. The flat band potentials of Pt–TiO₂(ref) were shifted positively by 50 mV, indicating that the CB edge position in Pt–TiO₂ is slightly lowered. Therefore, the charge separation of absorbed photons to electrons and holes occurs near the doped Pt ion. On the other hand, under UV irradiation, electrons are excited to the CB on all of the illuminated surfaces of TiO₂. That is, more holes and electrons are generated on the Pt–TiO₂ surface under UV irradiation, suggesting that the surface reaction with the adsorbed 4-CP is a rate-determining step. The presence of more 4-CP adsorbed on Pt–TiO₂ with a larger specific surface area can enhance the degradation rate of 4-CP. On the other hand, under VL irradiation, the migration of photogenerated holes and electrons to the Pt–TiO₂ surface is a rate-determining step and thus the amounts of 4-CP adsorbed on the Pt–TiO₂ surface do not affect the degradation rate.

**CONCLUSIONS**

Visible-light-responsive Pt–TiO₂ photocatalysts with the BET specific surface area larger than 200 m² g⁻¹ were prepared by conducting dialysis using the sol–gel method. In Pt–TiO₂, Pt(II) and Pt(IV) existed near the TiO₂ surface and only Pt(IV) existed in the TiO₂ bulk. The amount of Pt(II) as well as the Pt(II)/Pt(IV) ratio in 0.5 atom % Pt–TiO₂ increased by changing the TTIP concentration in aqueous HNO₃ solution during sol–gel synthesis. We can conclude that the Pt(II)/Pt(IV) ratio is an important factor determining the photocatalytic activity of Pt–TiO₂ under VL irradiation. It is often deduced that the presence of different valence states of a single metal ion would enhance the photocatalytic activity by suppressing the recombination of the photogenerated electrons and holes. We demonstrated for the first time that the photocatalytic activity increased linearly with the ratio of Pt(II)/Pt(IV) in Pt–TiO₂ by developing the characterization...
method for estimating the Pt(II)/Pt(IV) ratio as well as the synthetic method to prepare Pt–TiO₂ having various Pt(II)/Pt(IV) ratios. This finding was also demonstrated for Pt–TiO₂ prepared by the conventional sol–gel method, suggesting that many inconsistent results, which have been reported to date for optimal synthetic conditions of Pt–TiO₂, might be systematically understood by examining the Pt(II)/Pt(IV) ratio of Pt–TiO₂ used for their experiments. Many VL-responsive TiO₂ photocatalysts doped with various metal ions have been developed from the viewpoint of effective utilization of solar energy. Our results indicate that controlling the mixed valence states of metal dopants in TiO₂ is a new strategy to developing highly active photocatalysts under solar light.

■ EXPERIMENTAL SECTION

Preparation of Pt–TiO₂. TTIP (95%, 0.955 g cm⁻³, 0.75—20.0 mL) was added dropwise to 180 mL of aqueous solutions containing 1.3 mL of HNO₃. Unless otherwise noted, the TTIP amount of 15 mL is the standard condition. The obtained mixture was heated at the raising rate of 3 °C/min and then sintered at 200 °C. The powder was ground into 250 mL of H₂PtCl₆·6H₂O aqueous solutions containing 0.6 mL of HNO₃ (pH 1.5), in which the amount of H₂PtCl₆·6H₂O (content of Pt was 0.2—1.0 atom % against Ti + Pt) was added to the TiO₂ sol, followed by dialysis for another 1 day. The obtained sol was dried in an oven (ESPEC, ST-120) at 40 °C for 3 days, and the resulting xerogel was ground into fine powders using an agate mortar and pestle. The powders were sintered by ramping at 3 °C/min and keeping at 200 °C for 2 h. The concentration of Pt ions, which came out of the TiO₂ sol into water during the dialysis, was determined by inductively coupled plasma spectroscopy (Varian, ICP-AES Liberty Series II and Agilent technologies, 5110 ICP-OES) and was used for the calculation of the Pt ion content in Pt–TiO₂. Pure TiO₂ without Pt ions and Pt–TiO₂(ND) were also synthesized.

For comparison, Pt–TiO₂ powders were prepared by modifying the literature method. An ethanol solution (25 mL) containing TTIP (1.25—20 mL) was added dropwise to 250 mL of H₂PtCl₆·6H₂O aqueous solutions containing 0.6 mL of HNO₃ (pH 1.5), in which the amount of H₂PtCl₆·6H₂O was varied to keep the Pt content to be 0.5 atom %. The obtained mixture was stirred at room temperature for 5 days and then evaporated at 50 °C using a rotary evaporator. The obtained powder was ground into fine powders using an agate mortar and pestle and then sintered at 200 °C for 2 h after being heated at the raising rate of 3 °C/min.

Characterization of Pt–TiO₂. XRD (Rigaku, miniflex 600) analysis was performed with Cu Kα radiation (40 kV, 15 mA) at 2θ angles from 10 to 90° with a scan speed of 10° min⁻¹. The BET specific surface area was measured with nitrogen as the adsorptive gas by an automatic surface area analyzer (Shimadzu, Tristar II 3020). Diffuse reflectance UV—vis absorption spectra of the powder samples were obtained using a spectrophotometer (JASCO, V-670). The valence state of the Pt ion near the TiO₂ surface was analyzed by XPS (Thermo Scientific, K-Alpha). The Pt–TiO₂ powder was placed in a Clear Disk (JASCO, CD-05) and pressed into a pellet of 5 mm in diameter using a hand press. The binding energies were calibrated with reference to the C 1s peak (284.8 eV) originating from the surface impurity carbons. The valence state of Pt ion in the TiO₂ bulk was analyzed by XANES. The XANES spectra for the Pt L₃ edge were recorded on beamline 11 at Kyusyu Synchrotron Light Research Center. As reference samples, PtCl₂ and PtO₂ powders were used. Each powder was mixed with boron nitride in an agate mortar for 10 min and then molded into a pellet of 7 mm in diameter using the hand press. The XANES spectra of this pellet placed in a polyethylene bag were measured in the transmission mode. The synthesized Pt–TiO₂ powder sample was placed in the polyethylene bag, and the XANES spectrum was measured in fluorescence mode using a Lytle detector.

Photocatalytic Degradation of 4-CP. The synthesized Pt–TiO₂ (0.2 g) was suspended in 100 mL of 1.0 × 10⁻⁴ mol dm⁻³ 4-CP solution in a transparent Pyrex bottle, which was immersed in a water bath at 30 °C. Under air purging, the suspension was kept in the dark for 30 min to reach the adsorption—desorption equilibrium and then irradiated by a 150 W halogen lamp for 150 min. The light intensity through a long pass filter (Edmund, cut-on wavelength: 400 nm) was measured by a solar power meter (Sato Shouji Inc., SPM-SD) at the center of the Pyrex bottle to be 26 mW cm⁻². For comparison, photocatalytic experiments were performed using four 4 W black lights as the UV light source. The light intensity was measured to be 3.5 mW cm⁻² by a radiometer (Iuchi, UVR-400, S-365). An aliquot sample (7 mL) was withdrawn from the suspension at appropriate times and centrifuged at 2000 rpm for 15 min. The supernatant liquid was filtered through a 0.20 μm filter and then analyzed by a high-performance liquid chromatograph (Shimadzu) equipped with a UV detector (detection wavelength: 280 nm) and a C18 column (Shim-pack, VP-ODS 4.6 mm × 25 cm). The eluent was a mixture of water with methanol (1:1 by volume; flow rate: 1.0 mL min⁻¹).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01393.

XRD patterns of 0.5 atom % Pt–TiO₂ with or without dialysis; SEM images; method for obtaining the calibration curve of Pt(II); XPS spectra of the mixture of TiO₂ and PtCl₂ for making a calibration curve; relationship between moles of Pt(II) in the mixture of TiO₂ and PtCl₂ for making a calibration curve; relationship between moles of Pt(II) in the mixture of TiO₂ and PtCl₂ and the sum of peak areas of Pt(0), Pt(II), and Pt(IV) in the XPS spectra; moles of Pt(II) and their corrected values for making a calibration curve; calculation of a percentage of Pt(II) near the surface of TiO₂ XPS spectra of 0.5 atom % Pt–TiO₂ after the photocatalytic experiments (PDF)

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Notes

The authors declare no competing financial interest.
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