

Fabrication of Transparent Pt-TiO₂ Sol and Its Photocatalytic Activity for Hydrogen Evolution

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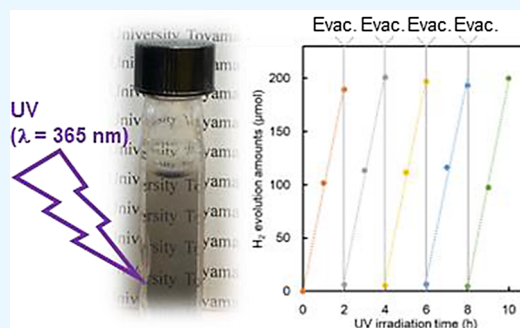


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ABSTRACT: Titanium dioxide doped with Pt(IV) ions was synthesized via a sol–gel method, incorporating a sol purification process through dialysis. The doped Pt(IV) ions were reduced by UV light irradiation to obtain a transparent Pt-TiO₂ sol, with Pt(0) acting as a cocatalyst for hydrogen evolution. The hydrogen evolution activity of Pt-TiO₂ sol was evaluated under UV light irradiation using methanol as a sacrificial reagent. 0.05 atom % Pt-TiO₂ sol remained in the sol state without precipitation after 10 h of UV light irradiation. The amount of hydrogen produced after 10 h of light irradiation was 1195 μmol, with a turnover number (TON) of 664.1, a turnover frequency (TOF) of 66.4 h⁻¹, and an apparent quantum yield (AQY) of 0.86%. The sol–gel synthesis from the molecular level is thought to result in Pt ions being doped inside the TiO₂ particles, maintaining high dispersibility by suppressing particle growth due to the aggregation of Pt(0) during the UV reduction of Pt(IV) ions. These results show that the Pt-TiO₂ photocatalyst has a high renewable energy factor because it can be synthesized at room temperature, and the aggregation of Pt-TiO₂ particles is suppressed by making full use of a sol–gel method.



1. INTRODUCTION

Since the Honda–Fujishima effect was reported, titanium dioxide (TiO₂) has always been a material of interest as an inorganic semiconductor that can be used for hydrogen production by water splitting.¹ For the use of TiO₂ in artificial photosynthesis, which converts solar energy into chemical energy, the required improvements of TiO₂ are to synthesize highly transparent photocatalytic particles with high hydrogen evolution activity and low aggregation/agglomeration in less energy-consuming processes such as low-temperature ones. TiO₂ synthesized by the room temperature sol–gel method reduces the input energy of the renewable energy factor (REF)² which is defined by REF = [Output energy]/[Input energy] and consequently increases the REF of the photocatalyst. Naturally, the REF must exceed 1 to be effective in reducing CO₂ emissions, and the smaller the input energy, the more desirable it is. On the other hand, as the output energy increases, REF also increases. TiO₂, which responds only to ultraviolet light, has the disadvantage of a low sunlight utilization efficiency. However, the adsorption of dyes that absorb visible light onto the TiO₂ surface allows it to respond to visible light.³ Recently, we have reported a water-splitting hydrogen evolution reaction on SWCNT/TiO₂ nanohybrid photocatalysts utilizing the visible light absorption band of SWCNTs.^{4,5} In this case, smaller TiO₂ particle size (nanoparticle) is advantageous because it allows for higher dye loading, but TiO₂ nanoparticles often aggregate and agglomerate, causing serious light scattering. This causes Anderson localization of photons in a disordered medium, which

prevents the absorption of the light by the dye.⁶ However, there are very few reported examples of metal-loaded TiO₂ nanoparticles with high transparency and high activity of hydrogen evolution by water splitting. Inoue and co-workers found that TiO₂ nanoparticles with high transparency were synthesized by the sol–gel method from TiCl₄ in 1 M HCl solution, and that aggregation/agglomeration was suppressed by the addition of MeOH.^{7,8} It is reported that the evolution of hydrogen was observed after the induction period by using the system of RhCl₃ was added to obtain TiO₂ sol (MeOH/H₂O, 9:1 v/v) and irradiated with LED light (365 nm, 5.4 mW). Therein, Rh(0), which acts as the cocatalyst for the hydrogen evolution, is deposited photochemically on the surface of TiO₂ nanoparticles by 30 at %, but there is room for improvement from the viewpoint of reducing rare metals. For these reasons, we decided to explore a new synthesis method for metal-doped TiO₂ sol with hydrogen evolution. Yamazaki et al. reported that anatase-type Pt(IV)-TiO₂ sol with high transparency and a particle size of ca. 4 nm in diameter could be obtained by adding H₂PtCl₆ as a Pt source during the sol–gel reaction by using titanium tetraisopropoxide as the raw material.^{9–11}

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Although Pt(IV)-TiO₂ has been confirmed to have photocatalytic activity for the degradation reactions of dyes or organochlorine compounds, there have been no reports of its use in water-splitting hydrogen production reactions. Since the Pt(IV) ions are present inside TiO₂ particles, the particle growth of Pt(0) acting as a cocatalyst is suppressed by the photoreduction of Pt(IV), and high activity is expected with the addition of a small dosage amount of Pt(IV). In this paper, we report on the photocatalytic activity on the evolution of hydrogen by water splitting using Pt-TiO₂ sol obtained by photoreduction of a highly transparent Pt(IV)-TiO₂ sol synthesized by a low-temperature sol-gel method. Interestingly, Pt-TiO₂ sol has maintained high transparency and stability for at least 1 week.

2. EXPERIMENTAL SECTION

2.1. Materials. Titanium tetraisopropoxide (TTIP, 95%, 0.955 g cm⁻³), hydrogen hexachloroplatinate hexahydrate (H₂PtCl₆·6H₂O, 98.5%), hydrochloric acid (HCl, 35.0–37.0%), and methanol (MeOH, 99.5%) were all purchased from FUJIFILM Wako Pure Chemical Corporation and used without purification. The water used was ultrapure water (Milli-Q water) purified from an ultrapure water production unit (Direct-Q UV-3, Merck) directly connected to tap water.

2.2. Synthesis of Pt-TiO₂ Sol. **2.2.1. Washing of Dialysis Membrane Tubes.** Two dialysis membrane tubes (Spectra/Por 3, MWCO 3500, width: 45 mm, Repligen) cut to ca. 17 cm were immersed in 1000 mL of Milli-Q water and stirred for 30 min at ca. 80 °C while being heated on a hot magnetic stirrer (RSH-1A, AS ONE corporation). The dialysis membrane tubes were then cooled to room temperature and washed thoroughly with water. Dialysis membranes were immersed in water and stored in a refrigerator until the time of use.

2.2.2. Synthesis of Pt(IV)-TiO₂ Sol. Pt-TiO₂ was synthesized by modifying the method of the previously reported paper.^{9–11} Briefly, the procedure for synthesizing Pt-TiO₂ sol with 0.05 atom % Pt ion doping against Ti is shown. Five mL of TTIP was added dropwise to 60 mL of aqueous solutions containing 0.52 mL of HCl (pH < 1) and 4.2 mg of H₂PtCl₆·6H₂O. The obtained mixture was peptized at room temperature for 4 days to form a highly dispersed colloidal solution. This Pt(IV)-TiO₂ sol was placed in a 17 × 4 cm dialysis membrane tube and dialyzed with 1000 mL of water. The Pt(IV)-TiO₂ sol was purified by changing the water every hour for a total of eight times. To investigate the optimum amount of Pt doping, Pt(IV)-TiO₂ sol was also synthesized by the above procedure with the amount of H₂PtCl₆·6H₂O adjusted so that the amount of Pt ion doping was 0.025–1.0 atom %.

2.2.3. Synthesis of Pt-TiO₂ Sol. Pt-TiO₂ was obtained by adding 2 mL of MeOH to 18 mL of Pt(IV)-TiO₂ in a 30 mL vial bottle and irradiating with a UV LED for 30 min (λ = 365 nm, 100 mW cm⁻²) while Ar was bubbling (50 mL min⁻¹).

2.3. Physical Property of Pt-TiO₂ Sol. **2.3.1. UV-Vis Absorption Spectra of Pt-TiO₂ Sol.** Pt-TiO₂ sol and methanol (10 vol %) were added to a 10 mm cuvette quartz cell with Ar purging (50 mL min⁻¹) for 30 min. After that, the quartz cell was covered by a screw cap and irradiated with 365 nm UV light (λ = 365 nm, 100 mW cm⁻²) for 4 h. The valence states of Pt in Pt-TiO₂ sol before and after UV light irradiation were analyzed by measuring the absorption spectra using a UV-Vis spectrophotometer.

2.3.2. Measurements of the Valence States of Pt by X-ray Photoelectron Spectroscopy (XPS). The xerogel was obtained by adding methanol to 0.1 atom % Pt-TiO₂ sol at 10 vol %, irradiating with UV light for 4 h, and drying at 90 °C for 24 h. The xerogel was ground in an agate mortar to obtain the Pt-TiO₂ powder. Clear discs (JASCO, CD-05) containing Pt-TiO₂ powder were placed in a pellet molding machine for an IR spectrometer and formed into a 5 mm diameter pellet using a hand press machine. For comparison, a pellet made from Pt-TiO₂ powder before UV irradiation was also prepared. XPS (ESCALAB 250Xi, Thermo Fisher Scientific) measurements were performed on these pellets. The binding energies were calibrated with reference to the C 1s peak (285.0 eV) originating from the surface impurity carbons on Pt-TiO₂.

2.3.3. Particle Size Measurements by Dynamic Light Scattering (DLS). Pt(IV)-TiO₂ (before UV light irradiation) or Pt-TiO₂ (after UV light irradiation) was placed in a 4-sided transmission cuvette cell (optical pass: 10 mm), and the particle size was measured by a particle sizing system (Otsuka Electronics Co., Ltd., ELSZ-2000).

2.3.4. Raman Spectra Measurements. Pt-TiO₂ powder was dispersed on a glass slide, and Raman spectra were measured using a micro-Raman spectrometer (JASCO, NRS-7100) at an excitation wavelength of 532 nm, exposure time of 5 s, and 16 integration times.

2.4. Evaluation of the Photocatalytic Activity. A glass vial with a volume of approximately 30 mL contained 18 mL of Pt-TiO₂ sol and 2 mL of methanol (Pt-TiO₂: 0.18 M; MeOH: 10 vol %; total volume of solution: 20 mL; the volume of the headspace; ca. 14 mL). The photocatalytic suspension was irradiated with 365 nm UV light at 100 mW cm⁻² for 30 min (irradiation distance: ca. 5 cm; irradiated area: ca. 28.3 cm⁻²) while purging and stirring dissolved oxygen with Ar (50 mL min⁻¹) to reduce doped Pt ions. After that, the glass vial bottle was then sealed with a butyl rubber stopper and aluminum tape by using a hand clip. The amount of photogenerated hydrogen was analyzed by inserting a glass gastight syringe (Hamilton, 1810N) into a butyl rubber stopper, collecting 100 μL of gas in the headspace, and injecting it into a gas chromatograph (Shimadzu, detector: TCD, column: molecular sieve 5 A: 2.0 m × 3.0 mm, carrier gas: Ar) every 1 h. The increase in the evolution of hydrogen up to 2 h of UV light irradiation was fitted with a linear function, the slope of which was used as the rate of hydrogen evolution (*r*). The apparent quantum efficiency (AQY) was calculated using the following eq 1. Here, the AQY was calculated using the amount of hydrogen at 1 h of UV irradiation.

$$\text{AQY (\%)} = \frac{2 \times \text{number of evolved hydrogen (mol)}}{\text{number of incident photons (mol)}} \times 100\% \quad (1)$$

Turnover number (TON) and turnover frequency (TOF) was calculated using the following eqs 2 and 3. Here, the TON was calculated using the amount of evolved hydrogen at 4 h of UV irradiation.

$$\text{TON} = \frac{\text{amount of evolved hydrogen after 4 h of UV irradiation (mol)}}{\text{amount of Pt (mol)}} \quad (2)$$

$$\text{TOF (h}^{-1}\text{)} = \frac{\text{TON}}{4 \text{ h}} \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Pt-TiO₂ Sol Synthesis. After refining the previously reported method, we synthesized Pt(IV)-TiO₂.^{9–11} Then Pt-TiO₂ was synthesized by adding MeOH as a reducing agent and irradiating with UV light to obtain highly transparent Pt(IV)-TiO₂ sol (Figure 1). In a typical run, 5 mL of titanium

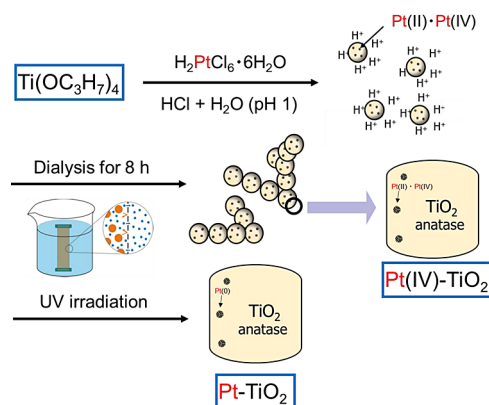


Figure 1. Synthesis of a transparent Pt-TiO₂ sol.

tetraisopropoxide was added dropwise to 60 mL of an aqueous solution containing 0.52 mL of HCl and 4.2 mg of H₂PtCl₆·6H₂O. The obtained mixture was peptized at room temperature for 4 days to form a highly dispersed colloidal solution. This highly dispersed 0.05 at % Pt(IV)-TiO₂ sol (ca. 0.2 M, 80 mL) was obtained by dialysis for 8 h using a molecularly porous dialysis tube immersed in 1000 mL of water. The water was exchanged once an hour. Pt-TiO₂ was obtained by adding 2 mL of MeOH to 18 mL of Pt(IV)-TiO₂ and irradiating with a UV LED for 30 min ($\lambda = 365$ nm, 100 mW cm⁻²) while Ar bubbling. Figure 2 shows photographs of 0.1 at % Pt(IV)-TiO₂

sol before and after UV irradiation and its UV–vis absorption spectra. Transparent Pt(IV)-TiO₂ sol before UV light irradiation changed to black transparent Pt-TiO₂ after the reduction treatment (Figure 2a,b). The increased absorption in the visible light region due to UV irradiation indicates the reduction of Pt(IV) to Pt(0), as reported by Choi and co-workers (Figure 2c).¹² Figure S1 shows Tauc plots of Pt(IV)- and Pt-TiO₂ and TiO₂. The band gap energies of TiO₂, Pt(IV)-TiO₂, and Pt-TiO₂ are 3.19, 3.17, and 3.08 eV, respectively. Therefore, the reduction of Pt(IV) and the formation of hydrogen proceed under UV LED irradiation. We have reported that during Pt(IV)-TiO₂ synthesis, almost all of the Pt(IV) ions are incorporated into TiO₂ nanoparticles when the amount of Pt(IV) ions added is less than 2 atom %.¹¹ This is thought to have maintained high dispersibility by suppressing particle growth due to aggregation of Pt(0) during the reduction of Pt(IV) ions by UV irradiation. In fact, Pt-TiO₂ is stable for at least 1 week at room temperature and does not precipitate at all. Particle size measurements using DLS showed that the particle size of Pt-TiO₂ after 6 h of UV light irradiation was ca. 57 nm, almost unchanged from that of Pt(IV)-TiO₂ sol before UV light irradiation (ca. 53 nm).

3.2. Valence States of Pt in Pt-TiO₂ Sol. Figure 3 shows XPS spectra of 0.1 at % Pt(IV)-TiO₂ and photoreduced Pt-TiO₂. In the case of Pt(IV)-TiO₂, only the peaks at 72.8 and 75.9 eV were observed to be derived from 4f_{7/2} and 4f_{5/2} of Pt(II), and at 74.6 and 77.6 eV from 4f_{7/2} and 4f_{5/2} of Pt(IV), with no Pt(0) detected (Figure 3a), the peaks around 71.0 and 74.3 eV were observed to originate from 4f_{7/2} and 4f_{5/2} of Pt(0).^{13,14} These results are consistent with the results of UV–Vis absorption spectra, indicating that UV irradiation of Pt(IV)-TiO₂ in the presence of MeOH reduced many if not all of the Pt ions to Pt(0). Figure S2 shows XPS spectra of Ti 2p and 1s for 0.1 atom % Pt(IV)-TiO₂ and photoreduced Pt-TiO₂. The Ti 2p spectra were almost unchanged before and after UV irradiation and could be attributed to Ti(IV) in TiO₂. From the results of the O 1s spectra, it is attributed to Oxygen in the TiO₂ crystal lattice and hydroxyl group on the Pt-TiO₂ surface. Figure S3 shows Raman spectra of 0.1 atom % Pt(IV)-TiO₂ and photoreduced Pt-TiO₂. The results of Raman spectral measurements indicate that this is an anatase-type crystal system (Figure S3). XPS and Raman spectra show that Pt(IV) and Pt-TiO₂ are anatase crystalline systems even without calcination.

3.3. Hydrogen Evolution from Water Using Pt-TiO₂ Sol as a Photocatalyst. Given the confirmed presence of Pt(0), which demonstrates cocatalytic activity in hydrogen generation, we proceeded to explore photocatalytic hydrogen evolution using Pt-TiO₂ as a photocatalyst and methanol as a sacrificial agent (Figure 4). By UV light irradiation, the holes generated in the valence band of Pt-TiO₂ oxidatively decompose methanol. At the same time, electrons in the conduction band are transferred to the Pt cocatalyst and consumed by the reaction of hydrogen generation by proton reduction.

Figure 5 shows the time course of the amount of hydrogen evolution on 0.05 atom % Pt-TiO₂ sol under UV light irradiation. Pt-TiO₂ sol was added to 10% (v/v) methanol and irradiated with UV LED ($\lambda = 365$ nm), and the evolved gases were analyzed every 1 h using a gas chromatograph. Every 2 h of UV light irradiation, the evolved hydrogen was removed by Ar bubbling for ca. 15 min (Evac. in Figure 5). This process was repeated 5 times for a total of 10 h to trace photocatalytic

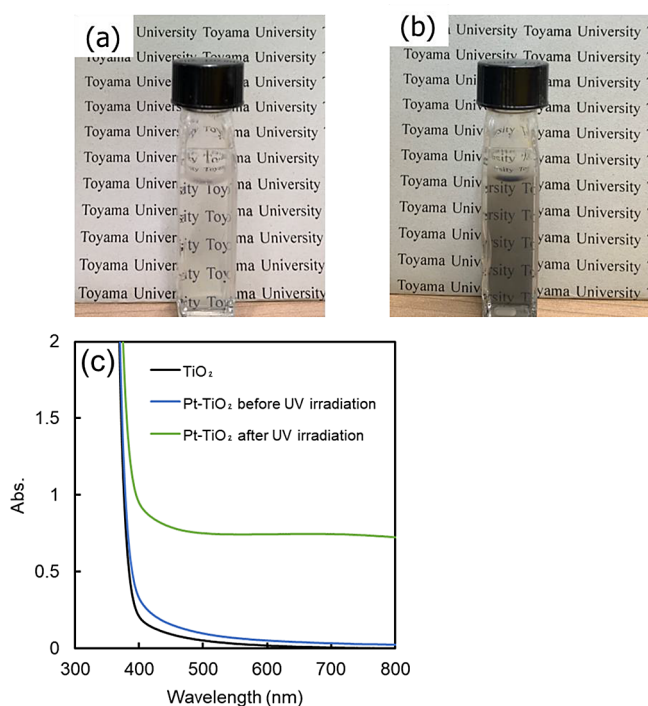


Figure 2. Photographs of Pt-TiO₂ sol (a) before UV irradiation, (b) after UV irradiation, and (c) their UV–Vis absorption spectra.

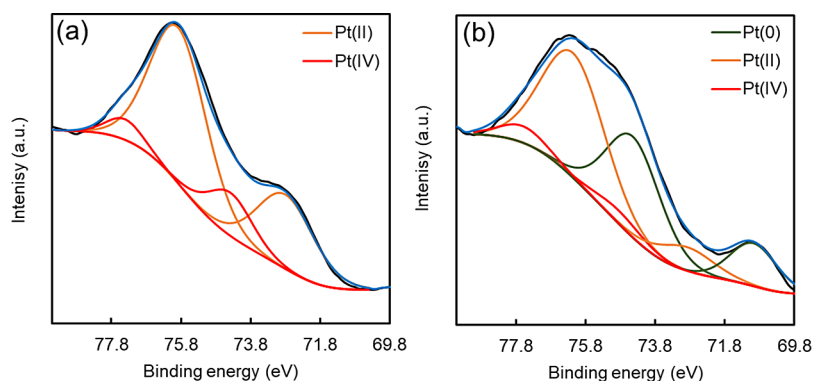


Figure 3. XPS spectra of 0.1 atom % Pt-TiO₂ before (a) and after (b) UV light irradiation.

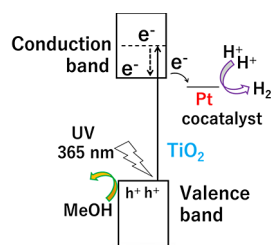


Figure 4. Mechanism of hydrogen evolution by the UV irradiation of Pt-TiO₂.

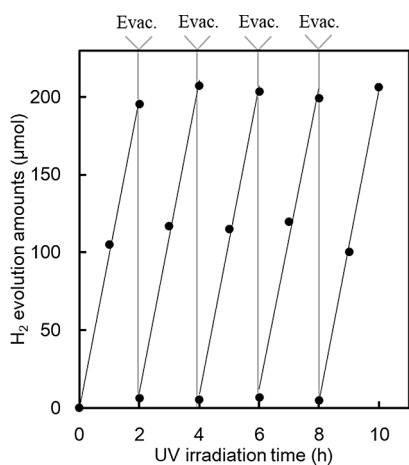


Figure 5. Time course of the hydrogen evolution using 0.05 atom % Pt-TiO₂ under UV light irradiation.

activity. It is notable that Pt-TiO₂ sol remained stable and transparent and did not lose activity during the experiment. The average of the rate of hydrogen evolution for five runs could be determined to be 96.1 $\mu\text{mol h}^{-1}$. The amount of evolution of hydrogen during 10 h of UV light irradiation was 1195 μmol . From these values, the turnover number (TON) and turnover frequency (TOF) were calculated to be 664.1 and 66.4 h^{-1} , respectively, and the apparent quantum efficiency (AQY) was about 0.86%. It is important to note that Pt-TiO₂ sol synthesized at room temperature can be used as a photocatalyst for hydrogen evolution from the viewpoint of REF.

3.4. Doping Amount of Pt. Finally, the effect of the amount of Pt doping on the photocatalytic activity was investigated. Figure 6a shows the time course of the amount of hydrogen evolution on 0.025–1.0 atom % Pt-TiO₂ sol under UV light irradiation. Figure 6b shows the effect of the rate of

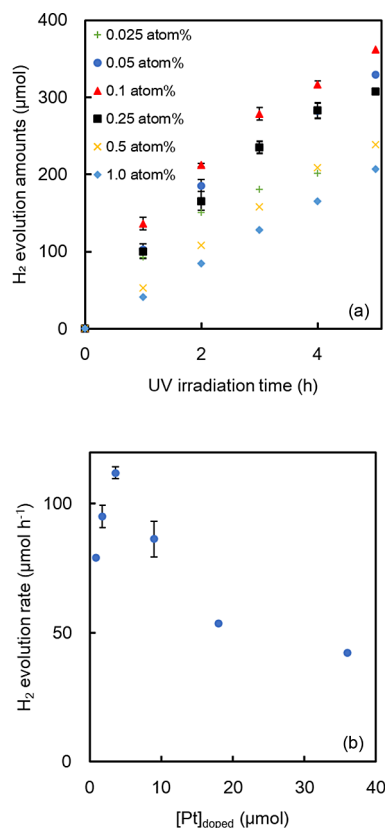


Figure 6. (a) Time course of the evolution of hydrogen on 0.025–1.0 atom % Pt-TiO₂ under UV light irradiation. (b) Effect of the amount of Pt doping on the rate of hydrogen evolution.

hydrogen evolution on the doping amount of Pt. Table 1 shows the moles of Pt, the rate of hydrogen evolution, TOF, TON (the amount of hydrogen evolution at 4 h of UV light irradiation), and AQY. The rate of hydrogen evolution and AQY showed maximum values at 0.1 atom % Pt ion doping. In general, it is often reported that photocatalysts using powders show maximum activity with a loading of 1–4 wt % of the cocatalyst.^{15–18} In this paper, we have found that high activity is exhibited at the amount of Pt doping of 0.025–1.0 atom %, which is about 1 order of magnitude lower than previously reported values. This result shows the superiority of Pt-TiO₂, exhibiting a significant reduction in cocatalyst loading compared to previously reported levels. This phenomenon is attributed to the incorporation of Pt ions within TiO₂ particles

Table 1. H₂ Evolution Rate, TOF, TON, and AQY, as Functions of the Pt Doping Amount

| Pt dope amount (atom %) | [Pt] _{doped} (μmol) | H ₂ evolution rate (μmol h ⁻¹) | TOF (h ⁻¹) | TON ^a | AQY ^b (%) |
|-------------------------|------------------------------|---|------------------------|------------------|----------------------|
| 0.025 | 0.90 | 79.0 | 56.1 | 224.3 | 0.66 |
| 0.05 | 1.8 | 94.9 ± 4.3 | 39.2 ± 1.4 | 156.9 ± 5.7 | 0.74 |
| 0.1 | 3.6 | 112.2 ± 2.2 | 22.0 ± 0.3 | 88.1 ± 1.2 | 0.98 |
| 0.25 | 9.0 | 86.3 ± 6.9 | 7.9 ± 0.3 | 31.5 ± 1.1 | 0.72 |
| 0.5 | 18.0 | 53.7 | 2.9 | 11.6 | 0.38 |
| 1.0 | 36.0 | 42.2 | 1.2 | 4.6 | 0.29 |

^aCalculated by the amount of hydrogen in 4 h of UV light irradiation. ^bCalculated by the amount of hydrogen in 1 h of UV light irradiation.

via the sol–gel method, consequently mitigating the aggregation of Pt(0) particles during photoreduction.

4. CONCLUSIONS

Pt-TiO₂ was synthesized by UV irradiation of Pt-doped titanium dioxide (Pt(IV)-TiO₂) in the presence of MeOH. Pt-TiO₂ showed activity as a hydrogen-evolution photocatalyst. UV light irradiation ($\lambda = 365$ nm) of a water–methanol dispersion (9:1, v/v) of 0.05 atom % Pt-TiO₂ sol (0.18 M) evolved 1195 μmol of hydrogen in 10 h, with TOF of ca. 66.4 h⁻¹ and AQY of ca. 0.86%. Pt-TiO₂ is synthesized by a room temperature process and is expected to have a high REF. Additionally, due to its high transparency and minimal light scattering, Pt-TiO₂ holds promise for integration into photocatalytic systems designed to harness visible light effectively by hybridizing with organic dyes and other materials responsive to visible light. We are currently conducting research on the development of innovative organic/inorganic hybrid photocatalysts based on Pt-TiO₂.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c05671>.

Tauc plots of 0.1 atom % Pt-TiO₂ before and after UV light irradiation and TiO₂; XPS spectra of Ti 2p and O 1s for 0.1 atom % Pt-TiO₂ before and after UV light irradiation; and Raman spectra of 0.1 atom % Pt-TiO₂ before and after UV light irradiation (PDF)

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Notes

The authors declare no competing financial interest.

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