

Synthesis of Titania-Supported Platinum Catalyst: The Effect of pH on Morphology Control and Valence State during Photodeposition

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Solid-supported metal catalysts have been widely used in industrial processes. The morphology of coated metal on the support is usually an important factor affecting the efficiency of the catalyst. In this study, a photocatalytic process is utilized to control the morphology of platinum particles deposited on titania (Degussa P-25). More specifically, the effect of pH on the morphology and the valence state of platinum nanoparticles was systematically investigated. It is found that, via a simple pH-controlled process, various states of platinum (Pt^0 , $Pt^{II}O$, or $Pt^{IV}O_2$) can be deposited onto the support directly at will. In this paper, the mechanism of morphology control and the key influencing factors at different pH regimes will be discussed. Followed by photodeposition, a H_2 thermal treatment process was employed to convert the oxides into metal platinum with narrow size distribution and even coverage on the supporting titania. Various techniques such as transmission electron microscopy, high-resolution transmission electron microscopy, energy-dispersive analysis of X-rays, and X-ray photoelectron spectroscopy were employed to characterize the prepared titania-supported platinum particles.

Introduction

One of the most challenging issues today is to design, fabricate, and manipulate nanostructured materials to achieve tailored chemical–physical characteristics for advanced applications. Among them, nanosized semiconductors and metals^{1,2} are of great research interest due to their unusual catalytic and electronic/optical properties. Nanocomposite systems that contain both metal and metal oxides^{3,4} are particularly interesting as they exhibit sharp contrast in properties in relation to typical bifunctional catalysts. In the nanosized regime, the oxide is not merely a support. The intimate metal–oxide interaction can have a significant impact on the properties of the metal component.^{3a} As an example, such an interaction often enhances the photocatalytic efficiency of oxide–noble metal⁴ composites by reducing the fast recombination of photogenerated charge carriers on the oxide.

Due to its high photocatalytic efficiency, chemical inertness, surface amphotericity, and nontoxicity, TiO_2 is the most studied semiconductor photocatalyst for various ap-

plications, especially environmental waste treatment. Platinum shows remarkable catalytic activity for hydrogenation, dehydrogenation, and cracking of hydrocarbons.⁵ It is also known that different valence states of platinum lead to diverse catalytic pathways.⁶ It is anticipated that the interaction between TiO_2 and Pt at the nanoscale will have a significant impact on the catalytic behavior of Pt and, thus, offer an unexplored opportunity for the realization of nanocomposite systems with enhanced and/or novel catalytic properties. To create a true nanocomposite material that contains titania and Pt particles, it is obvious that the traditional physical blending method is inadequate. Even with the chemical precipitation approach, the particle size of the active phase is usually quite broad and it is rather difficult to control the size and morphology.

Recently, several new techniques have emerged for the synthesis of Pt nanoparticles in an aqueous environment⁷ or in organic solutions^{8,9} and the deposition of platinum onto various supports such as Al_2O_3 ,¹⁵ TiO_2 ,^{20–29,31} CdS ,³⁰ carbon,¹¹ and mesoporous zirconia.¹⁰ Among these tech-

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niques are electron beam lithography,¹² colloidal lithography,¹³ spin-coating,¹⁴ microemulsions,^{15–19} and photoelectric and photocatalytic techniques.^{20–31} Although the size, shape, and interparticle distance of platinum particles on supports can be to some extent controlled by the above-mentioned techniques,^{10–19} the preparation process is usually complicated and contains multiple steps. In addition, the use of surfactant molecules in some of the techniques may introduce impurities that limit the applications of the final product. Even though photoelectric or photocatalytic deposition has been extensively investigated to coat and disperse noble metals onto semiconductors,^{20–31} little attention has been paid to the control of particle size, morphology, and interparticle distance between coated particles.

In a recent paper,³² we described an innovative approach to controlling the coating morphology of silver particles on TiO₂ particles during photocatalytic deposition. The morphology of silver particles was controlled by a combined use of surfactant, proper pH, and a source of silver such as silver oxide, AgCl, and AgBr. The objective of this study was to synthesize homogeneously dispersed platinum or its oxide with narrow size distribution onto titanium dioxide. More specifically, the pH variation is to be used as a handle to examine the hydrolytic behavior of PtCl₆²⁻ ions and its effect on the morphology and the valence state of platinum particles found on titania. The goal is to gain fundamental knowledge of the synthesis of nanocomposite materials with well-defined and predictable interparticle interactions.

Experimental Section

All commercial reagents and solvents used were of analytical grade without further purification. The water used was double distilled. TiO₂ was nonporous Degussa P-25, mainly anatase,

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with a surface area of ca. 50 m² g⁻¹. Transmission electron microscopy (TEM) was carried out on a Philips EM-120 TEM instrument with an accelerating voltage of 100 keV. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive analysis by X-rays (EDAX) were performed on a JEOL JEM-2010FEF ultrahigh-resolution transmission electron microscope working at 200 kV accelerating voltage. The particles obtained after the irradiation and workup were dropped onto the surface of a carbon membrane of a copper grid and dried at ambient conditions before analysis. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5300 ESCA commercial instrument (PHI Inc.) (Mg K α radiation; 1253.6 eV; 10⁻⁷ Pa) using the C 1s photoelectron peak (binding energy at 284.6 eV) as an energy reference. Atomic absorption spectrometry (AAS) was done using HTAZHI 180-80 (Japan).

The detailed photodeposition process was illustrated in our previous publication.³² A typical photodeposition was carried out in a 250 mL round-bottom flask using a 250 W high-pressure mercury light with the main wavelength of 365 nm as the light source. Unless stated, to 160 mL of 2 \times 10⁻³ M potassium hexachloroplatinate aqueous solution, 500 mg of TiO₂ and 8 mL of ethanol were added. The initial pH value of the slurry was adjusted to the desired range using either 1 M HCl or 1 M KOH aqueous solution. The suspension was purged with high-purity N₂ atmosphere to remove oxygen. The slurry was vigorously stirred throughout the process. During irradiation, the concentration of hexachloroplatinate and the pH of the solution were monitored at 10 min intervals. A slurry sample (ca. 6 mL each) was withdrawn and centrifuged at 7000 rpm for 10 min. The supernatant was analyzed by atomic absorption spectroscopy. After 6 h of irradiation, the particles were filtered, washed, and dried at ambient conditions. The samples were then analyzed by TEM and XPS.

H₂ thermal post-treatment of sample D prepared at the pH region of 9–11 was carried out in 573 K H₂ flow for 4 h to reduce platinum oxide species. The post-treated particles were characterized by HRTEM, the EDAX spectrum, and XPS spectra.

The hydrolytic behavior of PtCl₆²⁻ ions was monitored using UV-240 UV/vis spectroscopy at various pH values. HCl solution (1 M) and 1 M KOH solution were employed as pH regulators. Distilled water was employed as a reference sample, and the scan region was divided into two parts of 300–500 and 190–300 nm. Typical experimental concentrations of K₂PtCl₆ were selected at 6 \times 10⁻⁵ M close to the limit of measurement and 2 \times 10⁻³ M equal to the initial concentration of the preparation solution. The representative results are shown in Figure 1 and Figure 2 of the Supporting Information. Compared with the data in Table 1 of the Supporting Information, the 202(203), 258(259), and 360 nm bands can be explained as ¹A_{1g} \rightarrow C¹T_{1u}, ¹A_{1g} \rightarrow b¹T_{1u}, and ¹A_{1g} \rightarrow ¹T_{1g} transitions, respectively. The disappearance of the 206 nm absorption band and strengthening of the 210 nm signal in Figure 2b, compared with Figure 2a, suggested that the increase of pH value will promote the hydrolysis of potassium hexachloroplatinate, and the peak around 210 nm belongs to a hydrolyzed product. Although the exact structures of the hydrolyzed products have not been elucidated, the experimental results clearly indicate the pH effect on the hydrolysis of PtCl₆²⁻ ions.

Results

In our previous publication,³² a photocatalytic process was employed to control the morphology of deposited silver onto titania with a careful selection of pH value and source of silver such as silver oxide, AgCl, and AgBr. On the well-dispersed titania particles, Ag⁺ ions were first converted into silver oxide, AgCl, or AgBr which keep the local concentration of Ag⁺ ions extremely low. The pre-occupation of those water-insoluble particles and the low local silver ion contribution make the homogeneous dispersion of coated silver possible. For platinum deposition, the solution pH value affects not only the stability of the titania dispersion but also the hydrolytic behavior of platinum precursor ions. In other words, the solution pH value will have a direct impact on the local concentration

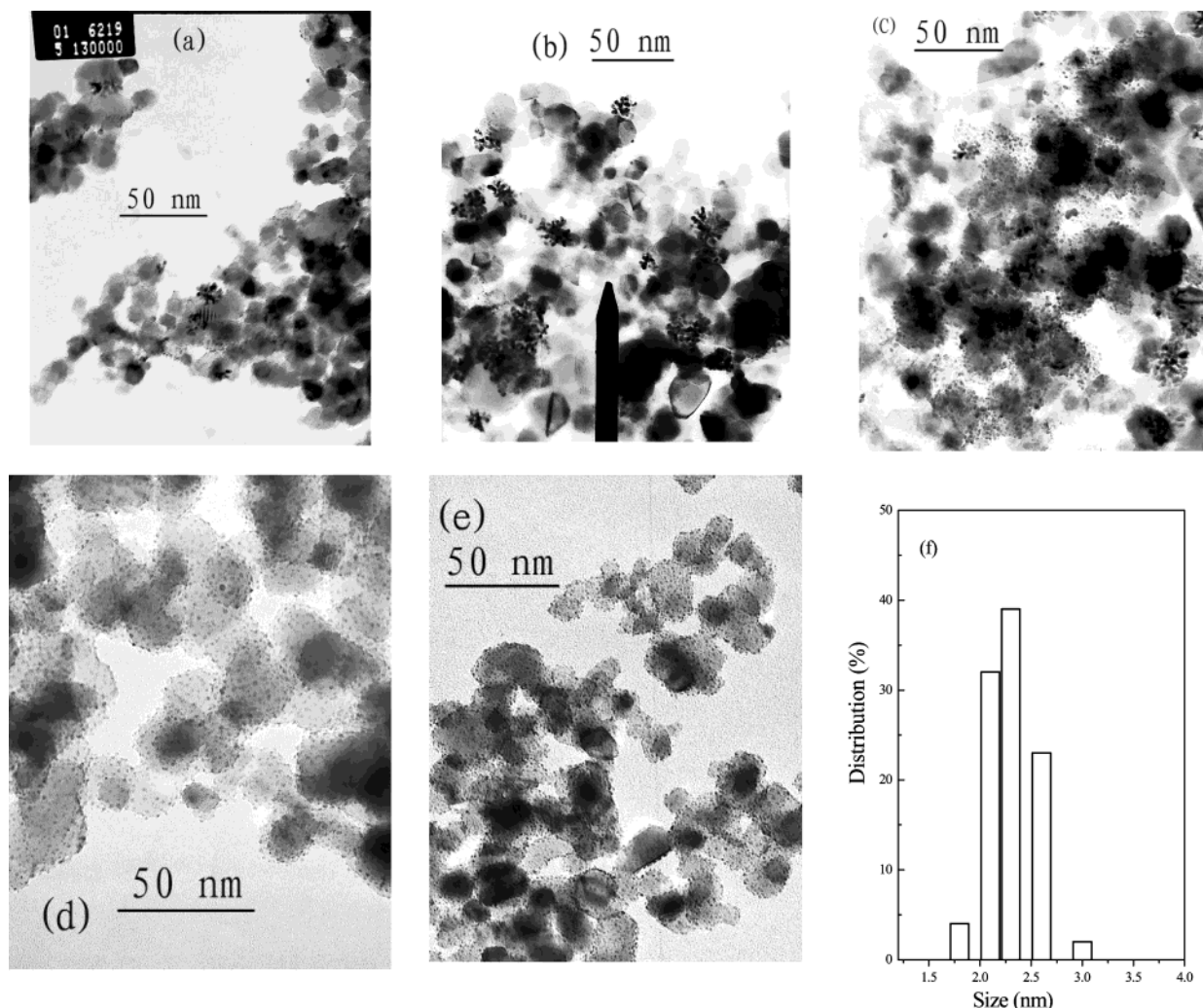


Figure 1. TEM images of (a) sample A prepared at the pH region below 5, (b) sample B prepared at the pH region of 5–7, (c) sample C prepared at the pH region of 7–9, (d) sample D prepared at the pH region of 9–11, and (e) sample E prepared at the pH region of 11–13. (f) The histogram of the size distribution of platinum particles in image d.

and exact structures of platinum anions on the surface of titania which may lead to different deposition morphology as well as the chemical nature of the deposited particles.

To investigate the effect of pH on the morphology and chemical nature of deposited platinum, a set of photo-deposition experiments were conducted using slurries with initial pH values at ca. 4.5, 6.5, 8.5, 10.5, and 12.5. During the photochemical experiments, the pH values of slurries were controlled at <5, 5–7, 7–9, 9–11, or 11–13, respectively, with NaOH or HCl solutions. The particles prepared under corresponding conditions are referred to as samples A–E. The key experimental parameters and results are summarized in Table 1. The representative TEM images of representative particles for each case are shown in Figure 1; the small black dots are platinum species. As indicated in Table 1 and Figure 1, the resulting samples have different physical appearance and chemical compositions. In an acidic medium (sample A, pH < 5), most of the deposited Pt exists as small Pt particles besides little aggregated Pt particles (Figure 1a). When the pH value of the solution is increased to nearly neutral (sample B, pH = 5–7), most Pt particles are present as large agglomerates with some diameters greater than that of the parent TiO₂. A remarkable improvement in dispersion of platinum deposits was found on sample C. Finally, the deposited particle size and distribution are much more

Table 1. Experimental Conditions and Results of As-Prepared Particles^a

sample	pH	appearance of resulting sample	TEM result shown in	major species	average deposition rate ^b
A	<5	white	Figure 1a	Pt	7.01
B	5–7	viridescent	Figure 1b	Pt + PtO	5.34
C	7–9	filemot	Figure 1c	PtO + PtO ₂	2.67
D	9–11	brown-yellow	Figure 1d	PtO ₂	1.78
E	11–13	brown-yellow	Figure 1e	PtO ₂	1.64

^a Other conditions: [K₂PtCl₆] = 2 × 10⁻³ M; 8 mL of ethanol; 500 mg of TiO₂ in 160 mL of twice-distilled water. ^b The average deposition rate was calculated by measuring the sample drawn in the time interval of 0.5 h at the initial pH value of ca. 4, 6, 8, 10, and 12, respectively (*r*: μmol min⁻¹).

uniform for samples D and E which were prepared at the pH region of 9–13. Figure 1f shows the histogram of the size distribution of sample D, which indicates an excellent size distribution. As a whole, a basic solution produces a narrower size distribution and homogeneous dispersion of platinum particles on the support.

Figure 2 shows the XPS spectra of samples A–E. Three different valence states of Pt⁰, Pt^{II}O, and Pt^{IV}O₂ were assigned to particles based on the corresponding binding energies of 70.5, 72.2, and 74.5 eV, respectively. The results are summarized in Table 1, which revealed an interesting trend that the valence states of deposited platinum depend

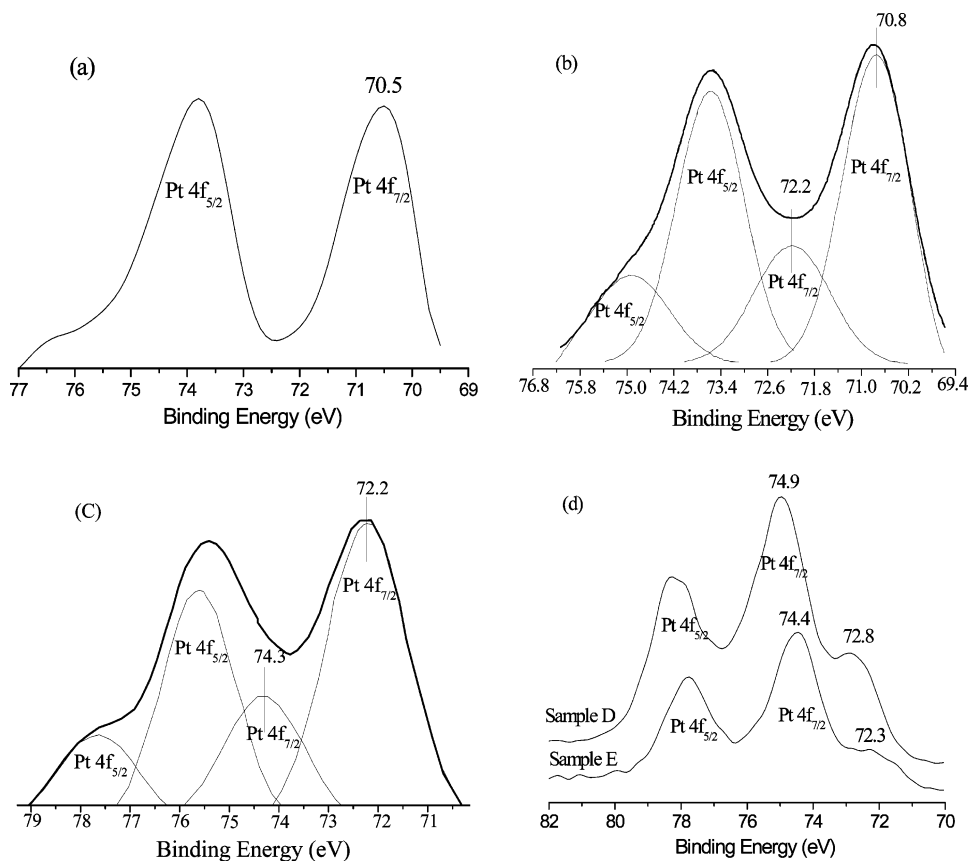


Figure 2. XPS spectra of (a) sample A prepared at the pH region below 5, (b) sample B prepared at the pH region of 5–7, (c) sample C prepared at the pH region of 7–9, (d) sample D prepared at the pH region of 9–11 and sample E prepared at the pH region of 11–13.

strongly on the solution pH value. The valence of the deposited particles increases when the pH value of the initial slurry increases. Sample A, prepared at pH < 5, has deposited particles mainly composed of metallic platinum, with binding energy of 70.5 eV (see the XPS spectrum in Figure 2a). Sample B, prepared in nearly neutral condition, contains both metallic platinum and PtO (Figure 2b). On the other hand, samples C, D, and E, prepared in basic solutions, have no metallic platinum but PtO and PtO₂, with binding energies of ca. 72.2 and 74.5 eV, respectively (see the XPS spectra in Figure 2c–e). Furthermore, the ratio of the two components changes with pH variation as well. The content of PtO₂ gradually increases with the strength of alkalinity of the slurry.

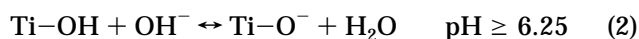
For many hydrogen-involving catalytic reactions, it is known that metallic platinum provides much more active sites than other states of platinum such as Pt^{II}O and Pt^{IV}O₂. To produce particles containing deposited metallic Pt with desired particle size and distribution, sample D was treated under H₂ flow at 573 K for 4 h to convert platinum oxides into metal platinum. The morphology and valence state of the treated particles were characterized by HRTEM, EDAX, and XPS. As shown in Figure 3, most platinum oxide particles originally on sample D have been converted to metallic platinum except a little PtO. It is important to point out that the treatment did not disturb the homogeneity and morphology of the deposited particles on the support.

Discussion

In our previous work on the photodeposition of nanosize silver particles onto a titania support,³² we introduced a novel approach in which a water-insoluble silver salt was

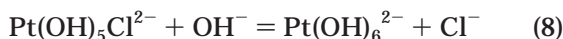
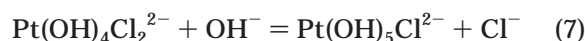
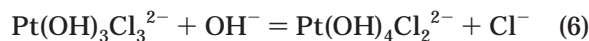
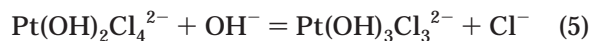
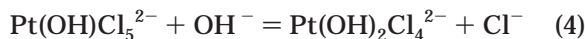
used to control the local silver ion concentration on the surface of titanium dioxide and hence the morphology of coated silver particles on the surface. In this paper, K₂-PtCl₆ was employed as an initial platinum source for the deposition of Pt on titania. As seen in the results section, the morphology of coated platinum particles can be controlled by regulating the initial pH value of the slurry. It is apparent that the strategy used in silver deposition also works for the platinum system. The key difference between the two systems is the actual species that received the electron from the conduction band of the illuminated titania. For the silver system, it is the Ag⁺ cation. For Pt, a series of hydrolytic products of PtCl₆²⁻ such as Pt(OH)_xCl_{6-x}²⁻ may coexist in a wide pH range,^{30a} making the Pt system much more complicated than its silver counterpart.

As the isoelectric point of titanium dioxide is ca. 6.25,³² the net surface charge of titanium dioxide will be different below or above 6.25 (eqs 1 and 2).



In other words, in a basic solution (or pH > 6.25) the surface of titania will be negatively charged, which will attract Ag⁺ ions to its surface but repulse platinum anions (Pt(OH)_xCl_{6-x}²⁻). Consequently, the deposition of Pt may undergo a completely different mechanism from that for silver.

In aqueous solution, a sequential hydrolysis of PtCl_6^{2-} occurs to give a series of hydrolytic products as indicated in eqs 3–8:^{30a,33}



It is obvious that the increase of pH value in solution will promote the hydrolysis of PtCl_6^{2-} ions and lead to a higher percentage of products containing fewer chlorides. For example,^{30a} in a solution containing 0.5 M HCl, the major hydrolytic ion is Pt(OH)Cl_5^{2-} ; in a nearly neutral solution, the predominate species is $\text{Pt(OH)}_2\text{Cl}_4^{2-}$. The highly hydrolyzed products $\text{Pt(OH)}_5\text{Cl}^{2-}$ and Pt(OH)_6^{2-} will become dominant in a more basic environment.

In addition to the fact that the degree of hydrolysis of PtCl_6^{2-} may vary at different pHs, the stability and aggregation of titanium dioxide particles are also affected by the pH value of the slurry. The interparticle interaction or aggregation among titania particles plays a significant role in determining the morphology for deposited particles (Pt or Ag).³² To achieve deposition with well-defined and uniform dispersion on the supporting particles, the residence time for the interparticle interaction among titania must be significantly shorter than that required for deposition. Otherwise, the imprint of such interparticle interaction will be seen through the pattern of the deposited particles. It is clear that such a short residence time among dispersed TiO_2 particles can only be obtained when the selected pH value is significantly away from the isoelectric point (IEP = 6.25) of TiO_2 .³² When the solution is in the acidic regime or below the IEP of TiO_2 , the surface of TiO_2 is positively charged and favors the adsorption of PtCl_6^{2-} and its hydrolyzed products. The local concentration of these anions is relative high. Thus the overall efficiency for those ions to accept electrons from the conduction band is also high (see Table 1). As a result of such high deposition rate, large Pt particles are found on the titania surface. It is therefore difficult to control the deposition morphology. When the solution pH is in the region of 5–7, closer to the IEP of TiO_2 , TiO_2 particles tend to aggregate and only parts of the TiO_2 surface are fully available to metal ions at all times. As a consequence, most deposited Pt particles are shown as large agglomerates. The size of these particles may even exceed that of the parent TiO_2 particles. When the solution pH is significantly high, the TiO_2 particles are kept away from each other and the local concentration of Pt anions is low. The low local concentration of those anions leads to a low deposition rate (see Table 1) and small deposition particles with narrower particle size distribution.

The remaining question is why the deposited platinum prefers different valence states in different pH environments. There seems to be a direct correlation between the

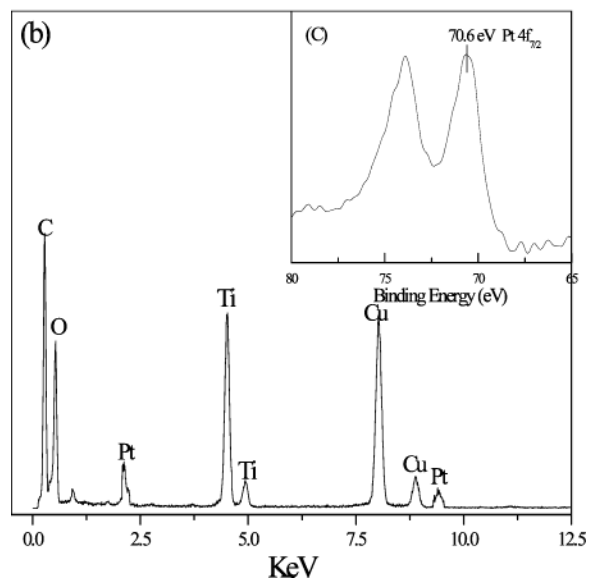
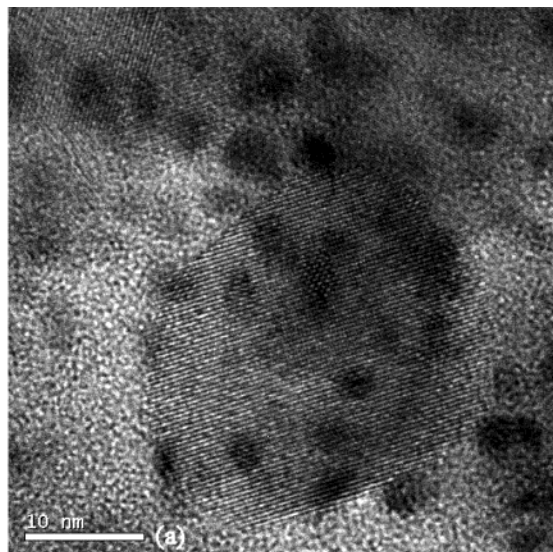


Figure 3. Photos of sample D post-treated by H_2 flow at 573 K for 4 h: (a) HRTEM images, (b) EDAX spectrum, and (c) XPS spectra.

degree of hydrolysis of PtCl_6^{2-} ions and the valence state of deposited platinum. More specifically, the slurry pH affects the relative concentration of hydrolyzed products and their redox potential which leads to deposited particles with different oxidation states of platinum. It is also possible that the deposited platinum may be a result of direct physical deposition without the involvement of photocatalysis.

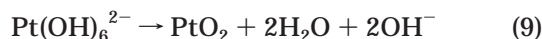
First, it is important to point out that the redox potential ($E_{1/2}$) for all platinum species and titania will change with pH value. It is reasonably safe to approximate the standard redox potential E° for platinum ions and titania as the corresponding half-wave potential value $E_{1/2}$ found in the literature.³⁴ For example, in an acidic solution, $E^\circ_{\text{PtCl}_6^{2-}/\text{PtCl}_4^{2-}} = 0.68$ V (vs normal hydrogen electrode (NHE)) and $E^\circ_{\text{PtCl}_4^{2-}/\text{Pt}} = 0.73$ V (vs NHE). In a basic solution, $E^\circ_{\text{Pt(OH)}_6^{2-}/\text{Pt(OH)}_2} = -0.1$ to 0.4 V (vs NHE) and $E^\circ_{\text{Pt(OH)}_2/\text{Pt}} = 0.15$ V (vs NHE). In addition, the photoexcited TiO_2 yields

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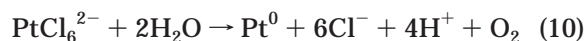
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a reductive potential ($E^\circ = -0.5$ V vs NHE) at pH = 7 and $E^\circ = -0.1$ V versus NHE at pH = 1 for the conduction band (CB) electrons (e_{CB}^-). For valence band electron holes, the oxidative potentials are also different at different pHs ($E^\circ = +2.7$ V vs NHE at pH = 7; $E^\circ = +3.1$ V vs NHE at pH = 1). Judging by the criterion of $\Delta_r G^\circ = -nFE^\circ < 0$, it can be concluded that the photogenerated electron can directly reduce the platinum precursor anions or its hydrolytic anions into metal platinum at the corresponding pH value (where $\Delta_r G^\circ$ is the change of standard Gibbs free energy, n is the gained or lost electron amount, F is the Faraday constant ($1F = 9.65 \times 10^4$ C mol $^{-1}$), and E° is the standard redox potential). Also, according to $\Delta_r G^\circ = -RT \ln K^\circ$ (where $\Delta_r G^\circ$ is the change of standard Gibbs free energy, R is the molar constant of an ideal gas, T is reaction temperature, and K° is the equilibrium constant of reaction), the deposition equilibrium constant is only correlated with E° and can be calculated as $e^{nFE^\circ/RT}$. Consequently, the effect of pH on the redox potential is inadequate to cause the difference in valence of deposited platinum.

To examine whether the valence difference of the deposited platinum is caused by processes other than photodeposition, such as direct photolysis followed by physical deposition or pure physical–chemical deposition without the influence of irradiation, two sets of experiments were conducted. First, a solution of platinum precursor was irradiated for 6 h without the presence of titania substrate. In a separate experiment, a slurry of platinum precursor containing titania substrate was stirred for 6 h without any irradiation. It was found that more than 97% of the precursor ions in both solutions remained after 6 h. The experiments clearly demonstrated that the deposited particles were coming from neither direct photolysis or physical–chemical deposition of Pt ions. In addition, the pH values of all irradiated slurries were found to decrease at various rates depending upon initial pH. This evidence further ruled out the possibility of direct deposition, as a direct deposition process as described in eq 9 will lead to a pH increase.

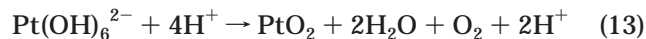


Therefore, it is more likely that the difference in the oxidation state of deposited platinum originated from the structural difference in hydrolyzed products at various pHs. Although the exact structures of the hydrolyzed product platinum ions at different pH solutions are not identified, the trend is clear. The increase of pH value in solution will promote the degree of hydrolysis and lead to a higher percentage of the products containing fewer chlorides. In an acidic solution, PtCl_6^{2-} ions, as majority, can easily adsorb onto a positively charged titania surface. The adsorbed ions can be photocatalytically reduced into metal platinum after accepting photogenerated electrons (eq 10).



With the increase of pH value, $\text{Pt(OH)}_2\text{Cl}_4^{2-}$ and $\text{Pt(OH)}_4\text{Cl}_2^{2-}$ anions will appear in sequence and may become dominant in concentration. These anions can be reduced or oxidized after accepting photogenerated electrons or holes. In sample B of Table 1, PtO is deposited together with metal platinum. For sample C, PtO_2 is deposited besides PtO. These results indicated that

$\text{Pt(OH)}_2\text{Cl}_4^{2-}$ may have received two photogenerated electrons to form PtO, and $\text{Pt(OH)}_4\text{Cl}_2^{2-}$ anions may receive four H^+ to give PtO_2 . Possible reactions are suggested in eqs 11 and 12.



In a strongly basic environment, the highly hydrolyzed product of platinum ions will dominate. Samples D and E in Table 1 show that PtO_2 is the major deposited species accompanied by some PtO. It is possible that Pt(OH)_6^{2-} ions accept four holes to produce PtO_2 as indicated in eq 13.

This is consistent with the fact that oxygen evolution was observed during photodeposition of platinum on titania²⁸ as well as PtO_2 on CdS^{30a} at pH = 13. Therefore, the chemical nature of the hydrolyzed product of platinum ions is the dominating factor in determining the valence state of the deposited platinum particles.

Conclusion

During the deposition of platinum, the pH value of the slurry not only affects the stability, surface charge, and dispersion of titania but also changes the hydrolytic components of PtCl_6^{2-} ions and their adsorption on the surface of titania. The morphology and the components of coated platinum on the surface of TiO_2 were influenced by the pH value of the preparation slurry. The experimental results demonstrate that $\text{PtO}_2/\text{TiO}_2$ particles can be synthesized to have a sharp size distribution and deployment dispersion by controlling the pH value at the region of 9–13. H_2 reduction is an efficient way to convert PtO_2 into metal platinum and to keep the morphology of platinum unchanged.

Supported platinum catalysts have a wide range of applications. For each targeted chemical transformation, a specific platinum species is desired. For example, platinum oxide is primarily used as an effective catalyst for oxidation reactions and metallic platinum is usually employed for H_2 -involving reactions. In some cases, however, an active site that contains both metal and metal oxide is more effective to facilitate the desired chemical transformation. This is particularly true for those reactions involving multiple simultaneous or sequential steps. For this purpose, supported platinum catalysts with multiple chemical compositions would be extremely valuable. The experimental techniques described in this work may serve as a blueprint for the preparation of such advanced nanomaterials.

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Supporting Information Available: The hydrolytic behavior of PtCl_6^{2-} ions monitored using UV/vis spectroscopy at various pH values and UV–visible absorption spectra of K_2PtCl_6 solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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