Highly porous Pt-Pb nanostructures as active and ultrastable catalysts for polyhydric alcohol electrooxidations

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ABSTRACT Highly porous materials have attracted intensive attention in the past decades due to their unique geometrical configuration, unusual structural features, and outstanding physicochemical properties, but the facile creation of porous metal nanomaterials remains a formidable challenge. Most reports focused on using hard templates to create porous metal nanomaterials *via* sacrificing the templates. Herein, we have created a new class of porous PtPb/Pt nanocrystals (NCs) with well-defined morphology, composition and porosity through a facile chemical etching approach. Due to the highly open three-dimensional (3D) structure and alloy effect, the porous PtPb/Pt NCs exhibit enhanced performances towards polyhydric alcohol electrooxidations with the optimized porous Pt₃Pb nanoplates exhibiting superior activities of 1.75 mA cm⁻² and 1.19 A mg⁻¹_{Pt} for ethylene glycol oxidation reaction (EGOR) and of 1.46 mA cm⁻² and 1.00 A mg⁻¹_{Pt} for glycerol oxidation reaction (GOR) that are much higher than the commercial Pt/C (0.34 mA cm⁻² and 0.22 A mg⁻¹_{Pt} for EGOR, 0.30 mA cm⁻² and 0.20 A mg⁻¹_{Pt} for GOR). In addition, the porous Pt₃Pb nanoplates can endure the long-term stability in EG and glycerol oxidation reactions with limited activity and structure change after 20,000 and 5,000 cycles, respectively, showing a highly promising class of porous Pt-based electrocatalysts for direct polyhydric alcohol fuel cells and beyond.

Keywords: nanoporous, Pt-Pb nanoplate, Pt-Pb octahedron, ethylene glycol oxidation, glycerol oxidation

INTRODUCTION

As a unique class of advanced structures, nanoporous materials have attracted considerable attention in the past few decades due to their unique geometrical configura-

tions, unusual structural features, and outstanding physicochemical properties [1–5]. Differing from conventional materials, nanoporous materials usually exhibit largely increased active sites and fast mass transport efficiency, all which are beneficial for the process of catalysis, reaction, or separation in applied catalysis, renewable energy, environmental cleanup and so forth [3,6–12]. Hence, it is highly demanding to develop efficient approach for the creation of the advanced nanoporous materials. To date, sophisticated synthetic methods such as direct synthesis, thermal decomposition, electrochemical deposition, and template-assisted method have been developed for the creation of various porous nanomaterials [2,13–17], such as zeolites, metals, metal oxides, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), carbons, inorganic-organic hybrid materials, and porous polymers [4,18–23]. As one of the most important nanomaterial members, noble metals such as platinum (Pt)-based nanomaterials play a critical role in a wide range of multidisciplinary fields [24,25], while the rare content and expensive cost largely hinder their practical applications [26,27]. Therefore, it is more urgent to construct the porous noble metal nanostructures (PNMNs) for improving performance and atomic utilization from the view of practical application. However, unlike the porous metal oxides and carbons, it is very hard to directly prepare the porous noble metal materials, mainly due to the weak interaction between noble metal precursors and pore-directing agents, along with the fact that the noble metal atoms are apt to form into the close-packed arrangement pattern caused by the minimized surface energy for structural stability during the crystal growth process [24,28]. While the most com-

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mon strategy to synthesize PNMNs is the hard-templating method, the procedure is usually complicated and is not beneficial for the efficient preparation of PNMNs [25,29]. Consequently, it is extremely urgent to search new approaches for fabricating the porous noble metal nanomaterials.

Recently, the structurally ordered Pt-based nanocrystals (NCs) have emerged as a class of promising electrocatalysts, mainly due to their outstanding performance as well as structural superiorities [30–32]. From the structural perspective, the ordered Pt-based NCs can be ideal candidates for the design of porous Pt-based electrocatalysts due to their predictable control over the surface composition, active sites distribution, and local geometry of metal atoms [25,33,34], which cannot be realized by the conventional alloys. For instance, while the Pt-based alloys with segregated features are fit for the formation of nanoframes [27,35,36], and the core-shell structured Pt-based nanomaterials can be used as the bases for creating the hollow nanostructures [37,38], these disordered Pt-based NCs cannot be acted as the foundation to realize the porous Pt-based electrocatalysts [33,34]. Moreover, because of the high enthalpy of mixing, the ordered nanomaterials can usually exhibit outstanding stability in catalytic reactions, which can be hardly afforded by the conventional disordered nanostructures [39–41]. Based on all the above considerations, rationally constructing the porous architectures based on ordered Pt-based NCs can be a viable strategy to create porous Pt-based electrocatalysts with enhanced electrocatalytic performance, but it is still an untapped subject to date.

Herein, we report a facile chemical etching approach to create a new class of porous PtPb/Pt NCs for the first time, namely porous PtPb/Pt nanoplates (porous PtPb/Pt NPs) and porous PtPb/Pt octahedra (porous PtPb/Pt OTs). The obtained series of porous PtPb/Pt NCs have controlled porosity, composition as well as well-defined morphology, which are highly beneficial for studying the shape, composition, alloy effect and the porosity on polyhydric alcohol electrooxidations, such as ethylene glycol and glycerol oxidation reactions (EG-G/OR). As a result, the porous PtPb/Pt NPs have been demonstrated largely enhanced EG-G/OR performances compared with the commercial Pt/C. The optimized porous PtPb/Pt NPs with composition of Pt₃Pb exhibit the highest activity for EG-G/OR among all the studied electrocatalysts. The unique 3D porous structure and the outstanding anti-poisoning ability also make the porous Pt₃Pb NPs highly durable with limited mass activity decay over 20,000 potential cycles for EGOR (29.9% loss) and 5,000

potential cycles for GOR (34.2% loss), respectively.

EXPERIMENTAL SECTION

Synthesis of PtPb NPs, porous Pt₃Pb₂ NPs, porous Pt₃Pb NPs, porous Pt₂₁Pb NPs, PtPb OTs, porous Pt₃Pb₂ OTs, porous Pt₃Pb OTs, and porous Pt₂₁Pb OTs

The PtPb NPs and PtPb OTs were initially synthesized according to our previous publications [42,43]. For the synthesis of porous Pt₃Pb₂ NPs, the PtPb NPs dispersed in cyclohexane/*N,N*-dimethylformamide (DMF)/nitric acid (HNO₃) (*v/v/v*=1/4/1) mixture were stirred intensively and heated at 60°C for 2 h. The products were collected by centrifugation. All the synthetic parameters for porous Pt₃Pb NPs, porous Pt₂₁Pb NPs, porous Pt₃Pb₂ OTs, porous Pt₃Pb OTs, and porous Pt₂₁Pb OTs are similar to those of porous Pt₃Pb₂ NPs but changing the etching temperature to 90°C, 120°C, 50°C, 70°C and 90°C, respectively.

Electrocatalytic measurements

The loading amounts of Pt for the PtPb NPs/C, porous Pt₃Pb₂ NPs/C, porous Pt₃Pb NPs/C, porous Pt₂₁Pb NPs/C, PtPb OTs/C, porous Pt₃Pb₂ OTs/C, porous Pt₃Pb OTs/C, porous Pt₂₁Pb OTs/C, and commercial Pt/C were all kept at 12.8 μg cm⁻², based on ICP-AES measurements. The EGOR (GOR) measurements were carried out in 0.1 mol L⁻¹ HClO₄ solution containing 0.5 mol L⁻¹ EG (0.5 mol L⁻¹ glycerol) at room temperature. In the cyclic voltammetry (CV) measurements of EGOR (GOR), the scanning rate was set at 50 mV s⁻¹. For the EGOR (GOR) stability tests, CV sweepings were conducted for more than 20,000 (5,000) cycles. All the other electrochemical measurements were described in our previous studies [42,43].

RESULTS AND DISCUSSION

By using PtPb NCs (i. e. PtPb NPs and PtPb OTs) as the starting materials (Figs S1, S2) [42,43], porous PtPb/Pt NCs were synthesized *via* a facile chemical etching strategy, in which nitric acid was used as the oxidative etching agent. Fig. 1 shows the schematic illustrations and representative transmission electron microscopy (TEM) images as well as the high-angle annular dark-field scanning TEM (HAADF-STEM) images of initial PtPb NPs, initial PtPb OTs, different porous PtPb/Pt NPs, and different porous PtPb/Pt OTs. To create well-defined porous PtPb/Pt NCs, we explored their synthetic parameters in details, especially the etching temperature and etching time (Figs S3, S4). As a result, the optimized

Figure 1 Schematic illustrations and corresponding TEM images as well as HAADF-STEM images of PtPb NCs and different porous PtPb/Pt NCs. (a) Initial PtPb NPs and initial PtPb OTs. (b) Porous PtPb/Pt NPs (I) and porous PtPb/Pt OTs (I). (c) Porous PtPb/Pt NPs (II) and porous PtPb/Pt OTs (II). (d) Porous PtPb/Pt NPs (III) and porous PtPb/Pt OTs (III). The scale bars, 50 nm. Insets are the magnified HAADF-STEM images. The scale bars, 10 nm.

porous PtPb/Pt NCs with well-controlled morphology, composition, and porosity were prepared by precisely controlling the etching temperature at the aid of nitric acid (see Experimental Section for details). As shown in Fig. 1a and Fig. S1, the unique PtPb NPs with hexagonal morphology were firstly selected as the seed to synthesize porous PtPb/Pt NPs with different compositions. After etching at 60 for 2 h in the nitric acid medium, we prepared the porous PtPb/Pt NPs with minimal etching extent, namely porous PtPb/Pt NPs (I), and the 3D model as well as the typical TEM images were shown in Fig. 1b and Fig. S5a, b. Large numbers of pores with the average size of 1.2 ± 0.7 nm were observed on the surface of the porous PtPb/Pt NPs (I) (Fig. S5c). Increasing the etching temperature from 60°C to 90°C while keeping other experimental parameters unchanged, we created the porous PtPb/Pt NPs with moderate etching level, namely porous PtPb/Pt NPs (II) (Fig. 1c and Fig. S5d, e). According to the statistics, the average pore size of these porous PtPb/Pt NPs was determined to be 1.5 ± 0.7 nm (Fig. S5f). When the etching temperature was changed to 120°C, the porous PtPb/Pt NPs (III) with the largest etching degree were obtained (Fig. 1d and Fig. S5g, h), and the average pore size was measured to be 1.9 ± 0.6 nm (Fig. S5i). When the etching temperature was increased to 130°C, the porous PtPb/Pt NPs underwent too heavy etching to maintain the structure (Fig. S3d–f).

We found that the optimized etching temperatures for creating porous PtPb/Pt OTs with different compositions are 50, 70, and 90°C, respectively, lower than that of the porous PtPb/Pt NPs, mainly due to the stable PtPb/Pt core/shell nanostructure of PtPb NPs [42,43]. According to our previous study, PtPb OTs show the non-core/shell structure (Fig. S2) [43], resulting in their milder etching condition than PtPb NPs. For the porous PtPb/Pt OTs, the porosity and pore size improved with the increased etching temperature, which is revealed by the TEM and HAADF-STEM images as well as the corresponding 3D models of porous PtPb/Pt OTs (Fig. 1b–d and Fig. S6a, c, e). As shown in Fig. S6b, d, f, the average pore size of porous PtPb/Pt OTs obtained by different etching temperature was measured to be 1.4 ± 0.8 nm, 1.7 ± 0.7 nm and 2.1 ± 0.8 nm, respectively.

Fig. 2a shows that the overall Pt/Pb ratios of PtPb NPs and porous PtPb/Pt NPs are 55.9/44.1, 60.4/39.6, 74.2/25.8, and 95.5/4.5, respectively, as revealed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES), which is consistent with the TEM energy-dispersive X-ray spectroscopy (TEM-EDS) results (Fig. S7a). In order to study the phase of porous PtPb/Pt NCs, powder X-ray diffraction (PXRD) was carried out in details. PXRD patterns demonstrate that the PtPb NPs and different porous PtPb/Pt NPs are highly crystalline (Fig. 2b). The PXRD pattern of PtPb NPs corresponds well with the intermetallic PtPb phase (Joint Committee on Powder Diffraction Standards (JCPDS) No. 06-0374) (Fig. 2b (1) and Fig. 2c (1)). After etching at 60°C for 2 h, the PXRD pattern of porous Pt₃Pb₂ NPs is hardly changed (Fig. 2b (2)), while the half-peak width of PtPb (102) facet became larger than that of the initial PtPb NPs from the enlarged PXRD patterns (Fig. 2c (1) and Fig. 2c (2)). When the etching temperature was set to 90°C, the PXRD pattern of the porous Pt₃Pb NPs underwent obvious change (Fig. 2b (3)). From their enlarged PXRD pattern in Fig. 2c (3), new diffraction peaks ($2\theta = 39.8^\circ$, 46.2°), corresponding to cubic Pt phase (JCPDS No. 04-0802), were found, while all the diffraction peaks of PtPb NPs were maintained, revealing the presence of different crystal phases in the porous Pt₃Pb NPs. This nanostructure is essentially an unconventional class of heterostructure for porous Pt₃Pb NPs, which can be hardly revealed in previous work. After etching under higher temperature, the PXRD pattern of the porous Pt₂Pb NPs underwent more significant change (Fig. 2b (4)). The enlarged PXRD pattern confirms the formation of new phase, which matches well with the cubic Pt phase (Fig. 2c (4)).

Figure 2 Compositions and phases of PtPb NCs and different porous PtPb/Pt NCs. (a) The changes on the Pt/Pb ratio of the PtPb NPs with different etching temperatures. (b) PXRD patterns and (c) enlarged PXRD patterns of PtPb NPs and porous PtPb/Pt NPs collected from the reactions at different etching temperatures. (d) The changes on the Pt/Pb ratio of the PtPb OTs with different etching temperatures. (e) PXRD patterns and (f) enlarged PXRD patterns of PtPb OTs and porous PtPb/Pt OTs collected from the reactions at different etching temperatures.

Similarly, the overall Pt/Pb ratios and phases of PtPb OTs and porous PtPb/Pt OTs underwent gradual changes with the increases of the etching temperature (Fig. 2d–f). According to the ICP-AES and TEM-EDS results (Fig. 2d and Fig. S7b), the overall Pt/Pb ratios of PtPb OTs and porous PtPb/Pt OTs were determined to be about 50.6/49.4, 60.2/39.8, 75.5/24.5, and 95.4/4.6, respectively. The variation tendency of PXRD patterns for porous PtPb/Pt OTs is similar to porous PtPb/Pt NPs (Fig. 2b, c, e, f). In particular, porous Pt₃Pb OTs with coexistence of two phases were also synthesized *via* controlling the etching conditions (Fig. 2e (3) and 2f (3)).

To further analyze the nanostructure of porous PtPb/Pt NCs with different morphologies and compositions, a series of characterization techniques, such as high-resolution TEM (HRTEM), fast Fourier transform (FFT), HAADF-STEM, elemental mapping, and line-scan have been carried out (Fig. 3). Compared with the initial PtPb NPs (Fig. 3a–c), the porosity of porous PtPb/Pt NPs with different compositions can be clearly observed from the HRTEM and HAADF-STEM images (Fig. 3d, e, g, h, j, k). The measured interplanar spacing of 0.212 nm and 0.219 nm shown in Fig. 3a, d, g are consistent with the (110) and (102) facets of PtPb intermetallic structure with hexagonal phase (*P6₃/mmc* (194)), while the displayed interplanar spacing of 0.227 nm matches well with the cubic Pt phase (*Fm-3m* (225)), as shown in Fig. 3g, j. We can see that the elemental distribution of Pt and Pb for

PtPb NPs and porous PtPb/Pt NPs are homogeneous throughout the whole nanoplates (Fig. 3b, e, h, k), as also confirmed by the corresponding line-scans (Fig. 3c, f, i, l). With the increase of etching degree, the relative content of Pb reduces gradually (Fig. 3c, f, i, l), consistent with the ICP-AES and PXRD analyses (Fig. 2a–c). Detailed morphology and structure characterizations of PtPb OTs and different porous PtPb/Pt OTs have also been carried out (Fig. 3m–x). From the HRTEM images of PtPb OTs and porous PtPb/Pt OTs, we can see that the present facet gradually changed from PtPb (101) plane (0.304 nm) to Pt (111) plane (0.227 nm) (Fig. 3m, p, s, v). The elements of Pt and Pb were distributed evenly throughout the OTs (Fig. 3n, q, t, w), which can be also confirmed by their corresponding line-scans (Fig. 3o, r, u, x). Here, porous PtPb/Pt NCs with well-controlled morphology, composition and phase have been created through an oxidative etching strategy. Integrating the advantages of porosity [24,25], modulated composition and phase [44], and the 3D structure, porous PtPb/Pt NCs are highly expected to possess excellent performances, such as EG-G/OR.

For studying the EG-G/OR properties of PtPb NCs and porous PtPb/Pt NCs, the different Pt-Pb NCs were loaded onto the commercial carbon black (C, Vulcan XC-72R). The resulting electrocatalysts were applied for EG-G/OR under acid medium (Figs S8–S15). For comparison, the commercial Pt/C purchased from Johnson Matthey (JM) Corporation was selected as the benchmarked catalyst

Figure 3 Morphological and structural characterizations of PtPb NCs and different porous PtPb/Pt NCs. (a, d, g, j) HRTEM images, (b, e, h, k) HAADF-STEM images and elemental mappings, and (c, f, i, l) corresponding line-scans of (a–c) PtPb NPs, (d–f) porous Pt₃Pb₂ NPs, (g–i) porous Pt₃Pb NPs, and (j–l) porous Pt₂₁Pb NPs, respectively. (m, p, s, v) HRTEM images, (n, q, t, w) HAADF-STEM images and elemental mappings, and (o, r, u, x) corresponding line-scans of (m–o) PtPb OTs, (p–r) porous Pt₃Pb₂ OTs, (s–u) porous Pt₃Pb OTs, and (v–x) porous Pt₂₁Pb OTs, respectively. The insets in (a, d, g, j, m, p, s, v) are their corresponding FFT patterns.

(Fig. S16a, b). Fig. 4a and Fig. S17a display the cyclic voltammograms (CVs) of different electrocatalysts in 0.1 mol L⁻¹ HClO₄ solution. According to the hydrogen adsorption charge calculated from the CVs, the electrochemically active surface areas (ECSAs) of these electrocatalysts were determined to be 56.1, 63.0, 68.3, 74.8, 40.5, 43.4, 47.5, 53.2, and 64.7 m² g⁻¹ for the PtPb NPs/C, porous Pt₃Pb₂ NPs/C, porous Pt₃Pb NPs/C, porous Pt₂₁Pb NPs/C, PtPb OTs/C, porous Pt₃Pb₂ OTs/C, porous Pt₃Pb OTs/C, porous Pt₂₁Pb OTs/C, and Pt/C (Fig. 4a, Fig. S17a and Table S1). The porous Pt₃Pb NPs/C exhibits the largest ECSA (68.3 m² g⁻¹) among all the catalysts except for the porous Pt₂₁Pb NP/C (74.8 m² g⁻¹), which even surpasses the ECSA of Pt/C (64.7 m² g⁻¹), mainly due to the presence of large number of pores and the 2D structure.

EGOR was firstly used to evaluate the electrochemical properties of porous PtPb/Pt NCs/C and PtPb NCs/C as well as the commercial Pt/C. The EGOR measurements were performed in 0.1 mol L⁻¹ HClO₄ solution containing

0.5 mol L⁻¹ EG at room temperature, and the scanning rate of CV measurements was 50 mV s⁻¹. As shown in Fig. 4b and Fig. S17b, all the porous PtPb/Pt NPs/C exhibit larger oxidation peak currents than those of the PtPb NPs/C, and the porous PtPb/Pt OTs/C have the similar situation, indicating the enhanced electrochemical activities of porous Pt-based NCs. With the same composition, the currents of porous PtPb/Pt NPs/C were higher than those of the porous PtPb/Pt OTs/C. Among all the compared electrocatalysts, porous Pt₃Pb NPs/C exhibits the highest oxidation peak current (Fig. 4c and Fig. S17c). To obtain the mass and specific activities of EGOR, the forward currents were normalized to Pt amount and ECSA, respectively. The EGOR mass activity of porous Pt₃Pb NPs/C reaches to 1.19 A mg⁻¹_{Pt}, which is 1.5, 1.2, 2.2, 1.9, 1.7, 1.3, 2.5, and 5.5 times higher than those of the PtPb NPs/C, porous Pt₃Pb₂ NPs/C, porous Pt₂₁Pb NPs/C, PtPb OTs/C, porous Pt₃Pb₂ OTs/C, porous Pt₃Pb OTs/C, porous Pt₂₁Pb OTs/C, and Pt/C, respectively (Table S1), showing the greatest enhancement fac-

Figure 4 EGOR performances of PtPb NCs/C, different porous PtPb/Pt NCs/C and Pt/C. (a) CVs of different electrocatalysts in 0.1 mol L⁻¹ HClO₄ solution. (b) CVs of different electrocatalysts in 0.1 mol L⁻¹ HClO₄ solution containing 0.5 mol L⁻¹ EG. (c) Histogram of maximum oxidation peak currents of different electrocatalysts for EGOR. (d) I_t/I_b ratios of different electrocatalysts for EGOR. (e) CVs of porous Pt₃Pb NPs/C before and after different CV cycles for EGOR. (f) Electrocatalytic durability of different electrocatalysts for EGOR. (g) HAADF-STEM image, (h) elemental mappings, and (i) the corresponding line-scan of porous Pt₃Pb NPs/C after 5,000 CV cycles for EGOR. The inset in (g) is the magnified HAADF-STEM image.

tor of mass activity versus the commercial Pt/C (Fig. S18a). Moreover, the porous Pt₃Pb NPs/C displays the EGOR specific activity of 1.75 mA cm⁻², which is 1.3, 1.1, 2.4, 1.1, 1.1, 2.0, and 5.2 times greater than those of the PtPb NPs/C, porous Pt₃Pb₂ NPs/C, porous Pt₂₁Pb NPs/C, PtPb OTs/C, porous Pt₃Pb₂ OTs/C, porous Pt₂₁Pb OTs/C, and Pt/C, respectively (Table S1), and has higher enhancement factor of specific activity than the commercial Pt/C (Fig. S18b). The unprecedented EGOR mass and specific activities make the porous Pt₃Pb NPs/C the most active electrocatalyst ever achieved in the Pt-based EGOR catalysts reported to date (Table S2).

Due to the complexity of EGOR, various reaction steps will take place [45,46]. Different reaction intermediates, including the carbonyl group, can unavoidably adsorb on

the surface of Pt-based electrocatalysts, leading to the CO poisoning of catalysts [45]. Generally, the ratio of forward current density (I_t) and backward current density (I_b) in the CV measurement is commonly used as the evaluation of the tolerance ability to CO poisoning [47]. As shown in Fig. 4d and Fig. S17d, the porous Pt₃Pb NPs/C exhibits the highest I_t/I_b ratio (1.81) among all the catalysts, and also higher ratio than those of the Pt-based EGOR electrocatalysts reported to date (Table S2), indicating the outstanding tolerance ability to CO poisoning, which is beneficial to the enhanced electrocatalytic stability. This can be ascribed to the key role of Pb in Pt-Pb NCs played in electrocatalysis [47]. X-ray photoelectron spectroscopy (XPS) was used to further analyze the unique electronic structure of Pt-Pb NCs (Fig. S19). The increased binding

energy of Pt 4f and decreased binding energy of Pb 4f clearly suggest that the electron transferred from Pt to Pb in Pt-Pb NCs could be facily occurred, which can be related to the strong electronic interaction between Pt and Pb and then contributing to the electrocatalytic stability.

The EGOR durability of these electrocatalysts was then investigated in details, since the durability can be seen as another significant evaluation criterion of electrocatalytic performance for catalyst [43,48]. To test the EGOR durability of catalysts, CV measurements were applied (Fig. 4e and Fig. S20). The mass activity of porous Pt₃Pb NPs/C for EGOR still reaches 1.00 A mg⁻¹_{Pt} and 0.84 A mg⁻¹_{Pb}, only 16.2% and 29.9% mass activity losses after 5,000 and 20,000 potential cycles, respectively, while the PtPb NPs/C, porous Pt₃Pb OTs/C, PtPb OTs/C, and commercial Pt/C exhibit 20.9%, 23.8%, 30.4%, and 96.8% mass activity losses after 5,000 potential cycles, showing that the porous Pt₃Pb NPs/C is the most stable catalyst among all the studied electrocatalysts (Fig. 4e, f and Fig. S20). These results make the porous Pt₃Pb NPs/C the best EGOR electrocatalyst with excellent tolerance ability to CO poisoning reported to date (Table S2). Further, the morphological and structural characterizations of porous Pt₃Pb NPs/C and commercial Pt/C after 5,000 CV cycles for EGOR were studied in details (Fig. 4g–i, Fig. S21 and Fig. S16c, d). After EGOR durability measurement, the shape, composition, phase, and elemental distribution of porous Pt₃Pb NPs/C had limited changes (Fig. 4g–i and Fig. S21). It is worth mentioning that the porous structure of porous Pt₃Pb NPs/C can be sustained well after durability test, as revealed in Fig. 4g, h and Fig. S21e, f. By the sharp contrast, the Pt nanoparticles on commercial Pt/C became bigger and aggregated after stability test (Fig. S16c, d), confirming the outstanding EGOR durability of the porous Pt₃Pb NPs/C.

In addition, the porous PtPb/Pt NCs/C, PtPb NCs/C, and commercial Pt/C were also studied as the anodic electrocatalysts for GOR in acid medium. The GOR measurements were conducted in 0.1 mol L⁻¹ HClO₄ solution containing 0.5 mol L⁻¹ glycerol with the scanning rate of 50 mV s⁻¹ at room temperature. Fig. 5a and Fig. S22a show the CV curves of different electrocatalysts, where the porous Pt₃Pb NPs/C has the highest current among these nine catalysts. The mass and specific activities of different electrocatalysts for GOR were calculated (Fig. 5b, c, Fig. S22b, c and Table S3). The GOR mass activity of porous Pt₃Pb NPs/C is measured to be 1.00 A mg⁻¹_{Pt}, which is 1.5, 1.3, 1.9, 1.7, 1.6, 1.5, 2.9, and 5.1 times higher than those of the PtPb NPs/C, porous Pt₃Pb₂ NPs/C, porous Pt₂₁Pb NPs/C, PtPb OTs/C, porous

Pt₃Pb₂ OTs/C, porous Pt₃Pb OTs/C, porous Pt₂₁Pb OTs/C, and Pt/C, respectively, demonstrating the highest mass activity among all the investigated electrocatalysts (Fig. 5b and Fig. S22b) and the highest enhancement factor of mass activity *versus* the commercial Pt/C (Fig. S23a). The porous Pt₃Pb NPs/C also exhibits the largest GOR specific activity of 1.46 mA cm⁻², and the order for GOR specific activity of other electrocatalysts is PtPb OTs/C (1.43 mA cm⁻²) > porous Pt₃Pb₂ OTs/C (1.41 mA cm⁻²) > porous Pt₃Pb OTs/C (1.40 mA cm⁻²) > porous Pt₃Pb₂ NPs/C (1.25 mA cm⁻²) > PtPb NPs/C (1.16 mA cm⁻²) > porous Pt₂₁Pb NPs/C (0.71 mA cm⁻²) > porous Pt₂₁Pb OTs/C (0.65 mA cm⁻²) > Pt/C (0.30 mA cm⁻²) (Fig. 5c and Fig. S22c). The porous Pt₃Pb NPs/C also shows the greatest enhancement factor of specific activity *versus* the commercial Pt/C (Fig. S23b). Among all these electrocatalysts, porous Pt₃Pb NPs/C, porous Pt₃Pb₂ NPs/C, porous Pt₃Pb OTs/C, and porous Pt₃Pb₂ OTs/C demonstrate more improved GOR activities than those of the commercial Pt/C, even better than those of PtPb NPs/C

Figure 5 GOR performances of PtPb NCs/C, different porous PtPb/Pt NCs/C and Pt/C. (a) CVs of different electrocatalysts in 0.1 mol L⁻¹ HClO₄ solution containing 0.5 mol L⁻¹ glycerol. Histogram of (b) mass activities and (c) specific activities of different electrocatalysts for GOR. (d) I_p/I_b ratios of different electrocatalysts for GOR. (e) CVs of porous Pt₃Pb NPs/C before and after different CV cycles for GOR. (f) Electrocatalytic durability of different electrocatalysts for GOR.

and PtPb OTs/C. Compared with other porous PtPb/Pt NCs/C, the porous Pt₂₁Pb NPs/C and porous Pt₂₁Pb OTs/C show less enhanced GOR activities than that of the commercial Pt/C, mainly due to their weak alloy effect (Fig. S23). Moreover, as summarized in Fig. 5d and Fig. S22d, porous Pt₃Pb NPs/C displays the largest I_f/I_b ratio (2.27) among these electrocatalysts in GOR, greater than those of PtPb NPs/C (2.08), porous Pt₃Pb OTs/C (2.13), PtPb OTs/C (2.05), commercial Pt/C (1.02), and even higher than those of the reported Pt-based GOR electrocatalysts (Table S4), indicating the superior tolerance to CO poisoning.

As shown in Fig. 5e and Fig. S24, the GOR durability of different electrocatalysts was also studied in details. After 5000 potential cycles, about 34.2% GOR mass activity for the porous Pt₃Pb NPs/C (0.66 A mg⁻¹_{Pt}) can be still maintained (Fig. 5e). While the GOR mass activity losses of other catalysts reach 35.3%, 38.3%, and 46.6% for PtPb NPs/C, porous Pt₃Pb OTs/C, and PtPb OTs/C, respectively (Fig. 5f and Fig. S24a–c). By sharp contrast, only 4.5% GOR mass activity for commercial Pt/C (0.009 A mg⁻¹_{Pt}) can be maintained after durability test (Fig. S24d), which reveal that the porous Pt₃Pb NPs/C is the most stable GOR electrocatalyst among all the investigated catalysts.

The highlights in our work are the largely enhanced EG-G/OR activities and long-term durability of the porous Pt₃Pb NPs compared with other porous PtPb/Pt NPs, different porous PtPb/Pt OTs, PtPb NPs and PtPb OTs as well as the commercial Pt/C. The superior EG-G/OR performances of porous Pt₃Pb NPs likely arise from their highly open 3D structure and the optimized synergistic effect between Pt and Pb. By precisely controlling the etching temperature with the aid of nitric acid, porous PtPb-based NCs with different morphologies, compositions and dimensionalities have been created, resulting in the substantial number of active sites [49] located inside and outside the nanoplates and therefore maximized Pt utilization, much higher than those of PtPb NPs and PtPb OTs. Consequently, the porous Pt₃Pb NPs exhibit much improved EG-G/OR activities than the commercial Pt/C. Furthermore, due to the stable and optimized composition resulting from chemical etching as well as the strong electronic interaction between Pt and Pb atomic orbits, the porous Pt₃Pb NPs demonstrate outstanding tolerance ability to CO poisoning and the excellent durability for EG-G/OR, compared with the PtPb NPs and the PtPb OTs as well as the commercial Pt/C. All these superiorities ensure the porous Pt₃Pb NPs high EG-G/OR performances, even much better than many state-of-art

Pt-based EG-G/OR electrocatalysts reported to date (Table S2 and Table S4).

CONCLUSIONS

To summarize, we have demonstrated a facile chemical etching strategy to create porous PtPb/Pt NPs and porous PtPb/Pt OTs with different compositions. The morphology, composition, and porosity of the porous PtPb/Pt NCs have been readily modulated. The porous Pt₃Pb NPs with 3D structures exhibit superior activity for EGOR (GOR) with about 5.5 (5.1) and 5.2 (4.8) times enhancements on mass activity and specific activity than the commercial Pt/C, respectively, which is also better than those of the PtPb NCs and porous PtPb/Pt NCs with other compositions, making them among the most promising EG-G/OR electrocatalysts to date. Due to the stable composition and the optimized synergistic effect between Pt and Pb, the porous Pt₃Pb NPs exhibit ultra-stable feature after long-term durability with only 29.9% mass activity loss after 20,000 CV cycles in EGOR. The present work will inspire the rational design of high-performance Pt-based NCs with well-controlled structure, composition, and porosity for fuel cells, batteries as well as heterogeneous reactions.

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- 1 Davis ME. Ordered porous materials for emerging applications. *Nature*, 2002, 417: 813–821
- 2 Zhang J, Li CM. Nanoporous metals: fabrication strategies and advanced electrochemical applications in catalysis, sensing and energy systems. *Chem Soc Rev*, 2012, 41: 7016–7031
- 3 Parlett CMA, Wilson K, Lee AF. Hierarchical porous materials: catalytic applications. *Chem Soc Rev*, 2013, 42: 3876–3893
- 4 Slater AG, Cooper AI. Function-led design of new porous materials. *Science*, 2015, 348: aaa8075
- 5 Kitagawa S. Future porous materials. *Acc Chem Res*, 2017, 50: 514–516
- 6 Eddaoudi M, Kim J, Rosi N, *et al.* Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science*, 2002, 295: 469–472
- 7 Li Y, Fu ZY, Su BL. Hierarchically structured porous materials for energy conversion and storage. *Adv Funct Mater*, 2012, 22: 4634–4667
- 8 Valtchev V, Tosheva L. Porous nanosized particles: preparation, properties, and applications. *Chem Rev*, 2013, 113: 6734–6760
- 9 Perego C, Millini R. Porous materials in catalysis: challenges for mesoporous materials. *Chem Soc Rev*, 2013, 42: 3956–3976
- 10 Saint Remi JC, Lauerer A, Chmelik C, *et al.* The role of crystal diversity in understanding mass transfer in nanoporous materials. *Nat Mater*, 2016, 15: 401–406
- 11 Kumar KV, Preuss K, Titirici MM, *et al.* Nanoporous materials for the onboard storage of natural gas. *Chem Rev*, 2017, 117: 1796–

- 1825
- 12 Wei J, Sun Z, Luo W, *et al.* New insight into the synthesis of large-pore ordered mesoporous materials. *J Am Chem Soc*, 2017, 139: 1706–1713
- 13 Braun PV, Wiltzius P. Electrochemical fabrication of 3D micro-periodic porous materials. *Adv Mater*, 2001, 13: 482–485
- 14 Choi M, Cho HS, Srivastava R, *et al.* Amphiphilic organosilane-directed synthesis of crystalline zeolite with tunable mesoporosity. *Nat Mater*, 2006, 5: 718–723
- 15 Fan W, Snyder MA, Kumar S, *et al.* Hierarchical nanofabrication of microporous crystals with ordered mesoporosity. *Nat Mater*, 2008, 7: 984–991
- 16 Zhang J, Bu JT, Chen S, *et al.* Urothermal synthesis of crystalline porous materials. *Angew Chem Int Ed*, 2010, 49: 8876–8879
- 17 Klope A, von Stetten F, Zengerle R, *et al.* Strategies for the fabrication of porous platinum electrodes. *Adv Mater*, 2011, 23: 4976–5008
- 18 Côté AP, Benin AI, Ockwig NW, *et al.* Porous, crystalline, covalent organic frameworks. *Science*, 2005, 310: 1166–1170
- 19 Pérez-Ramírez J, Christensen CH, Egeblad K, *et al.* Hierarchical zeolites: enhanced utilisation of microporous crystals in catalysis by advances in materials design. *Chem Soc Rev*, 2008, 37: 2530
- 20 Wu D, Xu F, Sun B, *et al.* Design and preparation of porous polymers. *Chem Rev*, 2012, 112: 3959–4015
- 21 Furukawa H, Cordova KE, O’Keeffe M, *et al.* The chemistry and applications of metal-organic frameworks. *Science*, 2013, 341: 1230444
- 22 Lang X, Hirata A, Fujita T, *et al.* Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors. *Nat Nanotech*, 2011, 6: 232–236
- 23 He W, Jiang C, Wang J, *et al.* High-rate oxygen electroreduction over graphitic-n species exposed on 3D hierarchically porous nitrogen-doped carbons. *Angew Chem Int Ed*, 2014, 53: 9503–9507
- 24 Xu Y, Zhang B. Recent advances in porous Pt-based nanostructures: synthesis and electrochemical applications. *Chem Soc Rev*, 2014, 43: 2439–2450
- 25 Zhu C, Du D, Eychmüller A, *et al.* Engineering ordered and nonordered porous noble metal nanostructures: synthesis, assembly, and their applications in electrochemistry. *Chem Rev*, 2015, 115: 8896–8943
- 26 Bing Y, Liu H, Zhang L, *et al.* Nanostructured Pt-alloy electrocatalysts for PEM fuel cell oxygen reduction reaction. *Chem Soc Rev*, 2010, 39: 2184–2202
- 27 Chen C, Kang Y, Huo Z, *et al.* Highly crystalline multimetallic nanoframes with three-dimensional electrocatalytic surfaces. *Science*, 2014, 343: 1339–1343
- 28 Xiong Y, Xia Y. Shape-controlled synthesis of metal nanostructures: the case of palladium. *Adv Mater*, 2007, 19: 3385–3391
- 29 Malgras V, Atae-Esfahani H, Wang H, *et al.* Nanoarchitectures for mesoporous metals. *Adv Mater*, 2016, 28: 993–1010
- 30 Maksimuk S, Yang S, Peng Z, *et al.* Synthesis and characterization of ordered intermetallic PtPb nanorods. *J Am Chem Soc*, 2007, 129: 8684–8685
- 31 Kang Y, Pyo JB, Ye X, *et al.* Synthesis, shape control, and methanol electro-oxidation properties of Pt–Zn alloy and Pt₃Zn intermetallic nanocrystals. *ACS Nano*, 2012, 6: 5642–5647
- 32 Zhang D, Wu F, Peng M, *et al.* One-step, facile and ultrafast synthesis of phase- and size-controlled Pt–Bi intermetallic nanocatalysts through continuous-flow microfluidics. *J Am Chem Soc*, 2015, 137: 6263–6269
- 33 Cui Z, Chen H, Zhao M, *et al.* Synthesis of structurally ordered Pt₃Ti and Pt₃V nanoparticles as methanol oxidation catalysts. *J Am Chem Soc*, 2014, 136: 10206–10209
- 34 Cui Z, Chen H, Zhou W, *et al.* Structurally ordered Pt₃Cr as oxygen reduction electrocatalyst: ordering control and origin of enhanced stability. *Chem Mater*, 2015, 27: 7538–7545
- 35 Niu Z, Becknell N, Yu Y, *et al.* Anisotropic phase segregation and migration of Pt in nanocrystals en route to nanoframe catalysts. *Nat Mater*, 2016, 15: 1188–1194
- 36 Wang C, Zhang L, Yang H, *et al.* High-indexed Pt₃Ni alloy tetra-hexahedral nanoframes evolved through preferential CO etching. *Nano Lett*, 2017, 17: 2204–2210
- 37 Wang L, Yamauchi Y. Metallic nanocages: synthesis of bimetallic Pt–Pd hollow nanoparticles with dendritic shells by selective chemical etching. *J Am Chem Soc*, 2013, 135: 16762–16765
- 38 He DS, He D, Wang J, *et al.* Ultrathin icosahedral Pt-enriched nanocage with excellent oxygen reduction reaction activity. *J Am Chem Soc*, 2016, 138: 1494–1497
- 39 Xiao C, Wang LL, Maligal-Ganesh RV, *et al.* Intermetallic NaAu₂ as a heterogeneous catalyst for low-temperature CO oxidation. *J Am Chem Soc*, 2013, 135: 9592–9595
- 40 Kim D, Resasco J, Yu Y, *et al.* Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold–copper bimetallic nanoparticles. *Nat Commun*, 2014, 5: 4948
- 41 Cui Z, Li L, Manthiram A, *et al.* Enhanced cycling stability of hybrid Li–air batteries enabled by ordered Pd₃Fe intermetallic electrocatalyst. *J Am Chem Soc*, 2015, 137: 7278–7281
- 42 Bu L, Zhang N, Guo S, *et al.* Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis. *Science*, 2016, 354: 1410–1414
- 43 Bu L, Shao Q, E B, *et al.* PtPb/PtNi intermetallic core/atomic layer shell octahedra for efficient oxygen reduction electrocatalysis. *J Am Chem Soc*, 2017, 139: 9576–9582
- 44 Yao Y, He DS, Lin Y, *et al.* Modulating fcc and hcp ruthenium on the surface of palladium-copper alloy through tunable lattice mismatch. *Angew Chem Int Ed*, 2016, 55: 5501–5505
- 45 Bambagioni V, Bianchini C, Marchionni A, *et al.* Pd and Pt–Ru anode electrocatalysts supported on multi-walled carbon nanotubes and their use in passive and active direct alcohol fuel cells with an anion-exchange membrane (alcohol=ethanol, ethanol, glycerol). *J Power Sources*, 2009, 190: 241–251
- 46 Hong W, Shang C, Wang J, *et al.* Bimetallic PdPt nanowire networks with enhanced electrocatalytic activity for ethylene glycol and glycerol oxidation. *Energy Environ Sci*, 2015, 8: 2910–2915
- 47 Yang S, Peng Z, Yang H. Platinum lead nanostructures: formation, phase behavior, and electrocatalytic properties. *Adv Funct Mater*, 2008, 18: 2745–2753
- 48 Xia BY, Ng WT, Wu HB, *et al.* Self-supported interconnected Pt nanoassemblies as highly stable electrocatalysts for low-temperature fuel cells. *Angew Chem Int Ed*, 2012, 51: 7213–7216
- 49 Wu Y, Wang D, Niu Z, *et al.* A strategy for designing a concave Pt–Ni alloy through controllable chemical etching. *Angew Chem Int Ed*, 2012, 51: 12524–12528

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Author contributions Huang X conceived and supervised the research. Huang X and Bu L designed the experiments. Huang X, Bu L, and Shao Q performed most of the experiments and data analysis. Bu L

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Supplementary information Supplementary figures and tables are available in the online version of the paper.

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高度多孔的铂铅纳米晶用作高效的多元醇电氧化催化剂

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摘要 本论文采用简便的湿化学刻蚀法首次成功合成了具有明确形貌、组分和多孔性的PtPb/Pt多孔纳米晶。由于具有高度开放的三维立体结构和合金效应, PtPb/Pt多孔纳米晶的多元醇电催化性能良好。其中, 最优化的Pt₃Pb多孔纳米片在乙二醇氧化反应中的催化活性为1.75 mA cm⁻²和1.19 A mg⁻¹_{Pt}, 在丙三醇氧化反应中的催化活性为1.46 mA cm⁻²和1.00 A mg⁻¹_{Pt}, 均远远高于商业Pt/C催化剂的催化活性。另外, Pt₃Pb多孔纳米片在乙二醇和丙三醇氧化反应中均表现出优异的电催化稳定性, 分别经过20000个循环和5000个循环后, 其催化活性没有发生明显衰减且纳米结构没有发生改变。因此, Pt₃Pb多孔纳米片可作为一种非常有发展前景的铂基电催化剂应用于多元醇燃料电池及相关领域中。