Surface composition-tunable octahedral PtCu nanoalloys advance the electrocatalytic performance on methanol and ethanol oxidation

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ABSTRACT The synthesis of surface composition-tunable Pt-based octahedral nanoalloys is key to unravel the structure-property relationship in fuel cells. Herein, we report a facile route to prepare composition-tunable PtCu octahedral nanoalloys by using halogen ions (Br^- or/and I^-) as composition modulators. Among these PtCu octahedral nanoalloys, $\text{Pt}_{59}\text{Cu}_{41}$ octahedron exhibits the highest catalytic activity and durability in alkaline solution. The specific activity/mass activity of $\text{Pt}_{59}\text{Cu}_{41}$ octahedron is $20.25 \text{ mA cm}^{-2}/3.24 \text{ A mg}^{-1}_{\text{Pt}}$, which is 6.64/5.3 times higher than commercial Pt black in $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$, respectively. In the case of using ethanol (0.5 mol L^{-1}) as fuel source, $\text{Pt}_{59}\text{Cu}_{41}$ octahedron shows much better catalytic activity, that is $34.84 \text{ mA cm}^{-2}/5.58 \text{ A mg}^{-1}_{\text{Pt}}$ for specific activity/mass activity, which is 9.16/7.34 times higher than commercial Pt black, respectively. *In situ* Fourier transform infrared spectroscopy is employed to detect the intermediate species and products for methanol/ethanol oxidation reaction and a plausible mechanism is proposed to explain the improved activity and durability of $\text{Pt}_{59}\text{Cu}_{41}$ octahedron toward methanol/ethanol oxidation in alkaline medium.

Keywords: octahedral PtCu alloy, composition and strain-tunable, *in situ* FTIR, direct methanol/ethanol fuel cells

INTRODUCTION

Fuel cells have attracted tremendous attention due to their high energy densities and environment-friendly technique. Among them, alcohol fuel cells (AFCs) are widely concerned by different research groups around the world [1–7]. Pt-based nanomaterials are commonly used

as electrode catalysts in cathode and anode of fuel cells. However, the commercialization of AFCs suffers from not only the high cost of Pt materials, but also the poisoning of Pt-based electrodes caused by CO-like intermediate. Great efforts have been devoted to addressing these issues and many promising progresses have been achieved. One of the most interesting and efficient strategies is to synthesize Pt-M nanoalloys by using cheap transition metal atoms (such as Cu, Co, Ru, and Pb). The introduction of those metal atoms into Pt crystal could significantly improve the durability of Pt materials because of the effective ligand effect and/or synergetic effect [8–17]. For example, Wang's group [18] reported that PtCu nanowires can respectively boost the mass activity of methanol/ethanol oxidation to $1.74/2.1 \text{ A mg}^{-1}_{\text{Pt}}$, together with enhanced durability compared with commercial Pt black in potassium hydroxide (KOH) solution. Xie's group [19] demonstrated enhanced durability and mass activity of $0.515 \text{ A mg}^{-1}_{\text{Pt}}$ on octahedral PtCo alloy compared with commercial Pt/C in sulfuric acid medium.

It is well-known that the shape and surface composition of Pt-based nanomaterials are greatly related to their catalytic performances, such as activity and durability [20–29]. Therefore, the shape and composition tunable synthesis of Pt-based nanocrystals is key toward optimizing the electrocatalytic performances of alcohols oxidation. Up to now, a variety of synthetic methods have been developed to achieve this goal, by employing surfactants (e.g. oleylamine, oleic acid, poly(ethyleneoxide)-*b*-poly(methyl methacrylate)), small molecules (e.g., amines and carbon monoxide), and halogen anions as

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structure-directing agents [30–39]. For instance, Dong's group [40] reported the shape-controlled synthesis of PtRu nanoalloys (nanowire, nanorod and nanocube) by changing the surfactants. Sun's group [41] and Wang's group [42] respectively used KI and NaI as structure-directing agent to achieve hierarchical Pt-Cu superstructures. However, the chemical composition largely depends on the feeding ratio between Pt precursors and other transition metal precursors [43–46]. Dimitrov *et al.* [47] recently have reported the synthesis of $\text{Pt}_x\text{Cu}_{100-x}$ nanocubes by changing the amount of Pt/Cu precursors. Very limited reports have focused on the synthesis of composition tunable Pt-M nanoalloys with the same morphology by changing the structure-directing agents. For example, the {111} faceted octahedral Pt nanoparticles show excellent electrocatalytic activity in fuel cells [48–51], which can be attributed to the specific geometry carrying abundant catalytic active sites (e.g., corner, edge and facet). Therefore, the preparation of composition-tunable Pt-based octahedral nanoalloys is a key step, yet challenging, for the applications in fuel cells.

Herein, we report a solvothermal method to synthesize surface composition tunable PtCu octahedrons by using sodium halides (NaBr and NaI) as structure-directing agents. The octahedral PtCu nanoalloys exhibit remarkable electrocatalytic activity and stability toward the electrocatalytic oxidation of methanol/ethanol in alkaline medium. Moreover, *in situ* Fourier transform infrared spectroscopy (FTIR) was employed to elucidate the intermediates on PtCu nanoalloys during the electrocatalytic reaction in alkaline medium for the first time. Finally, a plausible mechanism is proposed to explain the improved activity and durability of PtCu octahedrons toward methanol/ethanol oxidation in alkaline medium.

EXPERIMENTAL SECTION

Materials

NaI (A.R.), NaBr (A.R.), $\text{C}_2\text{H}_5\text{OH}$ (99.9%), CH_3OH (99.5%), KOH (A.R.) and *N,N*-dimethylformamide (DMF, 99.8%) were obtained from Aladdin. Pd black, Pt black, copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 97%) and platinum(II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 97%) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification.

Synthesis of PtCu octahedral nanocrystals

For $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys, 33 mg NaI, 46 mg NaBr (molar ratio of $\text{I}^-/\text{Br}^-=1:2$) were dissolved in 8 mL *N,N*-dimethylformamide containing 0.03 mmol $\text{Pt}(\text{acac})_2$,

0.06 mmol $\text{Cu}(\text{acac})_2$ and 30 mg polyvinyl pyrrolidone, and then the solution was placed in a Teflon-lined stainless-steel autoclave and kept at 150°C for 8 h. The dark products were washed with ethanol through centrifugation at 10,000 rpm for 10 min for several times. Finally, the product was kept in ethanol. The $\text{Pt}_{63}\text{Cu}_{37}$ (49.5 mg NaI, 35 mg NaBr (molar ratio of $\text{I}^-/\text{Br}^-=1:1$)), $\text{Pt}_{49}\text{Cu}_{51}$ (68.5 mg NaBr) and $\text{Pt}_{45}\text{Cu}_{55}$ (99.2 mg NaI) alloyed octahedrons were synthesized using the same process as that of $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys except for the deference of sodium halide. Contents of Pt and Cu in PtCu nanooctahedra were obtained *via* inductively coupled plasma optical emission spectrometer (ICP-OES) (Table S1).

Measurements of electrocatalytic performance

Electrocatalytic tests were performed by a conventional three-electrode cell equipped with salt bridge using a CHI 760E electrochemical analyzer (CHI Instruments, Shanghai, Chenghua Co., Ltd.) at room temperature. The ultrapure water (18.25 MΩ cm) was used as solvent and purified through a Milli-Q Lab system (Nihon Millipore Ltd.). The glassy carbon (GC, $\Phi=5$ mm) was used as the working electrode. Before the electrochemical test, the alumina powder with size of 0.05 μm was used to polish the GC electrode. The suspension of PtCu nanocrystals was spread on the polished GC electrode, and before the electrode was nearly dried, 1.5 μL of 1.0 wt.% Nafion solution was spread on the electrode surface. A platinum foil and Ag/AgCl electrode were utilized as the counter and reference electrode, respectively. The cyclic voltammograms (CVs) were recorded in N_2 -saturated 0.1 mol L⁻¹ KOH solution or 0.5 mol L⁻¹ KOH + 0.5 mol L⁻¹ methanol/ethanol solution, scanned from -0.8 to 0.2 V at a rate of 50 mV s⁻¹.

RESULTS AND DISCUSSION

Structure characterizations

Fig. 1a–e are the transmission electron microscopy (TEM) images and composition diagram of octahedral $\text{Pt}_{63}\text{Cu}_{37}$, $\text{Pt}_{59}\text{Cu}_{41}$, $\text{Pt}_{49}\text{Cu}_{51}$ and $\text{Pt}_{45}\text{Cu}_{55}$ nanoalloys synthesized by tuning the amount of NaI and/or NaBr while keeping other synthetic conditions the same. From Fig. 1a–d, we can see these PtCu nanocrystals are octahedral. The size of these PtCu nanocrystals is uniform, around 14 nm. The crystal phase of these PtCu octahedrons was determined by X-ray powder diffraction (XRD). Fig. 1f displays that there are four typical face-centered cubic (fcc) structure peaks which belongs to (111), (200), (220)

Figure 1 TEM images of (a) Pt₆₃Cu₃₇, (b) Pt₅₉Cu₄₁, (c) Pt₄₉Cu₅₁ and (d) Pt₄₅Cu₅₅. (e) Composition information on Pt and Cu for PtCu nanoalloys. (f) XRD patterns of the PtCu nanoalloys with different compositions.

and (311) crystal facets (JCPDS-04-0836 and JCPDS-65-2868). And these peaks shift to higher angles as the Cu content increases, which is caused by the incorporation of smaller Cu atoms into the lattice of Pt to form alloy structure and in accordance with Vegard's law [41–42,44–45]. It leads to the lattice contraction of PtCu nanoalloys associated with surface strain, which will enhance the catalytic performances of metal nanocrystals (Table 1)

[52–55]. The lattice fringes of Pt₅₉Cu₄₁ nanocrystals are clearly shown in Fig. 2a, b, with a lattice spacing of 0.216 nm, showing that the nanocrystals are bounded by {111} facets. The scanning TEM (STEM) image in Fig. 3a also indicates the PtCu nanocrystals are octahedral. Elemental mapping analysis (Fig. 3b–d) shows the Pt and Cu atoms have a uniform distribution in the nanocrystals, which also implies that the octahedral PtCu nanocrystals

Table 1 XRD results of standard Pt crystal and as-prepared PtCu octahedral crystals

Crystal	2θ ($^{\circ}$)(111)	Lattice parameter ($\text{\AA}^{-1}$)	Strain (%)
Pt-crystal	39.754	0.2205	/
Pt ₆₃ Cu ₃₇	40.471	0.2243	1.7
Pt ₅₉ Cu ₄₁	40.666	0.2253	2.2
Pt ₄₉ Cu ₅₁	41.084	0.2275	3.2
Pt ₄₅ Cu ₅₅	41.101	0.2277	3.3

have alloy structure.

As a sensitive technology for measuring the surface of materials, X-Ray photoelectron spectroscopy (XPS) is widely utilized to analyze the electronic structure and surface composition of substances within 2.0 nm. The two peaks centered at 71.5 and 74.8 eV for the Pt₅₉Cu₄₁ sample can be identified for the Pt 4f_{7/2} and Pt 4f_{5/2} (Fig. 4a). The binding energy for Pt 4f in the Pt₅₉Cu₄₁ sample has a positive shift, around 0.3 eV, compared with pure Pt (Pt 4f_{7/2}: 71.2 eV and Pt 4f_{5/2}: 74.5 eV). This implies that the d-band center of Pt has a downshift due to the introduced Cu atoms [11]. The binding energies of Cu 2p_{3/2} and Cu 2p_{1/2} are located at 932.1 and 952.1 eV for the Pt₅₉Cu₄₁ sample (Fig. 4b), which negatively shift to a lower value compared with pure Cu (Cu 2p_{3/2}: 932.5 eV, and Cu 2p_{1/2}: 952.5 eV). The analysis results of XPS demonstrate that Pt and Cu atoms coexist in nano surface and these exotic atoms have a strong electron interaction, which will build the synergistic active sites and improve the activity and durability of electrocatalysts [11,53,56].

Electrochemical measurements

The electrocatalytic performances of PtCu nanoalloys were investigated in alkaline solution with commercial Pt black as a contrast. The PtCu octahedral nanoalloys displayed a composition-dependent electrocatalytic perfor-

mance (Fig. S1 and Fig. 5).

The specific activity (SA) that stands for intrinsic electrocatalytic capacity of an electrocatalyst is generally accepted to compare the electrocatalytic activities of catalysts with different surface compositions. For methanol oxidation, the SA of commercial Pd black, commercial Pt black, Pt₆₃Cu₃₇, Pt₅₉Cu₄₁, Pt₄₉Cu₅₁ and Pt₄₅Cu₅₅ nanoalloys is 3.21, 3.05, 17.05, 20.25, 9.4 and 8.59 mA cm⁻², respectively (Fig. 5a, b and Fig. S3b). The Pt₅₉Cu₄₁ nanoalloys exhibit the best SA, 6.31/6.64 times higher than commercial Pd/Pt black. Similarly, Pt₅₉Cu₄₁ nanoalloys exhibit the best mass activity (MA) among these samples (Figs S2a and S3c). The MA of Pt₅₉Cu₄₁ nanoalloys is 3.24 A mg⁻¹_{Pt}, 5.7/5.3 times higher than that of commercial Pd black (0.57 A mg⁻¹_{Pd})/Pt black (0.61 A mg⁻¹_{Pt}). For ethanol oxidation (Fig. 5c, d, Figs S2b and S3e, f), the SA/MA of Pt₆₃Cu₃₇, Pt₅₉Cu₄₁, Pt₄₉Cu₅₁, Pt₄₅Cu₅₅ nanoalloys, commercial Pd black and commercial Pt black is 33.49/5.25, 34.84/5.58, 20.3/3.14, 17.42/2.67, 5.53/0.99 and 3.80/0.76 mA cm⁻²/A mg⁻¹_{Pt}, respectively. Among them, the Pt₅₉Cu₄₁ nanoalloys display the best SA/MA, 6.30/5.63 and 9.16/7.34 times higher than commercial Pd black and Pt black, respectively. Meanwhile, the onset potential of methanol/ethanol oxidation (Fig. 5a, c, inset) shows that the reaction dynamics of Pt₅₉Cu₄₁ octahedrons is much faster than that of commercial Pt black, which results in much better catalytic activity of Pt₅₉Cu₄₁ octahedral nanoalloys than that of commercial Pt black. The current-time (*i-t*) tests show that the durability of PtCu nanoalloys is better than that of Pt/Pd black for both methanol and ethanol electrooxidation (Fig. 5e, f and Fig. S3d, S3g). It is worth noting that the durability of PtCu nanoalloys for methanol oxidation is obviously better than that for ethanol oxidation. After 3600 s, for methanol/ethanol oxidation, the remaining current density of Pt₄₉Cu₅₁, Pt₄₅Cu₅₅, Pt₆₃Cu₃₇ and Pt₅₉Cu₄₁

Figure 2 High resolution TEM (HRTEM) images of Pt₅₉Cu₄₁ nanoalloys with different magnifications.

Figure 3 (a) High angle annular dark field-STEM (HAADF-STEM) image, (b) elemental maps of Pt (yellow), (c) Cu (red), and (d) overlap (Pt and Cu) of $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys.

nanoalloys are 1.95, 1.86, 2.15 and 2.44 mA cm^{-2} , while that of Pd/Pt black is $0.033/0.46 \text{ mA cm}^{-2}$. And the $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys display the best durability. We further utilized accelerated durability tests (ADT) to confirm the stability of $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys and Pt black in 0.1 mol L^{-1} KOH condition between -0.5 and 0 V at 100 mV s^{-1} . After 2000 cycles (Fig. 6a, b), the electrochemically active surface areas (ECSA) of $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys and Pt black only decrease by 1.2% and

17.25%, respectively, relative to initial ECSA, which also indicates the $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys have a better durability than commercial Pt black. The regeneration capacity of catalyst has also been generally used to evaluate the performance of catalyst. As shown in Fig. 6c–f, for both methanol and ethanol oxidation, the SA of $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys has a very small decrease, below 4%, while the SA of Pt black has an obvious decrease, beyond 15% (for methanol) and 33% (for ethanol). These results exhibit that the $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys have better regeneration capacity than commercial Pt black. Furthermore, the MA of $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys increases to $5.12/7.30 \text{ A mg}^{-1}_{\text{Pt}}$ when tested in 1.0 mol L^{-1} methanol/ethanol solution (Fig. S4). It is worth pointing out that these values are competitive compared with previous reports (Tables S2 and S3) [43,44,57–63].

In situ FTIR spectra of methanol/ethanol oxidation

In order to clarify the reasons why the octahedral $\text{Pt}_{59}\text{Cu}_{41}$ alloys have better durability than Pt black and why the durability of octahedral $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys in methanol oxidation is much better than that in ethanol oxidation, we performed *in situ* FTIR characterizations of octahedral $\text{Pt}_{59}\text{Cu}_{41}$ alloys and Pt black in 0.5 mol L^{-1} KOH+ 0.5 mol L^{-1} CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$ solution. The test potential ranges from -0.8 to 0.2 V with a 0.1 V interval. For methanol oxidation, as shown in Fig. 7a, b and Table 2, no carbon monoxide peak is observed, which agrees with previous reports, namely, alcohol oxidation in an alkaline solution has almost no carbon monoxide poisoning intermediate (generally observed at around 2050 cm^{-1}) [64]. The peaks around 1380 and 1590 cm^{-1} are attributed to formate [65]. Two peaks around 1380 cm^{-1} are observed on Pt black from -0.5 to -0.3 V , which are the typical peaks of formate (Fig. 7a); however, this phenomenon is not observed on octahedral $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys (Fig. 7b), and a strong peak of carbonate ap-

Figure 4 XPS spectra of Pt 4f (a) and Cu 2p (b) of $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys.

Figure 5 (a) CV curves of specific activity, (b) columns of specific activity and mass activity, (e) i - t curves (tested at -0.3 V for 3600 s) for catalysts in $0.5 \text{ mol L}^{-1} \text{ KOH} + 0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$. (c) Specific activity curves, (d) columns of specific activity and mass activity, (f) i - t curves (tested at -0.3 V for 3600 s) for catalysts in $0.5 \text{ mol L}^{-1} \text{ KOH} + 0.5 \text{ mol L}^{-1} \text{ C}_2\text{H}_5\text{OH}$ (insets in a and c are linear scanning curves of $\text{Pt}_{59}\text{Cu}_{41}$ and Pt black).

peaks at -0.6 V, which implies that carbonate is directly formed on octahedral $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys. Peaks around 2340 cm^{-1} belong to carbon dioxide [66], and Pt black has a stronger carbon dioxide peak than octahedral $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys, which indicates carbon dioxides are strongly adsorbed on Pt black and occupy the catalytic active sites, leading to less activity and durability than octahedral

$\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys. Another interesting phenomenon is, with the increase of potential, the peaks of carbon dioxide are much stronger on Pt black than that on octahedral $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys. However, the peaks of carbonate on Pt black are much weaker than that on octahedral $\text{Pt}_{59}\text{Cu}_{41}$ nanoalloys. These phenomena imply that the carbon dioxide adsorbs more strongly on the surface of Pt

Figure 6 CVs of Pt₅₉Cu₄₁ nanoalloys (a) and commercial Pt black (b) before and after ADTs at a rate of 100 mV s⁻¹. CVs of Pt₅₉Cu₄₁ nanoalloys in 0.5 mol L⁻¹ KOH + 0.5 mol L⁻¹ CH₃OH (c)/C₂H₅OH (d) before and after *i-t* test. CVs of Pt black in 0.5 mol L⁻¹ KOH + 0.5 mol L⁻¹ CH₃OH (e)/C₂H₅OH (f) before and after *i-t* test.

black and is harder to convert to carbonate. While the carbon dioxide adsorbs weakly on the surface of octahedral Pt₅₉Cu₄₁ nanoalloys and is more easily converted to carbonate, thus releasing the catalytic active sites and having higher energy conversion efficiency. On the other hand, water consumption bands are in the range of 2500–3000 and 1700–2000 cm⁻¹ (Fig. 7a, b), the intensities of water consumption bands on octahedral Pt₅₉Cu₄₁ nanoalloys are obviously higher than Pt black, indicating the better ability of Pt₅₉Cu₄₁ nanoalloys in activating water than Pt black, producing more reactive oxygen species

and resulting in much higher catalytic activity.

As for ethanol electrooxidation (Fig. 7c, d and Table 2), the symmetric and antisymmetric stretching vibrations of acetate anion appeared at around 1420 and 1550 cm⁻¹, respectively. The intensities of the two peaks are almost the same, generally accepted as the standard peak of acetate [67]. At -0.7 V, We can observe the two peaks of acetic acid and water consumption bands on octahedral Pt₅₉Cu₄₁ nanoalloys, but not on Pt black, indicating that the octahedral Pt₅₉Cu₄₁ nanoalloys can activate water and ethanol more easily, leading to better

Figure 7 *In situ* FTIR spectra of commercial Pt black (a) and Pt₅₉Cu₄₁ nanoalloy (b) in 0.5 mol L⁻¹ KOH + 0.5 mol L⁻¹ CH₃OH. *In situ* FTIR spectra of Pt black (c) and Pt₅₉Cu₄₁ nanoalloy (d) in 0.5 mol L⁻¹ KOH + 0.5 mol L⁻¹ C₂H₅OH (the range of test is between -0.8 and 0.2 V, and each step is 0.1 V).

Table 2 Assignments of the *in situ* FTIR spectrum of methanol/ethanol oxidation reaction

Wavenumbers (cm ⁻¹)	Peak assignment
2340	CO ₂ symmetric stretching vibration
1420 and 1550	Symmetric and asymmetric C-O bonds stretching vibration of acetate ions
1380 and 1590	Symmetric and asymmetric C-O bonds stretching vibration of formate
2500–3000	O-H stretching absorption
1700–2000	O-H stretching absorption
1380	CO ₃ ²⁻

catalytic activity. In addition, the peaks of acetic acid on octahedral Pt₅₉Cu₄₁ nanoalloys are weaker than Pt black from 0 to 0.2 V, because acetate species are CO-like intermediates in ethanol oxidation that would poison the electrocatalyst, and result in the durability decrease. At the beginning from 0 V, the peaks of carbon dioxide are detected on octahedral Pt₅₉Cu₄₁ nanoalloys, but cannot be observed on Pt black, indicating that the C-C bonds of ethanol are more easily broken on octahedral Pt₅₉Cu₄₁ nanoalloys than Pt black, resulting in more energy release and better activity. Compared with methanol oxidation, ethanol oxidation produces less carbon dioxide, which means the most C-C carbon bonds are not fully broken,

forming a lot of carboxylate species which are toxic species for electrocatalyst (Reactions 1, 2) [67,68].

Compared with ethanol oxidation (Reaction 3), methanol is prone to completely oxidized to CO₂ and only forms a small amount of carboxylate (Reaction 4), and thus the durability on octahedral Pt₅₉Cu₄₁ nanoalloys toward methanol oxidation is much better than that toward ethanol oxidation [67].

CONCLUSIONS

In summary, a series of composition-tunable PtCu octahedral nanoalloys were synthesized by using sodium halides (NaBr or/and NaI) as structure-directing agents. The as-prepared PtCu octahedral nanoalloys display composition-dependent catalytic performances toward methanol and ethanol oxidation. Taking advantages of the ligand effect, synergetic effect and strain effect, specific activity/mass activity on Pt₅₉Cu₄₁ octahedron can be 31.9 mA cm⁻²/5.12 A mg⁻¹_{Pt} toward methanol oxidation;

45.62 mA cm⁻²/7.3 A mg⁻¹_{Pt} toward ethanol oxidation, in 1.0 mol L⁻¹ methanol/ethanol solution, respectively. These values are much higher than that of commercial Pt/Pd black. The *in situ* FTIR spectroscopy indicated that the Pt₅₉Cu₄₁ octahedral nanoalloys show better capacity to activate water and methanol/ethanol, and as a result, less CO-like poisoning intermediates will be adsorbed on the surfaces of Pt₅₉Cu₄₁ octahedral nanoalloy, compared with commercial Pt black. Moreover, Pt₅₉Cu₄₁ octahedral nanoalloys are able to break C–C bonds of ethanol more easily than commercial Pt black. Our studies not only offer a simple route for the preparation of composition-tunable PtCu octahedral nanoalloys, but also give insights into the structural evidences in terms of activity and durability for both methanol and ethanol electrooxidation in alkaline medium.

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- Mao J, Chen W, He D, *et al.* Design of ultrathin Pt-Mo-Ni nanowire catalysts for ethanol electrooxidation. *Sci Adv*, 2017, 3: e1603068
- Huang W, Wang H, Zhou J, *et al.* Highly active and durable methanol oxidation electrocatalyst based on the synergy of platinum-nickel hydroxide-graphene. *Nat Commun*, 2015, 6: 10035
- Bu L, Shao Q, Huang X. Highly porous Pt-Pb nanostructures as active and ultrastable catalysts for polyhydric alcohol electro-oxidations. *Sci China Mater*, 2019, 62: 341–350
- Gamler JTL, Ashberry HM, Skrabalak SE, *et al.* Random alloyed versus intermetallic nanoparticles: a comparison of electrocatalytic performance. *Adv Mater*, 2018, 30: 1801563
- Zhang Y, Zhang J, Chen Z, *et al.* One-step synthesis of the PdPt bimetallic nanodendrites with controllable composition for methanol oxidation reaction. *Sci China Mater*, 2018, 61: 697–706
- Fan J, Qi K, Zhang L, *et al.* Engineering Pt/Pd interfacial electronic structures for highly efficient hydrogen evolution and alcohol oxidation. *ACS Appl Mater Interfaces*, 2017, 9: 18008–18014
- Liu H, Liu K, Zhong P, *et al.* Ultrathin Pt–Ag alloy nanotubes with regular nanopores for enhanced electrocatalytic activity. *Chem Mater*, 2018, 30: 7744–7751
- Gao D, Li S, Song G, *et al.* One-pot synthesis of Pt–Cu bimetallic nanocrystals with different structures and their enhanced electrocatalytic properties. *Nano Res*, 2018, 11: 2612–2624
- Xia T, Liu J, Wang S, *et al.* Nanomagnetic CoPt truncated octahedrons: facile synthesis, superior electrocatalytic activity and stability for methanol oxidation. *Sci China Mater*, 2017, 60: 57–67
- Song P, Cui X, Shao Q, *et al.* Networked Pt–Sn nanowires as efficient catalysts for alcohol electrooxidation. *J Mater Chem A*, 2017, 5: 24626–24630
- Fu QQ, Li HH, Ma SY, *et al.* A mixed-solvent route to unique PtAuCu ternary nanotubes templated from Cu nanowires as efficient dual electrocatalysts. *Sci China Mater*, 2016, 59: 112–121
- Du H, Luo S, Wang K, *et al.* High-quality and deeply excavated Pt₃Co nanocubes as efficient catalysts for liquid fuel electro-oxidation. *Chem Mater*, 2017, 29: 9613–9617
- Tao Z, Chen W, Yang J, *et al.* Ultrathin yet transferrable Pt- or PtRu-decorated graphene films as efficient electrocatalyst for methanol oxidation reaction. *Sci China Mater*, 2019, 62: 273–282
- Huang L, Han Y, Zhang X, *et al.* One-step synthesis of ultrathin Pt_xPb nerve-like nanowires as robust catalysts for enhanced methanol electrooxidation. *Nanoscale*, 2017, 9: 201–207
- Sun Y, Liang Y, Luo M, *et al.* Defects and interfaces on PtPb nanoplates boost fuel cell electrocatalysis. *Small*, 2018, 14: 1702259
- Chen Q, Yang Y, Cao Z, *et al.* Excavated cubic platinum-tin alloy nanocrystals constructed from ultrathin nanosheets with enhanced electrocatalytic activity. *Angew Chem Int Ed*, 2016, 55: 9021–9025
- Zhao Y, Liu J, Liu C, *et al.* Amorphous CuPt alloy nanotubes induced by Na₂S₂O₃ as efficient catalysts for the methanol oxidation reaction. *ACS Catal*, 2016, 6: 4127–4134
- Hong W, Wang J, Wang E. Facile synthesis of PtCu nanowires with enhanced electrocatalytic activity. *Nano Res*, 2015, 8: 2308–2316
- Chen Q, Cao Z, Du G, *et al.* Excavated octahedral Pt-Co alloy nanocrystals built with ultrathin nanosheets as superior multifunctional electrocatalysts for energy conversion applications. *Nano Energy*, 2017, 39: 582–589
- Din MAU, Saleem F, Ni B, *et al.* Porous tetrametallic PtCuBiMn nanosheets with a high catalytic activity and methanol tolerance limit for oxygen reduction reactions. *Adv Mater*, 2017, 29: 1604994
- Zhang Z, Luo Z, Chen B, *et al.* One-pot synthesis of highly anisotropic five-fold-twinned PtCu nanoframes used as a bifunctional electrocatalyst for oxygen reduction and methanol oxidation. *Adv Mater*, 2016, 28: 8712–8717
- Yan SY, Huang YR, Yang CY, *et al.* Enhanced activity of ethanol oxidation reaction on PtM (M=Au, Ag and Sn): The importance of oxophilicity and surface oxygen containing species. *Electrochim Acta*, 2018, 259: 733–741
- Kuttiyiel KA, Choi YM, Sasaki K, *et al.* Tuning electrocatalytic activity of Pt monolayer shell by bimetallic Ir-M (M=Fe, Co, Ni or Cu) cores for the oxygen reduction reaction. *Nano Energy*, 2016, 29: 261–267
- Eid K, Ahmad YH, Yu H, *et al.* Rational one-step synthesis of porous PtPdRu nanodendrites for ethanol oxidation reaction with a superior tolerance for CO-poisoning. *Nanoscale*, 2017, 9: 18881–18889
- Qi Z, Xiao C, Liu C, *et al.* Sub-4 nm PtZn intermetallic nanoparticles for enhanced mass and specific activities in catalytic electrooxidation reaction. *J Am Chem Soc*, 2017, 139: 4762–4768
- Xiang S, Wang L, Huang CC, *et al.* Concave cubic PtLa alloy nanocrystals with high-index facets: Controllable synthesis in deep eutectic solvents and their superior electrocatalytic properties for ethanol oxidation. *J Power Sources*, 2018, 399: 422–428
- Zhang E, Ma F, Liu J, *et al.* Porous platinum–silver bimetallic alloys: surface composition and strain tunability toward enhanced electrocatalysis. *Nanoscale*, 2018, 10: 21703–21711
- Xue S, Deng W, Yang F, *et al.* Hexapod PtRuCu nanocrystalline alloy for highly efficient and stable methanol oxidation. *ACS Catal*, 2018, 8: 7578–7584
- Liu T, Wang K, Yuan Q, *et al.* Monodispersed sub-5.0 nm PtCu nanoalloys as enhanced bifunctional electrocatalysts for oxygen reduction reaction and ethanol oxidation reaction. *Nanoscale*, 2017, 9: 2963–2968
- Sun X, Jiang K, Zhang N, *et al.* Crystalline control of {111} bounded Pt₃Cu nanocrystals: multiply-twinned Pt₃Cu icosahedra with enhanced electrocatalytic properties. *ACS Nano*, 2015, 9: 7634–7640
- Yin AX, Min XQ, Zhang YW, *et al.* Shape-selective synthesis and

- facet-dependent enhanced electrocatalytic activity and durability of monodisperse sub-10 nm Pt-Pd tetrahedrons and cubes. *J Am Chem Soc*, 2011, 133: 3816–3819
- 32 Hsu SW, Tao AR. Halide-directed synthesis of square prismatic Ag nanocrystals by the polyol method. *Chem Mater*, 2018, 30: 4617–4623
 - 33 Qin Y, Luo M, Sun Y, *et al.* Intermetallic hcp-PtBi/fcc-Pt core/shell nanoplates enable efficient bifunctional oxygen reduction and methanol oxidation electrocatalysis. *ACS Catal*, 2018, 8: 5581–5590
 - 34 Jiang B, Li C, Dag Ö, *et al.* Mesoporous metallic rhodium nanoparticles. *Nat Commun*, 2017, 8: 15581
 - 35 Luo S, Shen PK. Concave platinum-copper octopod nanoframes bounded with multiple high-index facets for efficient electro-oxidation catalysis. *ACS Nano*, 2017, 11: 11946–11953
 - 36 Xiong Y, Ma Y, Li J, *et al.* Strain-induced Stranski-Krastanov growth of Pd@Pt core-shell hexapods and octapods as electrocatalysts for methanol oxidation. *Nanoscale*, 2017, 9: 11077–11084
 - 37 Sahraie NR, Kramm UI, Steinberg J, *et al.* Quantifying the density and utilization of active sites in non-precious metal oxygen electroreduction catalysts. *Nat Commun*, 2015, 6: 8618
 - 38 Liu C, Ma Z, Cui M, *et al.* Favorable core/shell interface within Co₂P/Pt nanorods for oxygen reduction electrocatalysis. *Nano Lett*, 2018, 18: 7870–7875
 - 39 Dragoi B, Mazilu I, Chiriac A, *et al.* Highly dispersed copper (oxide) nanoparticles prepared on SBA-15 partially occluded with the P123 surfactant: toward the design of active hydrogenation catalysts. *Catal Sci Technol*, 2017, 7: 5376–5385
 - 40 Huang L, Zhang X, Wang Q, *et al.* Shape-control of Pt-Ru nanocrystals: tuning surface structure for enhanced electrocatalytic methanol oxidation. *J Am Chem Soc*, 2018, 140: 1142–1147
 - 41 Kuang Y, Cai Z, Zhang Y, *et al.* Ultrathin dendritic Pt₃Cu triangular pyramid caps with enhanced electrocatalytic activity. *ACS Appl Mater Interfaces*, 2014, 6: 17748–17752
 - 42 Nosheen F, Zhang Z, Xiang G, *et al.* Three-dimensional hierarchical Pt-Cu superstructures. *Nano Res*, 2015, 8: 832–838
 - 43 Eid K, Wang H, He P, *et al.* One-step synthesis of porous bimetallic PtCu nanocrystals with high electrocatalytic activity for methanol oxidation reaction. *Nanoscale*, 2015, 7: 16860–16866
 - 44 Li Z, Xu S, Xie Y, *et al.* Promotional effects of trace Bi on its highly catalytic activity for methanol oxidation of hollow Pt/graphene catalyst. *Electrochim Acta*, 2018, 264: 53–60
 - 45 Li D, Cai K, Wu L, *et al.* Ammonia mediated one-step synthesis of three-dimensional porous Pt_xCu_{100-x} nanochain networks with enhanced electrocatalytic activity toward polyhydric alcohol oxidation. *ACS Sustain Chem Eng*, 2017, 5: 11086–11095
 - 46 Bai J, Xiao X, Xue YY, *et al.* Bimetallic platinum-rhodium alloy nanodendrites as highly active electrocatalyst for the ethanol oxidation reaction. *ACS Appl Mater Interfaces*, 2018, 10: 19755–19763
 - 47 Xu D, Bliznakov S, Liu Z, *et al.* Composition-dependent electrocatalytic activity of Pt-Cu nanocube catalysts for formic acid oxidation. *Angew Chem Int Ed*, 2010, 49: 1282–1285
 - 48 Ding J, Bu L, Guo S, *et al.* Morphology and phase controlled construction of Pt-Ni nanostructures for efficient electrocatalysis. *Nano Lett*, 2016, 16: 2762–2767
 - 49 Strasser P. Catalysts by Platonic design. *Science*, 2015, 349: 379–380
 - 50 Li C, Liu T, He T, *et al.* Composition-driven shape evolution to Cu-rich PtCu octahedral alloy nanocrystals as superior bifunctional catalysts for methanol oxidation and oxygen reduction reaction. *Nanoscale*, 2018, 10: 4670–4674
 - 51 Beermann V, Gocyla M, Willinger E, *et al.* Rh-doped Pt-Ni octahedral nanoparticles: understanding the correlation between elemental distribution, oxygen reduction reaction, and shape stability. *Nano Lett*, 2016, 16: 1719–1725
 - 52 Xiao W, Liutheviene Cordeiro MA, Gong M, *et al.* Optimizing the ORR activity of Pd based nanocatalysts by tuning their strain and particle size. *J Mater Chem A*, 2017, 5: 9867–9872
 - 53 Fu S, Zhu C, Shi Q, *et al.* Highly branched PtCu bimetallic alloy nanodendrites with superior electrocatalytic activities for oxygen reduction reactions. *Nanoscale*, 2016, 8: 5076–5081
 - 54 Xiong Y, Shan H, Zhou Z, *et al.* Tuning surface structure and strain in Pd-Pt core-shell nanocrystals for enhanced electrocatalytic oxygen reduction. *Small*, 2017, 13: 1603423
 - 55 You H, Yang S, Ding B, *et al.* Synthesis of colloidal metal and metal alloy nanoparticles for electrochemical energy applications. *Chem Soc Rev*, 2013, 42: 2880–2904
 - 56 Zhao R, Liu Y, Liu C, *et al.* Pd@Pt core-shell tetrapods as highly active and stable electrocatalysts for the oxygen reduction reaction. *J Mater Chem A*, 2014, 2: 20855–20860
 - 57 Li ZY, Zhou J, Tang LS, *et al.* Hydroxyl-rich ceria hydrate nanoparticles enhancing the alcohol electrooxidation performance of Pt catalysts. *J Mater Chem A*, 2018, 6: 2318–2326
 - 58 Huang DB, Yuan Q, He PL, *et al.* A facile and general strategy for the synthesis of porous flowerlike Pt-based nanocrystals as effective electrocatalysts for alcohol oxidation. *Nanoscale*, 2016, 8: 14705–14710
 - 59 Jiang K, Bu L, Wang P, *et al.* Trimetallic PtSnRh wavy nanowires as efficient nanoelectrocatalysts for alcohol electrooxidation. *ACS Appl Mater Interfaces*, 2015, 7: 15061–15067
 - 60 Yuan X, Jiang X, Cao M, *et al.* Intermetallic PtBi core/ultrathin Pt shell nanoplates for efficient and stable methanol and ethanol electro-oxidation. *Nano Res*, 2019, 12: 429–436
 - 61 Liu H, Li J, Wang L, *et al.* Trimetallic PtRhNi alloy nanoassemblies as highly active electrocatalyst for ethanol electrooxidation. *Nano Res*, 2017, 10: 3324–3332
 - 62 Han SH, Liu HM, Chen P, *et al.* Porous trimetallic PtRhCu cubic nanoboxes for ethanol electrooxidation. *Adv Energy Mater*, 2018, 8: 1801326
 - 63 Wang Y, Wang W, Xue F, *et al.* One-pot synthesis of Pd@Pt₃Ni core-shell nanobranches with ultrathin Pt₃Ni{111} skins for efficient ethanol electrooxidation. *Chem Commun*, 2018, 54: 5185–5188
 - 64 Beyhan S, Uosaki K, Feliu JM, *et al.* Electrochemical and *in situ* FTIR studies of ethanol adsorption and oxidation on gold single crystal electrodes in alkaline media. *J Electroanal Chem*, 2013, 707: 89–94
 - 65 Zhang BW, Jiang YX, Ren J, *et al.* PtBi intermetallic and PtBi intermetallic with the Bi-rich surface supported on porous graphitic carbon towards HCOOH electro-oxidation. *Electrochim Acta*, 2015, 162: 254–262
 - 66 Li JT, Zhou ZY, Broadwell I, *et al.* *In-situ* infrared spectroscopic studies of electrochemical energy conversion and storage. *Acc Chem Res*, 2012, 45: 485–494
 - 67 Pech-Rodríguez WJ, González-Quijano D, Vargas-Gutiérrez G, *et al.* Electrochemical and *in situ* FTIR study of the ethanol oxidation reaction on PtMo/C nanomaterials in alkaline media. *Appl Catal B-Environ*, 2017, 203: 654–662
 - 68 Christensen PA, Jones SWM, Hamnett A. *In situ* FTIR studies of ethanol oxidation at polycrystalline Pt in alkaline solution. *J Phys Chem C*, 2012, 116: 24681–24689

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Author contributions Zhao F synthesized the PtCu nanocrystals and performed the electrochemical test. Zhao F, Luo B, Li C, Yang F and Yang X carried out the structure characterization. Zhou Z tested the *in situ* FTIR. Yuan Q and Zhao F conceived this work and wrote the manuscript. All authors discussed the experiment results.

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表面组成和应变可调的PtCu八面体纳米合金促进甲醇和乙醇电催化性能

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摘要 本文介绍了一种以卤素离子(Br⁻或I⁻)为成分调变剂制备组成和应变可调的PtCu八面体纳米合金的简便方法. 由于纳米合金化所产生的配位效应、协同效应和应变效应, PtCu八面体纳米合金在碱性介质中对甲醇和乙醇电氧化表现出优于商业Pt黑的催化性能. 在这些PtCu八面体纳米合金中, 优化的Pt₅₉Cu₄₁八面体纳米合金具有较高的催化活性和耐久性. 对于甲醇氧化, Pt₅₉Cu₄₁八面体的比活性/质量活性为20.25 mA cm⁻²/3.24 A mg⁻¹_{Pt}, 分别是商业铂黑的6.64/5.3倍. 对于乙醇氧化, Pt₅₉Cu₄₁八面体的比活性/质量活性为34.84 mA cm⁻²/5.58 A mg⁻¹_{Pt}, 分别是商业铂黑的9.16/7.34倍. 利用原位傅立叶变换红外光谱技术, 对甲醇/乙醇氧化反应中的中间物种和产物进行了检测, 并探讨了Pt₅₉Cu₄₁八面体催化活性和耐久性较好的原因, 同时解释了在碱性介质中甲醇氧化耐久性优于乙醇的原因. 本文对探索制备高性能的碱性甲醇/乙醇燃料电池纳米电催化剂具有一定的科学意义.