Simple and low-cost preparation method for highly dispersed Pd/TiO$_2$ catalysts

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Abstract

Supported metal catalysts have been applied in many current industrial processes. The morphology of metal particles coated on support has been proven to affect the performance of catalysts greatly. In this study, a simple photodeposition process will be introduced to coat palladium onto titanium dioxide with an emphasis on the morphology control and size distribution of palladium particles. The effect of pH on the morphology of palladium particles was systemically investigated. It is found that the deposited palladium particles can be controlled to have narrow particle size distribution and homogeneous dispersion by a simple pH-controlled process during photodeposition. Experimental results demonstrate that the adsorption competition between OH$^-$ and PdCl$_4$$^{2-}$ or it's hydrolytic anions can efficiently keep local concentration of palladium ions on titanium dioxide extremely low to control the morphology of deposited palladium particles on titania. The as-prepared Pd/TiO$_2$ particles are found to be crystallitic stable indicated by TEM, XRD and XPS measurements.
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Keywords: Palladium particles; Titania; Coating; Photodeposition; Morphology

1. Introduction

Supported metal catalysts play a crucial role in industrial chemistry and have been used extensively in many important industrial processes such as refining of petroleum, conversion of automobile exhaust, hydrogenation of carbon monoxide and hydrogenation of fats, etc. [1–7]. Many results have been reported about how the morphology of metal particles affects the specific activity of catalysts [8]. A suitable size of metal clusters and higher dispersion for a given metal loading are preferred for the activity [9]. The smaller the metal particles are, the larger the fraction of the metal atoms that are exposed at surfaces, where they are accessible to reactant molecules and available for catalysis. For industrial applications, the preparation of supported metal catalysts is not only required to have good performance of catalysts, but also is eager for having high efficient of metal coating because of the expensive metal cost. The preparation of supported metal catalysts with deployment dispersion and narrow size distribution of metal particles, especially having average size of 1–5 nm (usually showing

high performance for most reactions), becomes particularly desirable for the improvement of performance of catalysts [10,11] and the understanding of mechanism of some size-dependent or structure-sensitive reactions such as the breaking or making of C–C, N–N, or C–O bonds [4,5,8].

In recent years, the study of metal nanostructured materials has also attracted intense research due to many new unusual properties such as electromagnetic, and optical properties [12,13]. The uniformity of nanoscaled metal particles is crucial in controlling their novel collective properties, which differ from those of bulk material [14,15]. As special material exploitation, the synthesis of nanostructured supported noble metals with high surface area and sharp size distribution also presents a significant challenge for material scientists [16,17].

Traditionally, supported metal catalysts are typically prepared by impregnation of high-area support with an aqueous solution of a metal salt, followed by heating in air (calcining) and reduction in hydrogen. The resultant metal particles on support are usually heterogeneously dispersed with broad size distribution, and some metals cannot deposit onto the surface of support. Although many new techniques have been developed to improve the dispersion of metal particles and control the size distribution of metal particles on support in the recent years [18–22], the coating amount

of metal was usually low and incompletely conversion of metal precursor still remains.

In this study, a simple and straightforward photodeposition method was employed to deposit palladium nanoparticles on titanium dioxide (Deggussa P-25) with a certain degree of control in coating morphology. Unlike conventional chemical routes, the simple method can be performed at room temperature without introducing any foreign reducing agent and the photodeposition of palladium ions is nearly 100%. As a result of the pH-controlled process, homogeneous dispersion and sharp size distribution of palladium particles can be prepared in the basic pH region of 10–13, where OH^- can efficiently compete with palladium anions to adsorb on titanium dioxide to control the morphology of deposited palladium particles.

2. Experimental

2.1. Preparation of catalysts

An amount of 1 g Na_2PdCl_4 was dissolved in 100 ml bidistilled water as the precursor of palladium ions. A typical photodeposition was carried out in a 250 ml round bottom flask using a 250 W high-pressure mercury light with main wavelength of 365 nm as outer-irradiating light source. A suspension containing 500 mg TiO_2 (Degussa P-25 with anatase/rutile crystalline ratio of 8:2 and surface area of 50 m^2/g) and certain amount of above mentioned Na_2PdCl_4 solution in 120 ml twice-distilled water were prepared, and then 8 ml ethanol were added. The initial pH value of the slurry was adjusted to the desired value by a solution of NaOH (0.1 M) or HNO_3 (0.1 M). The suspension was purged with high-purity N_2 atmosphere to remove oxygen. The slurry was mechanically stirred throughout the process. During irradiation, the concentration of $PdCl_4^{2-}$ and the pH of the solution were monitored at 30 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 in N_2 flow at 473 K for 3 h. The samples were then analyzed by TEM, XRD and XPS.

For a concise demonstration of our method, this paper reports mainly the results of high loading (16 wt.%) samples, for which high dispersion is generally considered more difficult to obtain than low loadings.

2.2. Characterizations

Transmission electron micrographs were obtained on a Philips EM-120 TEM with an accelerating voltage of 100 KeV. The particles obtained after the irradiation and work-up were dropped onto the surface of carbon membrane and dried at ambient conditions before analysis.
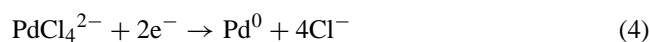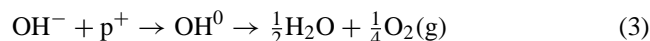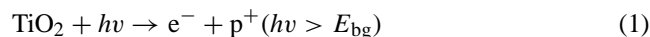
X-ray photoelectron spectroscopy (XPS) was performed using PHI 5300 ESCA instrument (Mg Kα radiation; 1253.6 eV; 10^{-7} Pa). The C 1s photoelectron peak (binding energy at 284.6 eV) was used as energy reference.

X-ray diffraction (XRD) patterns were collected on D/max-2500 commercial instrument (Cu Kα, λ = 1.54178 Å) with a scan speed of $2\theta = 8.0°$/min.

Atom absorption spectroscopy (AAS) was done using HTAZHI 180-80 (Japan). An amount of 100 mg as-prepared catalysts were dissolved in aqua regia solution and centrifuged to analyze the concentration of palladium in the supernatant.

3. Results

Unlike conventional chemical routes, the reduction reaction described here can be performed at room temperature, and introduction of additional reducing agents into the reaction system is not required. The results of AAS analysis show that the photodeposition of palladium ions is nearly 100% to the completion after 6 h irradiation in all cases. According to the deposition mechanism Eqs. (1)–(5) of palladium, one point can be found that the pH value of solution will decrease because of the formation of H^+ ions during photodeposition.

$$TiO_2 + h\nu \rightarrow e^- + p^+ (h\nu > E_{bg}) \tag{1}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{2}$$

$$OH^- + p^+ \rightarrow OH^0 \rightarrow \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2(g) \tag{3}$$

$$PdCl_4^{2-} + 2e^- \rightarrow Pd^0 + 4Cl^- \tag{4}$$

$$mPd^0 \rightarrow Pd_m \tag{5}$$

To investigate the pH effect on the morphology of deposited palladium, a set of photodeposition experiments were carried out by controlling the pH value of slurry at the region of: below 6; 6–8; 8–10; 10–12; 12–13, respectively.

Table 1
The preparing conditions and TEM results of Pd/TiO_2 particles prepared in different pH region[a]

Sample name	Preparing pH region	Average diameter (nm)	Statistic histogram	TEM result
Sample A	Below 6	–	–	Fig. 1a
Sample B	6–8	–	–	Fig. 1b
Sample C	8–10	3.87 ± 0.5	Fig. 2b	Fig. 2a
Sample D	10–12	2.2 ± 0.2	Fig. 3b	Fig. 3a
Sample E	12–13	2.0 ± 0.15	Fig. 4b	Fig. 4a

[a] Other conditions: TiO_2: 500 mg; distilled water: 120 ml; Na_2PdCl_4 solution: 23 ml; reduction time: 6 h.
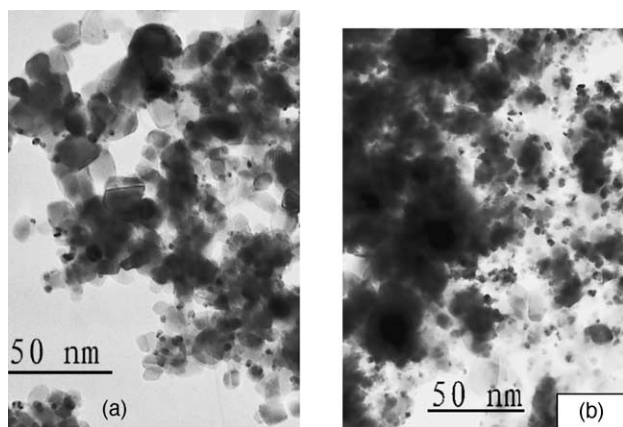
Fig. 1. TEM images of Pd/TiO$_2$ particles prepared at: (a) pH < 6; (b) pH = 6–8.

The particles prepared under corresponding conditions are referred 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 Figs. 1–4.

As shown in Figs. 1–4, the dispersion morphology and size distribution of deposited palladium particles are distinctly affected by the pH value of slurries. When a simple dispersion of TiO$_2$ particles containing palladium ions, without any pH adjustment, was exposed to ultraviolet irradiation, the pH values of slurry was usually kept at below 6. The surface-adsorbed palladium ions can be reduced and subsequently accumulated on TiO$_2$ particles via a photodeposition process (sample A). The size of these metal islands is typically large and heterogeneously dispersed. Fig. 1a shows its representative TEM image.

As for sample B, prepared at the pH region of 6–8, most coated palladium particles are polydispersed and overshadowed on TiO$_2$ particles. The typical TEM result is shown in Fig. 1b.

With the increase of pH value of preparation slurry, a remarkable improvement in dispersion of palladium deposits was found on sample C. Finally, the deposited particle size and distribution are much more uniform for samples D and E which were prepared at the pH region of 10–13. Figs. 2a-4a show their representative TEM results and Figs. 2b-4b show their corresponding histogram of size distribution, which
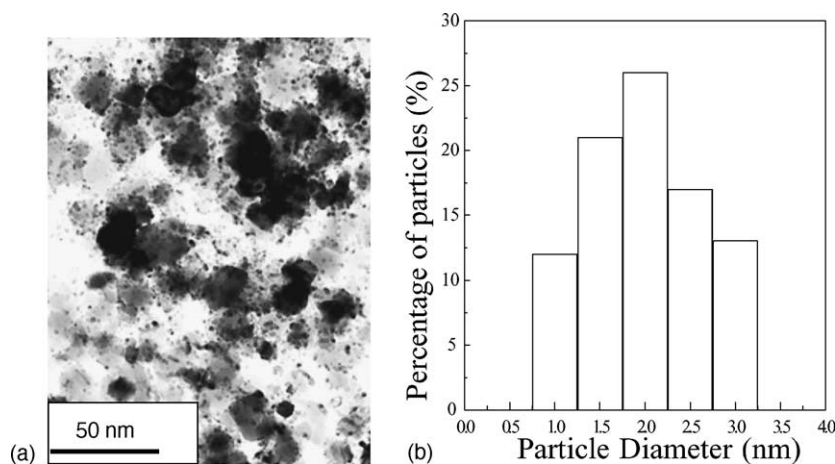

Fig. 2. TEM images (a) and its statistics histogram (b) of Pd/TiO$_2$ particles prepared in the pH region of 8–10.
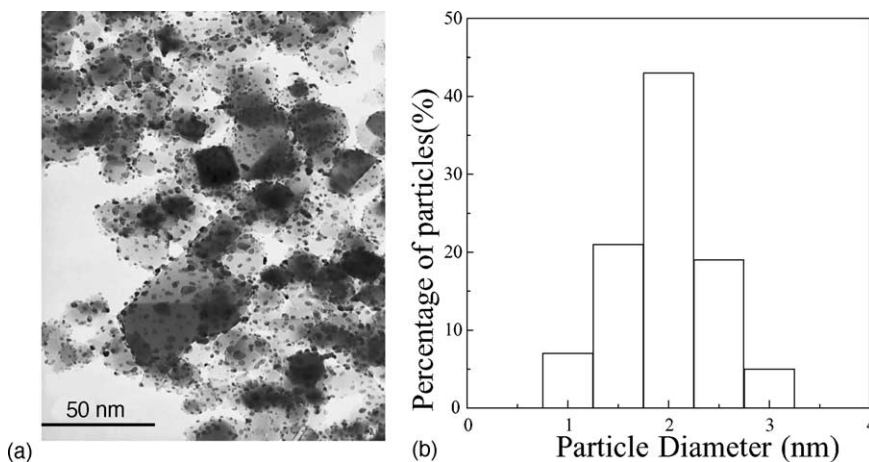

Fig. 3. TEM images (a) and its statistics histogram (b) of Pd/TiO$_2$ particles prepared in the pH region of 10–12.
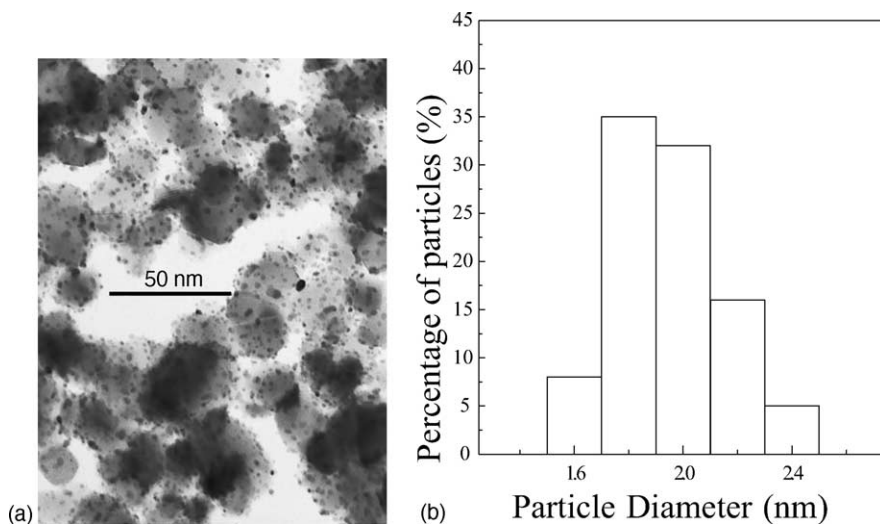
Fig. 4. TEM images (a) and its statistics histogram (b) of Pd/TiO$_2$ particles prepared in the pH region of 12–13.

show the improvement of size distribution. As a whole, a basic solution produces narrower size distribution and homogeneous dispersion of palladium particles on the support.

For many catalytic reactions, the valence of coated metal greatly affects the reactivity of catalysts. To confirm the existed states of palladium coated on TiO$_2$, above as-prepared five samples were characterized by XPS and XRD measurement. Figs. 5 and 6 show their XPS profiles and XRD patterns of samples A–E, respectively. Based on the binding energy, metal state of coated palladium can be estimated. The powder XRD patterns of the pure TiO$_2$ substrate (Fig. 6) confirmed the presence of rutile and anatase with proportion as described in Section 2. For Pd/TiO$_2$ particles, three additional peaks, $2\theta = 40.12°$, $46.52°$, and $82.6°$ are assigned to the metal crystals, which not only further confirm the metallic state of the coated palladium particles, but also shows their existed state as stable palladium crystals, which may be promising on improving the performance of catalysts. The average size of palladium phase of the Pd/TiO$_2$ was estimated according to the following equation:
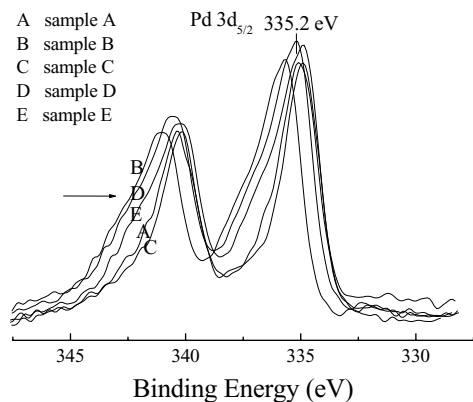

Fig. 5. The XPS spectra of Pd/TiO$_2$ particles prepared in different pH region: (a) pH < 6 (sample A); (b) pH = 6–8 (sample B); (c) pH = 8–10 (sample C); (d) pH = 10–12 (sample D); (e) pH = 12–13 (sample E).

Fig. 6. The XRD patterns of Pd/TiO$_2$ particles prepared in different pH region: (a) pH < 6 (sample A); (b) pH = 6–8 (sample B); (c) pH = 8–10 (sample C); (d) pH = 10–12 (sample D); (e) pH = 12–13 (sample E).
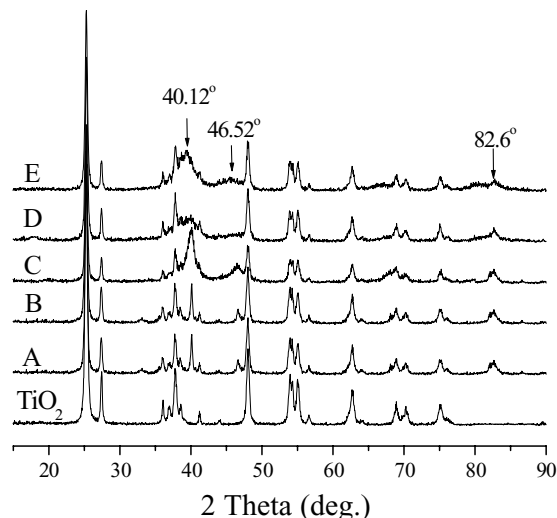
$$D = \frac{k\lambda}{(\beta_c - \beta_s)}\cos\theta \qquad (6)$$

where D is the grain size, λ the X-ray wavelength, β_c and β_s are the FWHM of the calculation phases and the standard (single-crystal silicon), respectively. The number $K = 0.89$ is a coefficient; θ the diffraction angle. The calculated results showed that the average size of palladium particles of sample A–E was 14.5, 19.5, 4.1, 2.4 and 2.2 nm respectively, in agreement with the results observed in the TEM.

4. Discussions

Many excellent properties have been found on TiO$_2$ (P-25 type), which were widely used in many industrial fields,

mainly as photocatalyst or catalyst support [23–27]. TiO$_2$ usually shows amphoteric and occurs as-named acid–base equilibrium. Eqs. (7)–(8)) because of the existence of "titanol" (Ti–OH) on the surface [28].

$$TiOH + H^+ \leftrightarrow TiOH_2^+, \quad pH < 6.25 \qquad (7)$$

$$TiOH \leftrightarrow TiO^- + H^+, \quad pH > 6.25 \qquad (8)$$
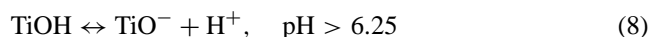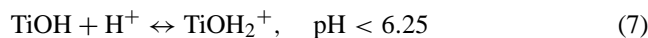
The absorption property of TiO$_2$ greatly changes with environment of different pH value. If the pH value of solution is higher or lower than the identical electric point (IEP = 6.25) of TiO$_2$, the surface of which will be negatively or positively charged respectively. The further the pH value of solution is from the IEP of TiO$_2$, the more stable and the better dispersed titanium dioxide particles will be. Oppositely, if near the identical electric point, TiO$_2$ particles will be aggregated.

As a prerequisite factor of coating metal, TiO$_2$ particles must be stable and well dispersed in the solution to allow their surfaces to wholly expose to metal ions, otherwise the adsorption and deposition of metal ions onto those covered surfaces will become impossible. Once metal ions adsorb onto those exposed surfaces, they will be photoreduced to initially form metal nucleus centers, which can act as the reservoir of photoinduced electrons to accelerate the metal photodeposition. If not controlled, these metal particles will fast grow and even overshadow the original TiO$_2$. That is why most palladium particles in sample B (Fig. 1b), prepared in the pH region of 6–8 close to the IEP of TiO$_2$ leading to the aggregation of TiO$_2$ particles, are large and typically polydispersed.

Both nucleation kinetics and growth kinetics of metal will influence the morphology and size distribution of coated metals. The simultaneous nucleation on different active sites and slow growth of these metal nucleuses are preferred for the preparation of homogeneously dispersed metal particles with sharp size distribution. It can be easily understood that if the growth of metal nucleus is too fast, minute diversity of nucleation rate on different active sites in the initial stage of irradiation will cause great growth difference of nucleus. The former deposited nucleus, acting as electron reservoir to inhibit the recombination of photoinduced electron, can accelerate the growth of metal particles and become big more rapidly than those latter deposited nucleuses, which broadens the resultant size distribution of metal particles. An anticipated way to weaken the influence of nucleation kinetics and growth kinetics of metal particles is to keep the local concentration of palladium ions on the surface extremely low.

If the pH value of slurry is changed, both the surface charge of TiO$_2$ and the adsorption of palladium ions will be influenced. This phenomenon was expected contributing to effectively control the local concentration of palladium ions on the surface and the nucleation kinetics of metal particles. In basic solution, on the one hand, TiO$_2$ particles can be stably dispersed by adsorption of OH$^-$ ions on the surface; on
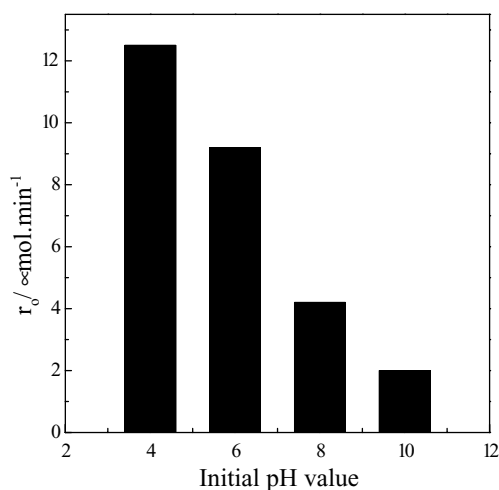

Fig. 7. Variation of the initial photodeposition rate of palladium as a function of the initial pH value of solution.

the other hand, the potential species of palladium ions are expected to include mixed complexes such as PdCl$_3$OH^{2-}, PdCl$_2$(OH)$_2^{2-}$, PdCl(OH)$_3^{2-}$, and Pd(OH)$_4^{2-}$, etc. besides PdCl$_4^{2-}$ [29] because of hydrolysis. As the presence of stronger covalent ligand of OH$^-$ than Cl$^-$, an adsorption competition between OH$^-$ ions and palladium anions or its hydrolytic anions occurs to effectively keep the concentration of palladium ions on titanium dioxide surface particularly low and inhibit the fast nucleation and the fast growth of metal particles. Consequently, homogeneously dispersed palladium particles with narrow size distribution can be prepared at the pH region of 10–12 or 12–13 (Fig. 3a, Fig. 4a). Although the above-mentioned adsorption competition also exists in the pH region of 8–10, the concentration of OH$^-$ ions is too low to effectively keep the local concentration of palladium ions extremely low. In addition, the pH value is not far enough from the IEP of TiO$_2$ to assure the TiO$_2$ particles stable in the whole process. Accordingly the resultant palladium particles prepared in the pH region of 8–10 can be disparted but a few aggregated metal particles are still found (Fig. 2a). As a result of the fail in or disappear of the as-named adsorption competition in the pH region of below 6, it is hard to control the coating morphology of palladium particles with homogeneous dispersion (Fig. 1a) for the rapid deposition of metal ions, even though TiO$_2$ particles in this solution can be well dispersed. By comparing the TEM results of Fig. 2a, Fig. 3a and Fig. 4a, one conclusion can be drawn that control the pH of the solution, providing competitor of palladium ions, is a simple and effective way to control the nucleation and growth kinetic and at last control the morphology of coated metal particles.

In our experiments, no attempts were done to study the mechanism of morphology control except that the initial deposition rate in different initial pH value was carried out, and the results of which are shown in Fig. 7 that the photodeposition rate decreases with the increase of initial pH value, in

agreement with the assume in the discussion. Further work is doing to study the performance of the catalysts.

5. Conclusion

This paper introduces an innovative approach in controlling the coating morphology of palladium particles on TiO_2 surface during photocatalytic deposition. The control of local palladium ion concentration on TiO_2 surface by introducing OH^- into preparation system was employed. The results demonstrated that homogeneously dispersed palladium particles with sharp size distribution on titanium dioxide could be prepared in the basic solution of 10–13. Both XPS and XRD characterized the coated palladium particles existed as metal state. The approach that validates in this study can be easily extended to deposit other metals onto reactive surface, and has the potential to be applied in larger scale manipulation or synthesis.

Acknowledgements

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