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Introduction

During the past decades, noble metal nanomaterials have attracted considerable interest for a variety of research fields ranging from organic synthesis and fuel cells to environmental protection, especially for catalytic/electrocatalytic applications because of their specific physicochemical properties.^{1–4} In general, the properties of metal nanoparticles (NPs) mostly depend on their composition, size and morphology.^{5–9} Therefore, it is possible to tune the properties of metal NPs by tailoring their composition, size and morphology. For example, the catalytic activity of reported metal NPs, such as nanosheetconstructed Pd particles,¹⁰ three dimensional PtPd bimetallic NPs¹¹ and hollow PtPd alloyed nanocubes¹² *etc.* is largely dependent on their morphologies.

Until now, Pt has always been considered as the best electrocatalyst for methanol oxidation in the direct methanol fuel cell.¹³⁻¹⁶ Moreover, the Pt-based materials are also developed as efficient electrocatalysts for methanol oxidation reactions in

A green synthesis of "naked" Pt and PtPd catalysts for highly efficient methanol electrooxidation[†]

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Up to now, green synthesis of "naked" nanoobjects with clean surfaces is still a great challenge since structure-directing agents such as surfactants are usually used to induce the anisotropic particle growth for interesting nanostructures in solution. Here, a green synthesis approach for preparing "naked" Pt nanoparticles (NPs) in acetic acid solution was reported. Interestingly, Pt NPs with different morphologies (well-defined polyhedrons, irregular polyhedron-constructed chain networks and nanoflower-constructed chain networks) could be successfully synthesized at different concentrations of acetic acid without adding additional structure-directing agents and reducing agents. The acetic acid itself works both as structure-directing agent and reducing agent for the formation of these interesting Pt NPs. Specifically; the synthesized NPs are "naked" with clean surfaces since the acetic acid is a weakly-capping agent which can be easily removed after the washing process. The versatility of this method is further demonstrated by preparation of "naked" PtPd alloy NPs. In particular, the as-prepared "naked" Pt_5.20 and Pt_3Pd_{1_5.20} NPs are demonstrated to be excellent catalysts with much higher electroactivity and better durability than the commercial Pt black catalyst (HispecTM 1000) for the methanol oxidation reaction. The method reported in this work may pave the way for simple, low-cost, green and eco-friendly synthesis of "naked" metal catalysts for advanced electrocatalytic applications.

fuel cells.^{17–20} Among the Pt-based catalysts, it is reported that Pd can largely enhance the performance of Pt catalysts for various catalytic reactions.^{21–25} Specifically, Pt and Pd in PtPd electrocatalysts show an obvious "synergistic effect" leading to superior activity in comparison with individual Pt or Pd electrocatalysts in the oxidation of methanol.^{11,26} The "synergistic effect" of Pt and Pd in the alloys for methanol oxidation can be attributed to the bifunctional methanol oxidation mechanism.^{27,28} Pt catalyzes methanol dehydrogenation to form Pt–CO while Pd mainly make water dehydrogenation form Pd–OH. The Pt–CO and Pd–OH react together to produce CO₂ and therefore the active metal surfaces refresh. However, the water dehydrogenation on pure Pt occurs at a higher potential without Pd, resulting in the overall oxidation process on pure Pt sluggish.

The synthesis of morphology-controlled NPs including Pt and PtPd NPs is generally based on the classical solution synthesis method, in which NPs are synthesized with the help of additives such as surfactants, polymers, fatty acids and fatty amine *etc.*²⁹ These additives are often defined as structuredirecting agents. However, it was reported that these agents often strongly adsorb and cap the surfaces of NPs, blocking the exposure of the surface active sites. Specifically, they are very difficult to remove, leading to a subsequent reduction in catalytic activity.^{30–32} Therefore, partly loss of activity of these synthesized catalysts is unavoidable during the catalytic or electrocatalytic reactions. Moreover, the introduction of

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additional structure-directing agents such as surfactants and polymers will make the synthesis risk toxicity since some surfactants or polymers themselves are not low toxic chemicals.¹⁰ In principle, to ensure the successful formation of metal NPs from metal salts, the synthesis system usually contains additional reducing agents. The reducing agents like hydrazine hydrate, NaBH₄, and CO are often used, which certainly increases the toxic/unsafe risk from these chemicals.^{10,33-36} Therefore, a facile green method for the preparation of "naked" metal nanocatalysts with clean surfaces is still of great challenge. To achieve this goal, a simple synthesis system without additional surfactants, polymers and toxic chemicals will be highly demanded.

Herein we describe a simple, low-cost, green and eco-friendly method to synthesize the "naked" Pt NPs with clean surfaces in acetic acid solution without using additional structure-directing agent or reducing agent. The acetic acid itself works both as structure-directing agent and reducing agent for the formation of the Pt NPs. Specifically, the synthesized NPs have clean surface since the acetic acid is a weakly-capping agent which can be removed after the washing process. Various interesting Pt morphologies such as well-defined polyhedrons, irregular polyhedron-constructed chain networks and nanoflowerconstructed chain networks can be successfully synthesized. This method can be further extended for the synthesis of "naked" PtPd alloy NPs. Furthermore, the as-prepared "naked" Pt_5.20 and Pt3Pd1_5.20 show superior electrocatalytic performance in comparison with the commercial Pt black catalyst for the electrooxidation of methanol.

Experimental section

Materials

 $H_2PtCl_6 \cdot 6H_2O$ and K_2PdCl_4 were purchased from Aladdin Industrial Corporation. Nafion solution was purchased from Sigma-Aldrich. Johnson-Matthey platinum black catalyst (HispecTM1000) was purchased from Alfa Aesar. All the regents were used without further purification.

Synthesis

In a typical synthesis of Pt particles, 245 μ L of 0.1 M H₂PtCl₆· 6H2O (0.0245 mmol) was injected into 16 mL aqueous solution with the acetic acid concentration of 0.10 M, 0.21 M, 0.52 M, 1.04 M, 3.11 M, 4.16 M, 5.20 M, 8.33 M, 10.41 M, 14.57 M, respectively. Then the solution was sonicated for a few minutes to form a uniform solution. Subsequently, the resultant solution was put into a Teflon-lined autoclave and the autoclave was heated at 180 °C for 2 h. The autoclave was then cooled to room temperature naturally. Finally, the resultant products were recovered by repeated centrifugation and washed with ethanol and water, respectively. The synthesized product was then dried at 60 °C for 5 h. The procedure for synthesizing PtPd (Pt₃Pd₁ was synthesized as the typical samples) bimetallic NPs was similar as that described above with the molar ratio $H_2PtCl_6 \cdot 6H_2$ -O: K₂PdCl₄ equal to 3:1 (0.0184 mmol: 0.0061 mmol) while the total molar number of metal salt was same as that for the

synthesis of pure Pt NPs. The synthesized Pt and Pt_3Pd_1 NPs with different concentrations of acetic acid were labeled as Pt_x and $Pt_3Pd_{1_x}$ (*x* presents the concentration of acetic acid).

Characterization

X-ray diffraction (XRD) was performed using a Rigaku Dmax-rc X-ray diffractometer with Ni-filtered Cu K α ($\lambda = 1.5418$ Å) radiation. Transmission electron microscopy (TEM) was performed using a JEM 1400 TEM operating at 120 kV. HAADF-STEM-EDS mapping were performed with a JEM-2100F. For the measurement of particle size, over 100 particles were measured using photoshop. Fourier transform infrared spectroscopy (FTIR) spectra were performed on Nicolet 6700 Fourier transform infrared spectrometer. The composition of the bimetallic particles was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, VISTAMPX).

Electrocatalytic activity

Electrochemical measurements were performed on an electrochemical workstation (CHI model 660C). The conventional three electrode test cell contained a glassy carbon electrode (GCE, diameter: 3 mm) as working electrode, a Pt wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The GCE was first polished carefully with alumina powder, and then washed by sonication in ethanol and water respectively. 5 μ L aqueous solution (2 mg mL⁻¹) of asprepared Pt, Pt₃Pd₁ particles or the commercial Pt black was dropped onto the surface of the GCE, respectively. After the solution was dried, 5 µL of Nafion (0.5 wt%) was added to the surface of the modified electrode. The GCE was dried naturally before using. The cyclic voltammetry (CV) profiles were first recorded at a scan rate of 50 mV s^{-1} within the potential range from -0.25 V to 1.0 V vs. SCE in a 0.5 M HClO₄ solution. For methanol oxidation, the CV profiles were measured in 0.5 M $HClO_4 + 1.0 \text{ M CH}_3OH$ solution at a scan rate of 50 mV s⁻¹ within the potential range from -0.2 V to 1.0 V vs. SCE. The accelerated cycling tests for methanol oxidation were conducted for 3000 cycles. All CVs were obtained at room temperature and the electrolyte solutions were purged with high purity N₂ gas prior to the test.

Results and discussion

Here, the synthesis of Pt NPs was performed in a wide range of acetic acid concentrations. The resultant Pt NPs at different concentrations of acetic acid were labeled as Pt_x (*x* presents the concentration of acetic acid). The typical synthesis process was illustrated in Fig. 1A. Fig. 1B shows the XRD patterns of the selected synthesized Pt particles with typical morphologies at the acetic acid concentration of 0.21 M, 3.11 M and 5.20 M, respectively. All diffraction peaks can be indexed as the face-centered cubic (fcc) Pt (JCPDS card, 04-0802). The XRD result confirms that the formation of pure Pt powers with highly crystallization. The intensity of diffraction peaks in XRD patterns is closely related to the crystallinity of prepared nanomaterials. In general, the higher intensity of diffraction



Fig. 1 Typical schematic illustration (A) for the preparation of Pt NPs at various concentration of acetic acid. XRD patterns (B) of the asprepared $Pt_{-0.21}$, $Pt_{-3.11}$ and $Pt_{-5.20}$ particles synthesized at the acetic acid concentration of 0.21 M (a), 3.11 M (b) and 5.20 M (c), respectively.

peaks represents the higher crystallinity. From Fig. 1, it shows that the intensity of diffraction peaks Pt NPs decreases with the increasing of acetic acid concentration. This indicates that the crystallinity of Pt NPs decreases with the increasing of acetic acid concentration. The ratio between the intensities of (111) and (200) peaks for Pt_{0.21}, Pt_{-3.11} and Pt_{-5.20} is 2.49, 2.29, and 2.20, respectively. Compared with the reported value (JCPDS card, 04-0802) for the conventional Pt powder sample (1.89), it indicates that the diffraction from {111} planes is enhanced for the synthesized Pt_{0.21}, Pt_{-3.11} and Pt_{-5.20} particles, reflecting the predominant growth of the (111) planes in Pt_{0.21}, Pt_{-3.11} and Pt_{-5.20} NPs.

TEM characterization is used to understand the morphologies of the typical synthesized Pt_0.21, Pt_3.11 and Pt_5.20 NPs. Fig. 2a and b shows the low and high magnification TEM images of the as-prepared Pt_0.21 NPs synthesized at 0.21 M acetic acid. From the TEM images in Fig. 2a and b, it can be seen that well-defined polyhedron particles consisting of cube, octahedra, tetrahedra and pentahedra form. Most of the particles are cubes, whereas spherical particles are virtually absent. The average size of the Pt $_{0.21}$ particles is 11.7 \pm 2.5 nm. Fig. 2c and d shows the TEM images of Pt 3.11 NPs synthesized at 3.11 M acetic acid. The average size of the Pt 3.11 particles is 16.1 \pm 2.8 nm. However, the morphology of Pt _{3.11} NPs is obviously different from the Pt 0.21 NPs. Clearly, there are a lot of interconnected chains across the whole section (Fig. 2c). Each chain is fused with the adjacent ones to form Pt chain networks. High magnification TEM image (Fig. 2d) reveals each



Fig. 2 Low and high magnification TEM images of $Pt_{0.21}$, $Pt_{3.11}$ and $Pt_{5.20}$ particles synthesized at the acetic acid concentration of 0.21 M (a, b), 3.11 M (c, d) and 5.20 M (e, f).

chain is composed of irregular polyhedrons. These irregular polyhedrons are linearly interconnected and further selfassemble to chains. For the Pt 5.20 particles synthesized at 5.20 M acetic acid, Pt nanoflower-constructed chain networks form, as shown in Fig. 2e and f. The size of the nanoflowers is 22.9 \pm 3.9 nm. The enlarged TEM image in Fig. 2f further reveals that the Pt flowerlike nanostructures are composed of small nanoparticle subunits, in which the small NPs are with the size of 4.3 \pm 1.1 nm. Such three-dimensional hierarchical structure could be very useful in the catalytic application since each nanoflower structure shows a bumpy surface which benefits for the active sites such as high density of atomic steps, ledges and kinks.^{37,38} From Fig. 2, it also shows that the particle size of the synthesized Pt increases with the acetic acid concentration. With the increase of acetic acid concentration, the formation of Pt becomes faster as the higher acetic acid concentration can reduce the platinum salt faster. In this case, the Pt crystal grows faster. Therefore larger Pt particles form at higher acetic acid concentration.

We also performed the synthesis in a wide range of acetic acid concentrations from 0.10 M to 14.57 M. The morphology and size of these synthesized Pt NPs were summarized in Table 1. The related TEM images are shown in Fig. S1 (ESI[†]).

We have succeeded in synthesizing the Pt particles according to the procedure above without using any additional reducing agents. This indicates that the successful formation of Pt particles is attributed to the acetic acid which works as the

 Table 1
 Summary of morphology and size of the Pt NPs synthesized in a wide range of acetic acid concentrations

Pt NPs	Morphology	Size (nm)
Pt 0.10	Well-defined polyhedrons	19.2 ± 3.4
Pt $_{0.21}$	Well-defined polyhedrons	11.7 ± 2.5
Pt 0.52	Well-defined polyhedrons	12.2 ± 2.4
Pt 1.04	Well-defined polyhedrons	27.1 ± 4.3
Pt_3.11	Irregular polyhedron-constructed	16.1 ± 2.8
	chain networks	
Pt_4.16	Irregular polyhedron-constructed	13.2 ± 2.9
	chain networks	
Pt_5.20	Nanoflower-constructed	22.9 ± 3.9
	chain networks	
Pt_8.33	Nanoflower-constructed	113.1 ± 8.9
	chain networks	
Pt_10.41	Nanoflower-constructed	345.2 ± 14.3
	chain networks	
Pt_14.57	Nanoflower-constructed	309.6 ± 18.2
	chain networks	

reducing agent. To further investigate the reduction mechanism, we took the supernatant after the reaction for FTIR characterization, as shown in Fig. 3. The FTIR spectrum of the supernatant exhibits typical absorption peaks, which is similar to the controlled acetaldehyde solution. Thus, it can be conclude that the acetic acid is partly changed into acetaldehyde during the reaction. This agrees with the previous reported work,^{39,40} that acetic acid can decompose into hydrogen, acetaldehyde and carbon dioxide at heating condition. Therefore, the actual reducing agent in the present synthesis could be attributed to the generated H₂ upon the decomposing of acetic acid. The FTIR spectrum of the as-prepared Pt NPs after the reduction by using acetic acid is shown in Fig. S2 (ESI†), which demonstrates the negligible organic agent surrounding the surface of the as prepared Pt NPs.

The observed different morphologies at various acetic acid concentrations in Table 1 can be explained as follows. As the acetic acid concentration is low, the reduction rate of platinum ions to platinum particles is low. Specifically, since (111) facets has the lowest surface energy for a face-centered cubic structure,41 the formation of polyhedrons such as cubes with maximized expression of (111) facets is thermodynamically favorable to reduce the total surface energy. Therefore, the morphologies of as-prepared Pt NPs at low concentration of acetic acid are well-defined polyhedrons, which mostly are cubes (agree with the XRD results). As the concentration of acetic acid increases, the morphology of resultant Pt particles is irregular polyhedronconstructed chain network, in which the adjacent Pt NPs are often in close contact within the chains. In this case, the primary Pt particles are firstly formed via the reduction of platinum ions by the acetic acid and there is enough acetic acid for selectively tuning the Pt growth into irregular polyhedron particles based on that small molecule can also act as a structure-directing agent for crystal growth.⁴² The formed irregular polyhedron Pt NPs can further follow an attachment growth mode^{41,43} to form chain networks. As the concentration of acetic acid further increases, the abundant acetic acid molecules can result in rapid nucleation to form numerous Pt NPs. The initial formed Pt NPs are more energetically favorable to grow into a flowerlike shape since such aggregation can reduce the surface energy.⁴⁴ The as-prepared Pt nanoflowers can further have a growth through an attachment growth mode, resulting in nanoflower-constructed chain networks.

We further extended the present method to synthesize Pt-based bimetallic NPs. We selected PtPd as the studied system since PtPd bimetallic nanomaterials are among the most interesting bimetallic nanomaterials11,45-47 with excellent catalytic performance. Here, we studied on the synthesis of PtPd NPs with the concentrations of acetic acid at 0.21 M, 3.11 M and 5.20 M since typical interesting Pt particles can be obtained at these acetic acid concentrations. As we mainly focus on the green, simple and eco-friendly synthesis of "naked" PtPd NPs with clean surfaces but not on the study of compositiondependent PtPd particles, we choose Pt₃Pd₁ as the model PtPd bimetallic particles for the synthesis. The synthesis process of Pd₃Pt₁ NPs was similar to that of Pt NPs. The only difference was that the metal salt of $H_2PtCl_6 \cdot 6H_2O$ was replaced by the combination of H₂PtCl₆·6H₂O and K₂PdCl₄ with the molar ratio of $H_2PtCl_6 \cdot 6H_2O$: K_2PdCl_4 equal to 3 : 1 while the total amount of metal salt was the same as that for pure Pt NPs. The resultant Pt₃Pd₁ NPs at various acetic acid concentrations are labeled as Pt_3Pd_{1x} (x presents the concentration of acetic acid). The composition of the Pt₃Pd₁ NPs was characterized by ICP-AES. The atomic ratios of Pt to Pd for Pt₃Pd_{1_0.21}, Pt₃Pd_{1_3.11}, and Pt₃Pd_{1,5,20} synthesized with the concentrations of acetic acid at 0.21 M, 3.11 M and 5.20 M were determined to be 3.52:1, 3.29:1 and 3.41:1, respectively, which is well consistent with the ratio of precursors supplied. This indicates the complete reduction of the reaction due to the addition of acetic acid.

To visualize the morphology of the synthesized Pt_3Pd_1 NPs, a detailed TEM study of these NPs was undertaken. TEM images of the as-prepared $Pt_3Pd_{1_0.21}$, $Pt_3Pd_{1_3.11}$, and $Pt_3Pd_{1_5.20}$ are presented in Fig. 4a–f. The morphologies of $Pt_3Pd_{1_0.21}$, $Pt_3Pd_{1_3.11}$, and $Pt_3Pd_{1_5.20}$ NPs are almost similar to the as-prepared $Pt_{-0.21}$, $Pt_{-0.21}$



Fig. 3 FTIR spectra of the supernatant after the reaction (a) and the controlled acetaldehyde (C_2H_4O) solution (b).

corresponding Pt particles could be attributed to the addition of K_2PdCl_4 .

Fig. 5 shows the XRD patterns of the as-prepared various Pt₃Pd₁ particles. All the particles show four diffraction peaks corresponding to (111), (200), (220) and (311) of the typical facecentred cubic (fcc) phase, respectively. The corresponding diffraction peaks of the Pd₃Pt₁ NPs are located between that of pure Pt (JCPDS. no. 04-0802) and Pd (JCPDS. no. 65-2867), which demonstrates their alloyed structure. The XRD result confirms the formation of pure PtPd powders with highly crystallization and alloyed structure. From Fig. 5, it shows that the intensity of diffraction peaks Pt₃Pd₁ NPs increases with the increasing of acetic acid concentration. This indicates that the crystallinity of Pt₃Pd₁ NPs increases with the increasing of acetic acid concentration. Comparing the result of Fig. 1 with that of Fig. 5, it is obviously the change of the crystallinity with the increase of acetic acid concentration is completely different between Pt NPs and Pt₃Pd₁ NPs. Such difference could be attributed to the addition of K₂PdCl₄ for the synthesis of Pt₃Pd₁ NPs.

To further analyze the structure and elemental composition of the synthesized Pt_3Pd_1 , the high-angle annular dark-field scanning TEM (HAADF-STEM) and the element mapping of the typical $Pt_3Pd_{1_{5,20}}$ sample are characterized (Fig. 6). The uniform color distribution verifies that both Pt and Pd are homogeneously distributed throughout the NPs, indicating that the as-prepared particle is an alloy structure which is consistent with the result of the XRD. The Pt and Pd have extremely high



Fig. 4 TEM images of $Pt_3Pd_{1_0.21}$, $Pt_3Pd_{1_3.11}$ and $Pt_3Pd_{1_5.20}$ particles synthesized with various acetic acid concentrations: 0.21 M (a, b), 3.11 M (c, d) and 5.20 M (e, f).



Fig. 5 XRD patterns of the as-prepared Pt_3Pd_1 particles synthesized with various acetic acid concentrations: 0.21 M (a), 3.11 M (b) and 5.20 M (c).

lattice match (99.23%)⁴⁸ and similar redox potential ($[PdCl_4]^{2-}/$ Pd: 0.755 V *versus* SHE, $[PtCl_6]^{2-}/Pt$: 0.591 V *versus* SHE),⁴⁹ therefore the successful formation of alloy structure could be easily understood.

The electrocatalytic property of the typical synthesized Pt and Pt₃Pd₁ alloy NPs towards methanol oxidation was tested to understand their potential application in direct methanol fuel cells (Fig. 7). Here the typical Pt_{_0.21}, Pt_{_3.11}, Pt_{_5.20}, Pt₃Pd_{1_0.21}, Pt₃Pd_{1_3.11} and Pt₃Pd_{1_5.20} NPs are selected for the electrocatalytic performance evaluation since these particles are unique and representative. The commercial state-of-the-art Johnson-Matthey platinum black catalyst (HispecTM1000) is used as a reference for comparison. Fig. 7a and b shows the cyclic voltammograms (CVs) of the different catalysts at a scan rate of 50 mV s⁻¹ in 0.5 M HClO₄ solution. The current densities are normalized to the electrochemically active surface areas



Fig. 6 HAADF-STEM images (a-b), and EDS mapping images (c-e) of $Pt_3Pd_{1_5,20}$ bimetallic particles ((c) overlap, (d) Pt green, (e) Pd red).

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(ECSA). The semi-reversible peaks appeared at around -0.1 V correspond to the hydrogen adsorption and desorption while irreversible peaks at around +0.6 V are due to the platinum oxidation and reduction.⁵⁰ From the CVs in HClO₄ solution, the ECSA of the as-prepared Pt and PtPd electrocatalysts can be estimated by integrating the charge passed during the hydrogen adsorption–desorption from the electrode surface.^{28,29,51-54} The calculated ECSAs are 11.4 m² g⁻¹, 13.7 m² g⁻¹, 13.5 m² g⁻¹, 9.1 m² g⁻¹, 9.0 m² g⁻¹, 11.8 m² g⁻¹, 17.5 m² g⁻¹ for the

as-prepared $Pt_{0.21}$, $Pt_{3.11}$, $Pt_{5.20}$, $Pt_3Pd_{1_{0.21}}$, $Pt_3Pd_{1_{3.11}}$, $Pt_3Pd_{1_{5.20}}$ NPs and the commercial Pt black, respectively. The ECSA of the commercial Pt black is slightly higher than the asprepared Pt and Pt_3Pd_1 NPs because the size of the commercial Pt black (5.6 nm⁵⁵) is smaller than as-prepared Pt and Pt_3Pd_1 NPs. To test the electrocatalytic activity of various catalysts toward the oxidation of methanol, the ECSA normalized initial CVs of 1 M methanol in a 0.5 M HClO₄ were recorded, as shown in Fig. 7c and d. Characteristic anodic peaks in the forward and



Fig. 7 (a and b) ECSA-normalized CVs of $Pt_{0.21}$, $Pt_{3.11}$, $Pt_{5.20}$, $Pt_3Pd_{1_0.21}$, $Pt_3Pd_{1_3.11}$, $Pt_3Pd_{1_5.20}$ NPs and the commercial Pt black in 0.5 M HClO₄, (c and d) ECSA-normalized and (e and f) mass-normalized initial CVs of $Pt_{0.21}$, $Pt_{3.11}$, $Pt_{5.20}$, $Pt_3Pd_{1_0.21}$, $Pt_3Pd_{1_{3.11}}$, $Pt_3Pd_{$

observed. The peak current densities are 0.83, 0.59, 1.01, 0.94, 0.99, 1.37 and 0.42 mA cm⁻² for as-prepared Pt $_{0.21}$, Pt $_{3.11}$, Pt 5.20, Pt₃Pd_{1 0.21}, Pt₃Pd_{1 3.11}, Pt₃Pd_{1 5.20} NPs and commercial Pt black, respectively. Thus, the peak current densities of all asprepared Pt and Pt₃Pd₁ are higher than the commercial Pt black. Moreover, the Pt_5.20 exhibits the highest peak current density among the studied Pt catalysts while Pt₃Pd_{1,5,20} exhibits the highest peak current density among the studied PtPd bimetallic catalysts. Among all of the studied catalysts, the peak current density of Pt₃Pd_{1 5.20} NPs is the highest, about 3.26 times higher than commercial Pt black. Following Pt₃Pd_{1 5.20} is the as-prepared Pt_{_5.20} NPs, about 2.40 times higher than the commercial Pt black. The mass-normalized current densities of as-prepared Pt _{0.21} (0.095 A mg⁻¹), Pt _{3.11} $(0.082 \ A \ mg^{-1}), \ Pt_{5.20} \ (0.137 \ A \ mg^{-1}), \ Pt_{3}Pd_{1_{-0.21}} \ (0.102$ A mg⁻¹), $Pt_3Pd_{1\ 3.11}$ (0.106 A mg⁻¹), $Pt_3Pd_{1\ 5.20}$ (0.189 A mg⁻¹) NPs and commercial Pt black $(0.075 \text{ A mg}^{-1})$ are also presented (Fig. 7e and f). The peaks of mass-normalized current density of Pt₃Pd_{1 5.20} and Pt 5.20 are 2.52 and 1.83 times higher than the commercial Pt black, respectively. Both Pt 5.20 and Pt3Pd1 5.20 are with similar morphology (nanoflower-constructed chain networks), therefore one can imagine that such morphology is superior to other morphologies towards methanol oxidation in our case. This can be attributed that the electrocatalytic activity of Pt depends not only on the surface-to-volume ratio, but also on the structure or arrangement of the surface atoms. Here the synthesized Pt 5,20 and Pt3Pd1 5,20 NPs have a three-dimension (3D) nanoflower-constructed chain network structure. On one hand, the present 3D structure is helpful for the transport of the reactant due to the porous characteristic in the structure. On the other hand, each nanoflower structure shows a bumpy surface providing more catalytically active sites such as high density of atomic steps, ledges and kinks.35,36 The reason that the electrocatalytic activity of Pt₃Pd_{1 5.20} bimetallic NPs is better than monometallic Pt 5.20 NPs can be explained as follows. For Pt₃Pd_{1 5.20}, Pt catalyzes methanol dehydrogenation into Pt-CO while Pd makes water dehydrogenation into Pd-OH.27,28 The reaction between Pt-CO and Pd-OH produces CO2 and therefore the active metal surfaces refresh, resulting in higher electrocatalytic activity. However, the water dehydrogenation on pure Pt occurs at a higher potential without Pd, which makes methanol oxidation process sluggish in this case. Therefore the electrocatalytic activity of the synthesized Pt₃Pd_{1 5.20} bimetallic NPs is better than the synthesized monometallic Pt 5.20 NPs. We further used accelerated durability tests to characterize the cycling durability of the as-prepared catalysts. Here, the $Pt_{5.20}$ and Pt₃Pd_{1,5,20} NPs are selected for the study of catalytic durability since Pt $_{\rm 5.20}$ and $\rm Pt_3Pd_{1_5.20}$ represent the best Pt catalyst among the studied Pt catalysts and the best PtPd alloy among the studied PtPd alloy catalysts, respectively. Fig. 7g shows the ECSA-normalized current densities of the of Pt 5.20, Pt₃Pd_{1 5.20} NPs with increasing cycle number up to 3000 cycles in the solution of 1 M CH₃OH and 0.5 M HClO₄ solution. For comparison, the corresponding result of the commercial Pt black is also included. It is clear that all the current densities of Pt_5.20 and Pt₃Pd_{1_5.20} NPs are much higher than commercial Pt

reverse sweeps associated with methanol oxidation are

black in the corresponding cycles. For example, the current densities of Pt $_{5.20}$ and Pt₃Pd₁ $_{5.20}$ are 0.61 and 0.82 mA cm⁻², respectively at 3000 cycles, while the corresponding value of commercial Pt black is only 0.30 mA cm⁻². Comparing the current density at 3000 cycles with the maximum current density for each catalyst, the loss of activity of commercial Pt black is 67.6%, which might be caused by Pt nanoparticle ripening and aggregation.⁵⁶ In contrast, the Pt 5 20 and Pt₃Pd_{1 5.20} NPs lose 53.7% and 47.1%, respectively. The above results evidently show that the Pt 5.20 and Pt3Pd1 5.20 have much better durability in comparison with the commercial Pt black for the methanol oxidation, thanks to their structural advantages. Fig. 7h shows the corresponding mass-normalized current densities of Pt 5.20, Pt3Pd1 5.20 and Pt black with increasing cycle number up to 3000 cycles. The massnormalized current densities of Pt 5.20 and Pt3Pd1 5.20 are all much higher than commercial Pt black in the corresponding cycles, demonstrating the advantage of the as-prepared Pt 5.20, and Pt₃Pd_{1 5.20} catalysts in the long-term use. Thus, the as-prepared Pt 5.20 and Pt3Pd1 5.20 have superior cycling durability for methanol electrooxidation in comparison with commercial Pt black catalyst. The onset potential (E_{onset}) of the Pt 5.20, Pt₃Pd_{1 5.20} and the commercial Pt black for the oxidation of methanol is shown in Table S1 (ESI[†]). Generally speaking, the much negative E_{onset} is more beneficial for the oxidation of methanol. From the Table S1,† the *E*_{onset} of Pt₃Pd_{1 5.20} at 3000 cycles is lower than commercial Pt black while the Eonset of Pt 5.20 is similar to the commercial Pt black. Therefore, it is clear that the Pt_5.20 and Pt3Pd1_5.20 have superior electrocatalytic properties toward methanol oxidation in comparison with commercial Pt black.

Conclusions

In this work, we proposed a very simple, green and eco-friendly route to synthesize "naked" Pt and PtPd alloy NPs with clean surfaces in acetic acid solution. The synthesis does not need any additional reducing agents and structure-directing agents such as surfactants. The acetic acid itself acted as the reducing agent and the structure-directing agent for the formation of the Pt and PtPd alloy particles. Pt and PtPd alloy NPs with various interesting morphologies (well-defined polyhedrons, irregular polyhedronconstructed chain networks and nanoflower-constructed chain networks) could be controllable synthesized by tuning the concentration of acetic acid. Particularly, the electrochemical results showed that as-prepared Pt 5.20 and Pt3Pd1 5.20 exhibit much higher activity and better durability than the commercial Pt black for the methanol oxidation reaction, verifying their promising application in fuel cell areas. The present synthesis strategy thus provides a promising way for the synthesis of "naked" metal catalysts for advanced electrocatalytic applications.

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