Nanoporous twinned PtPd with highly catalytic activity and stability†

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Growing needs for highly efficient energy storage devices have prompted increasing research efforts in energy-efficient and sustainable materials. In this context, nanoporous noble metals have been studied extensively because of their extraordinary properties. However, existing electrochemical/chemical dealloying approaches for their synthesis largely lack the ability to optimize their structure/function relationships. To overcome this limitation, we developed a thermal-decomposition strategy for the synthesis of component-controllable nanoporous PtPd alloys composed of ~2 nm sawtooth-like ligaments induced by a high density of twinning boundaries (boundary spacing ~ 1 nm). Such twinned and ultrathin ligaments exhibit large curvatures between concave and convex regions, associated with abundant low-coordination surface atomic steps and kinks. These low-coordination atoms are sites of high catalytic activity, as confirmed by theoretical simulations. The optimized Pt25Pd75 sample exhibits the best catalytic performance among all the currently reported catalysts, and has a mass activity of 1110 mA mg−1 Pt−1 and high stability for the electro-oxidation of methanol.

Introduction

Direct methanol fuel cells (DMFC) that exhibit high energy density have attracted considerable interest for portable energy storage applications. However, during the electro-oxidation process, methanol is dehydrogenated into adsorbed carbonaceous intermediates on Pt atoms,1 which heavily affect the catalytic capacity by the formation of strong Pt–CO bonds that lead to the degradation of catalytic activity. These issues have been addressed by combining Pt with other transition metals in various forms, known as the bi-functional catalytic mechanism, which is responsible for accelerating the oxidation and removal of carbonaceous molecules generated in the process.1–12 For example, Pd can weaken the Pt–CO bond and promote the oxidation process of CO to CO2 via water dehydrogenation, i.e. the formation of Pd–OH. By adjusting the atomic ratio between Pt and Pd, the degradation and dehydrogenation processes of methanol can be coordinated effectively.7,8,12

Conventional routes for improving catalytic activity, either by reducing particle size13,14 or by constructing high-index facets15 have proven effective, but they are structurally unstable when downsized to 5 nm or smaller. Therefore, the agglomeration and coarsening of catalysts cannot remain a desirable stability during reaction processes. To enhance the catalytic stability, porous structures, providing 3-dimentional skeleton support, have been achieved, which are usually synthesized by chemical/ electrochemical dealloying procedures.7,8,16–19

Results and discussion

Here we describe a thermal-decomposition strategy for the synthesis of highly miscible PtPd nanostructures composed of ultrathin ligaments with 2–5 nm diameter having a high density (boundary spacing ~ 1 nm) of twinning boundaries that induce significant surface steps and kinks. The composition of PtPd nanoporous samples can be rationally adjusted by changing the raw material ratio of palladium(u) chloride (PdCl2) and platinum(u) acetylacetonate [Pt(acac)2], as detailed in the ESI.† The structures of Pt, PtPd, and Pd samples were characterized using bright-field scanning transmission electron microscopy (BF-STEM) and high angle annular dark field STEM (HAADF-STEM). The HAADF-STEM image in Fig. 1a represents the mass contrast, whereby regions with higher-density and/or heavier elements are imaged with brighter contrast. From Fig. 1a, a typical nanoporous Pt35Pd65 sample structure has an average size of 50–100 nm in the form of a cluster with a mean ligament diameter of 2.3 ± 0.6 nm. The three-dimensional Pt25Pd75...
structure is composed of randomly oriented branches, in which the central brighter regions correspond to the overlapped ligaments. The yield of these nanostructures in the final product reaches 100% by statistical analysis using STEM.

The composition distribution of Pt and Pd was visualized through a sequence of annular dark-field (ADF) images and X-ray energy-dispersive (EDX) maps, which presents the microstructural bimetallic interfaces. As shown in Fig. 1b, the distribution of Pd and Pt of the Pt25Pd75 sample throughout the entire domain of a single cluster is clearly observed and shows a slight fluctuation of the composition ratio. Further magnification and focusing of the EDX analysis on the growth tip of a branch (Fig. 1c) demonstrates that Pt and Pd are highly miscible.

By adjusting the raw material ratio of PdCl₂ and Pt(acac)₂, we synthesized the following compositions of nanoporous structures: Pt₈Pd₆₂, Pt₁₄Pd₆₈, Pt₂₅Pd₇₅, Pt₄₃Pd₅₇, Pt₅₈Pd₂₂, as well as polyhedral Pt nanoparticles. The composition ratios of Pt versus Pd for all PtPd samples were determined by elemental analysis using energy-dispersive X-ray spectroscopy (ESI Table S1, and Fig. S1–S6†). Comparisons of Pt and Pd compositions in products and precursors shown in Fig. 2a and b confirm that there is almost no loss of metal components during the preparation processes. The X-ray diffraction (XRD) patterns (Fig. 1d and ESI Fig. S7 and Table S2†) show five broad diffraction peaks corresponding to the face-center-cubic (FCC) metal structure. The average grain size estimated using Scherrer’s formula exhibits an initial decrease with increasing Pd component and reaches a minimum value of 2.3 ± 0.6 nm for Pt₂₅Pd₇₅ composition (Fig. 1e). The value of the computed grain size is slightly lower than the ligament diameter estimated by statistical analysis of STEM images, indicating the presence of polycrystalline domains confined within a ligament.

HAADF-STEM imaging was also employed to gain insight on the growth mechanism of the nanoporous structure. The Pt₂₅Pd₇₅ sample image (inset of Fig. 1a) reveals a detailed structure of the primary branch consisting of multiple sub-branches in the early stage of growth. The image confirms that all the branches grow initially along the [111] direction. TEM and STEM observations provide the detailed microstructures of PtPd catalysts, confirming the product is porous structure with continuous growth at [111] crystalline plane directions, which is absolutely different from agglomerated nanoparticles with random crystalline planes. In addition, the presence of a monolayer of oleylamine (OAm) molecules adsorbed on the surface of the Pt₂₅Pd₇₅ ligaments was confirmed by combined SEM/STEM analysis (Fig. 3) and Fourier transform infrared (FTIR) spectroscopy (Fig. 4). These results suggest that channel-mediated growth previously reported for ultrathin noble metal nanowires is the dominant mechanism in the case of PtPd nanoporous structures.⁶,20–22 A high density of twin boundaries appears for all the compositions of PtPd samples (ESI Fig. S1–6†). The formation of twinning boundaries plays a critical role in exponential reduction of the surface energy for FCC metals at the nanoscale.²³ Such structural features result in abundant atomic steps and low-coordinated surface atoms, associated with multiple exposed (111) and {100} facets, which provide the energetically favorable conditions for multi-branched growth. Subsequently, PtPd branches could be “welded” at connecting junctions by mechanical and thermal activation, similarly to the welding of ultrathin nanowires (Au and Ag) by mechanical contact⁴,15 or low-energy light irradiation.²⁶

In the absence of the Pd precursor, however, the final product consists solely of polyhedral Pt nanoparticles (ESI Fig. S1†). This may be a consequence of the relatively higher redox potential of Pt²⁺/Pt (+1.188 V) that results in a nucleation burst leading to the formation of a very large number of small Pt particles followed by their rapid agglomeration, which thus
limits the growth of Pt branches with insufficient feedstock [Pt(acac)₂]. In comparison, the lower redox potential of Pd⁺²/Pd⁺(+0.915 V) together with the slower decomposition rate of PdCl₂, favor the growth of Pd branches along the energetically preferential [111] directions. The scheme of growth process is shown in Fig. 5. In addition to Pd⁺² and Pd nuclei, the supersaturated Pt nucleus provides a stable feedstock for the growth of PtPd branches by Ostwald ripening. Under thermal assistance, Pt and Pd diffuse and finally form a highly miscible composition.

The electrochemical catalysis of methanol oxidation was evaluated systematically in an Ag/AgCl three-electrode reaction cell at room temperature. The PtPd samples were deposited on Vulcan XC-72 carbon support with 20 wt% of metals, following an ultra-sonication dispersion of 1 hour and a treatment of 99% acetic acid overnight. The cyclic voltammetry (CV) curves for each catalyst were recorded at room temperature in an N₂-purged solution of 0.5 M H₂SO₄ and 1 M methanol by scanning the voltage from 0 to 1 V at 50 mV s⁻¹ sweep rate. The PtPd samples exhibit significant improvement for catalytic performances of methanol electro-oxidation, as shown in Fig. 6 (ESI Fig. S8–11 and Table S3†). Because Pd has no electrocatalytic activity for methanol oxidation in sulfuric acid medium, we therefore counted the mass activity of bimetallic PtPd catalysts only based on the Pt fraction. The mass current densities and normalized residual currents of Pt-based catalysts reported in the literatures were compared with the PtPd samples presented herein, as shown in Fig. 6a. It should be noted that Pt₂₅Pd₇₅ exhibits the largest mass current of 1110 mA mg⁻¹ Pt⁻¹, which is higher than Pt₄₃Pd₅₇ and Pt₅₈Pd₄₂ although they own relatively larger electrochemical surface areas (ECSAs). In the methanol oxidation, Pd and Pt are responsible for the water dehydrogenation (Pd–OH formation) and methanol dehydrogenation (Pt–CO formation), respectively. The reaction between Pd–OH and Pt–CO produces CO₂ and regains the active metal surface, which is significantly co-affected by both the Pt/Pd ratio and their reaction dynamics. Therefore, although Pt₄₃Pd₅₇ catalyst presents the maximized ECSAs among all the samples, Pt₂₅Pd₇₅ catalyst has the best catalytic performance due to its suitable Pt/Pd match related to the electrochemical dynamics. In comparison to polyhedral Pt nanoparticles, the current densities of Pt₅₈Pd₄₂, Pt₄₃Pd₅₇ and Pt₂₅Pd₇₅ samples curves exhibit significantly higher and more stable values with enhancement ratios ranging from 140% to 390% despite the lower Pt content. Additionally, the optimized current density is higher than those of Pt-on-Pd nanodendrites (490 mA mg⁻¹ Pt⁻¹ (ref. 7) and 647 mA mg⁻¹ Pt⁻¹ (ref. 8)) which have a spatial phase-separation of the Pt and Pd domains with limited Pd/Pt interfaces. The
Fig. 6 Catalytic performance of nanoporous PtPd with controllable compositions in the electro-oxidation of methanol. (a) Electro-oxidation peak current of methanol as a function of Pt/Pd composition (upper panel); residual current extracted from chronoamperometric curves recorded at 0.6 V for 2000 s, exhibiting better durability of nanoporous PtPd structures than that of polyhedral Pt nanoparticles (lower panel). (b) Redox potentials and their ratio in the forward and backward sweeps (\(I_F/I_B\)), showing an increase from 0.75 to 1.93 as increasing the Pd content. (c) Comparison of catalytic activity and stability of Pt and Pt-based catalysts in various forms. The normalized residual currents are recorded at 2000 s for our Pt and nanoporous PtPd samples whose compositions are marked, or at shorter time for some cited references. Detailed descriptions and cited references are provided in ESI Table S3,† in which several catalysts having higher mass activities but quite lower stabilities are not integrated into Fig. 2c.

Fig. 7 Catalytic stability of nanoporous PtPd. (a) Electro-oxidation peak current of methanol as a function of Pt/Pd composition (upper panel); residual current extracted from chronoamperometric curves recorded at 0.6 V for 2000 s of nanoporous PtPd structures than that of polyhedral Pt nanoparticles; (c) column pattern of residual current density (normalized) after 2000 s measurement.

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chronoamperometric curves of Pt_{25}Pd_{75} sample indicate the presence of 75.9% residual current after 2000 s reaction (Fig. 6b and 7). The enhancement for the stability is evidently ascribed to the bi-functional catalytic mechanism from the synergistic effect of Pd and Pt,\textsuperscript{1-12,20-32} in which the intermediate carbonaceous residues can be effectively oxidized and removed, resulting in a sustainable electro-oxidation process. Electrocatalytic cycling stability has also been measured by using CV cycling, as shown in Fig. 8, indicating only a 21% loss of activity after 500 cycles. The microstructures analyzed by TEM (Fig. 9), for the as-made Pt_{25}Pd_{75} and after 500 CV cycles, further confirm high structural stability at electrochemical reactions.

The tolerance towards intermediate carbonaceous species is also evaluated by the ratio of the peak current values in the forward and backward sweeps (\(I_F/I_B\)). The low \(I_F/I_B\) ratio is an indication of poor methanol electro-oxidation and excessive accumulation of carbonaceous residues on the catalyst surface in the forward sweep.\textsuperscript{30-32} As shown in Fig. 6b, the \(I_F/I_B\) ratio exhibits a significant increase from 0.75 to 1.93 when the Pd content is increased. This confirms the enhanced ability to remove carbonaceous species formed on the catalyst during the forward sweep. In addition, with the increasing Pd content, the forward and backward peaks gradually shift to the lower potential values, indicating an enhanced kinetics of methanol electro-oxidation. From the comparisons summarized in Fig. 6c, the Pt_{25}Pd_{75} sample exhibits an overall better performance than Pt and Pt-based catalysts previously reported, possessing both high activity and high stability. Catalytic activity and stability are correlated with the microstructure of the catalysts. The HAADF-STEM image in Fig. 10a reveals a three-dimensional porous architecture consisting of sawtooth-like ligaments with characteristic diameters of 2–5 nm, associated with a complex arrangement of convex and concave surfaces. The stepped surface facets shown in the magnified image (Fig. 10b) give rise to a curvature that change along the surface line where the twinning boundaries terminate, as indicated by arrows. The kinks induced by twinning boundaries result in an inward surface curvature, a phenomenon that was not observed in any other nanoporous metal or alloy reported to date.\textsuperscript{1,7,18,19,33-35} Adjacent to the twin boundaries, a column of surface atoms protruding from the regular surface was observed. This complex structure is associated with a high density of atomic steps where the atoms are thought to be low-coordination. These low-coordination atoms play an important role that is responsible for the high catalytic activity of nanoscale catalysts.\textsuperscript{11-15} Specifically, low-coordination metal atoms interact more strongly with molecules due to a local up-shift and narrowing of the d-band, which weakens chemical bonding.
Fig. 9  Structural stability of nanoporous PtPd catalysts during electrochemical reactions. TEM images of Pt\textsubscript{25}Pd\textsubscript{75}/Vulcan XC-72 carbon catalyst (a) before and (b) after 500 cycles of cyclic voltammograms in N\textsubscript{2}-saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} containing 1 M methanol (scan rate: 50 mV s\textsuperscript{-1}).

Fig. 10  Enhanced surface strain by twinning boundaries. (a) High-resolution HAADF-STEM images near center region of a Pt\textsubscript{25}Pd\textsubscript{75} cluster, showing the microstructure of nanopores and high lattice coherence on junctions. Scale bar, 5 nm. (b) Sawtooth-like ligaments induced by a high density of twinning boundaries with a twinning space of \textasciitilde 1 nm were further observed. Careful identification reveals that most of the exposed facets on the PtPd ligaments were \{111\} and \{110\} planes with a large number of low-coordinated surface stepped atoms arising from the concave and convex architectures. Scale bar, 2 nm. (c) High-resolution HAADF-STEM image of a Pt\textsubscript{25}Pd\textsubscript{75} ligament containing two twining boundaries, revealing the atomic-scale lattice structure. Scale bar, 1 nm. (d) Strain maps of $\varepsilon_{xx}$ and $\varepsilon_{zz}$ corresponding to the atomic structure as shown in (c) were obtained by first principle calculations. Color represents variation of strain from $-10.0$ to $10.0\%$. 

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of molecules and reduces reaction barriers relative to close packed metal surfaces.\textsuperscript{33}

The surface strain of nano-scale catalysts is directly related to the density and catalytic activity of low-coordination surface atoms.\textsuperscript{33,35,36} While large positive out-of-plane strain can be induced by the intrinsic nature of the curved ligaments of nanoporous structures,\textsuperscript{35} the exact role that the twinning boundaries play in the surface strain is still unclear. A comprehensive study of lattice distortion near the twinning boundary for nanoporous PtPd is crucial for understanding the origin of high-performance electro-oxidation of methanol. From Fig. 10c, a representative region is examined to uncover two crossed twinning boundaries that are confined within a ligament having a $\sim$3 nm diameter. These twinning boundaries induce sawtooth-like surface steps along the highly active $\{111\}$ and $\{110\}$ facets. This structure was employed as the basis for a model constructed to further study the effect of the twinning boundary on the surface strain using \textit{ab initio} calculations (Fig. 10d). For the strain mapping analysis, predefined directions ($x$ and $z$) were chosen parallel and perpendicular to the $\{111\}$ surface plane, respectively. After structural relaxation, the calculated strains were obtained by comparison with the $\{111\}$ lattice spacing of bulk Pt metal. Strain mapping analysis provides intrinsic insights into this experimental configuration, showing that the strain occurs only slightly in the in-plane direction, while it becomes more pronounced out-of-plane. The local strains, particularly those in the regions of twinning boundary and the induced convex corner, are enhanced up to $\pm$10\%, and more than $\sim$5\% at the normal ligament surface. These results indicate that the enrichment of twinning boundaries provides more active sites for catalysis that are the origin of high-performance electro-oxidation of methanol.

To understand the role of highly miscible Pt/Pd interfaces in suppressing the excessive accumulation of carbonaceous residues on the catalyst surface, CO molecules adsorbed onto four sites with different distances to the interface were characterized using spin-polarized first-principles calculations (Fig. 11a). From Fig. 11b, on the site closest to the interface (denoted as Pt\textsubscript{1}), the CO adsorption energy associated with triple Pt–C bonding corresponds to 1.756 eV, which is significantly lower than those at more distant sites (Pt\textsubscript{2}, Pt\textsubscript{3} and Pt\textsubscript{4}). Density functional theory (DFT) calculations provide the charge density distributions of the four configurations. As shown in Fig. 11c, the charge density increase located at Pt\textsubscript{1} is evidently reduced in comparison to those at sites Pt\textsubscript{2}, Pt\textsubscript{3} and Pt\textsubscript{4}. It suggests that the interactions between Pt\textsubscript{1} and CO molecules are weakened, which is consistent with the result of adsorption energy calculation. This is further demonstrated by quantitative DOS analysis for four different sites of Pt atoms without CO absorption, as shown in Fig. 11d. Pt\textsubscript{1} atoms exhibit anomalous DOS in comparison with the other three sites, which implies that the local electronic structure of Pt atoms at Pt/Pd interfaces is affected by coordinated Pd atoms. These atomic-scale insights confirm that Pt\textsubscript{1} is the most favourable site for the bi-functional catalytic mechanism.\textsuperscript{1} At this location, Pt atoms coordinate with Pd atoms resulting in the weakest Pt–CO bonding, which promotes the oxidation process of CO to CO\textsubscript{2}. With high miscibility of Pt and Pd, the exposed Pt/Pd interfaces confined within ultrathin ligaments thus provide the optimal configuration. In relation with the three-dimensional open porous

Fig. 11  Theoretical simulation for the effect of atomic-scale Pt/Pd interfaces of nanoporous PtPd alloy on the methanol electro-oxidation. (a) Four configurations of CO adsorption on various sites around Pt/Pd interfaces. (b) Dependence of absorbance energy and C–O bond length on the four indexed sites in (a). (c) Charge density distribution of Pt\textsubscript{1} and Pt\textsubscript{4} sites, indicating the weaker Pt–C bond at Pt\textsubscript{1} site than Pt\textsubscript{4}. (d) Quantitative DOS in various configurations, indicating the origin of electronic structures for the weakened Pt–C bond at Pt\textsubscript{1}.
structure, these Pt/Pd interfaces can accelerate the catalytic process of carbonaceous residues and effective renewal of ions and molecules.

**Conclusions**

In summary, a simple thermal-decomposition strategy was employed to synthesize component-controllable PtPd nanoporous catalysts including an optimized \( \text{Pt}_{25}\text{Pd}_{75} \) composition which exhibits the smallest ligament size, a high density of twinning boundaries, as well as sub-nanometre scale Pt/Pd interfaces. These nanoporous PtPd catalysts are both highly active and stable, as demonstrated by their performance in methanol electro-oxidation. Additionally, the synthesis strategy we employed holds great potential for large-scale industrial production due to the processing simplicity and low cost, which is a promising avenue for many energy-related applications.

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