Synthesis of an excellent electrocatalyst for oxygen reduction reaction with supercritical fluid: graphene cellular monolith with ultrafine and highly dispersive multimetallic nanoparticles

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ABSTRACT: Graphene cellular monolith (GCM) can be used as an excellent support for nanoparticles in widespread applications. However, it's still a great challenge to deposit the desirable nanoparticles in GCM that have small size, controllable structure, composition, and high dispersion using the current methods. Here we demonstrate a green, efficient and large-scale method to address this challenge using supercritical fluid (SCF). By this superior method, graphene hydrogel can be transferred into GCM while being deposited with ultrafine and highly dispersive nanoparticles. Specifically, the bimetallic PtFe/GCM and the trimetallic PtFeCo/GCM catalysts are successfully synthesized, and their electrocatalytic performances toward oxygen

reduction reaction (ORR) are also studied. The resultant PtFe/GCM shows the significant enhancement in ORR activity, including a factor of 8.47 enhancement in mass activity ($0.72 \text{ A mg}_{\text{Pt}}^{-1}$), and a factor of 7.67 enhancement in specific activity (0.92 mA cm^{-2}), comparing with those of the commercial Pt/C catalyst ($0.085 \text{ A mg}_{\text{Pt}}^{-1}$, 0.12 mA cm^{-2}). Importantly, by introducing the Co, the trimetallic PtFeCo/GCM exhibits the further improved ORR activities ($1.28 \text{ A mg}_{\text{Pt}}^{-1}$, 1.80 mA cm^{-2}). The high ORR activity is probably attributed to the alloying structure, ultrafine size, highly dispersive, well-defined, and a better interface with 3D porous graphene support.

1. Introduction

Highly porous graphene cellular monolith (GCM), combining extraordinary mechanical, electrical, and thermal properties, large specific surface area, as well as the efficient transport pathways of ions and electrons, holds great promise to be a macroscopic device for widespread applications [1-4]. Nowadays, integrating nanoparticles into GCM has attracted tremendous attention. It is not only important for the enhancement of the merits of monolith materials, but also crucial for building complex macroscopic graphene monolith with interesting properties [5,6]. Recent reports have shown that GCM can be used as porous electrode material for fuel cells when it was deposited with Pt-based nanoparticles [7]. Theoretically, the porous architectures provide higher specific surface areas and larger pore volumes, which help to maximize the availability of nanosize electrocatalyst surface area for electron transfer, and improve the mass transport of reactants to electrocatalyst. However, the electrocatalytic performances of such porous electrode materials reported in previous works still need to be further improved. Controlling the structure of Pt-based nanoparticles in GCM at the atomic level,

and optimizing the structural and compositional effect between GCM and nanoparticles would be an available strategy to enhance the electrocatalytic performance.

Until now, a series of metal-based nanoparticles have been constructed into GCM, and the popular methods are still the hydrothermal method and self-assembly method. Briefly, porous materials were prepared through gelatinization of graphene oxide (GO) sheets assembled with nanoparticles to form the 3D hydrogels using the hydrothermal method or self-assembly method, and then dried to aerogels [8-10]. However, it is still highly challenging to integrate nanoparticles into 3D porous graphene with beneficial structure while maintaining good dispersion. High concentration of GO colloid has been proven to be a key to fabricate the 3D porous graphene through gelatinization of GO sheets, and block linkers are sometimes needed [11,12]. Thus, the interfacial tension and viscosity of metal precursors or nanoparticles in GO colloid are very high. It is difficult for precursors or nanoparticles to diffuse and disperse uniformly on the GO sheets, which results in particle aggregation and big particle size in final porous structure. Furthermore, the quality of porous graphene would be affected because of uncontrollable porous architectures during the depositing of nanoparticles. Some researchers have tried to directly deposit the nanoparticles into prepared porous graphene [13,14]. However, it is difficult to control the composite structure in liquid phase due to the hierarchical porous structure and strong hydrophobic property of porous graphene. Moreover, the porous structure might be compromised due to the immersing and second drying processes. Above analysis suggests that it is highly desirable to develop new strategies to tackle this challenging and very significant problem.

Supercritical fluid (SCF) technique has been developed to synthesize and process nanomaterials such as metal films, metal and metal oxide nanoparticles, and porous materials

[15-17]. Especially supercritical carbon dioxide (scCO₂) is widely used since it is non-toxic, non-flammable, and abundant [17]. Due to the unique properties such as low viscosity, high diffusivity, near-zero surface tension, and tenability, scCO₂ technique can be used to uniformly deposit metal-based nanoparticles on the support. For example, Han, et. al investigated uniform deposition of metal-oxide nanoparticles on carbon nanotube (CNT) using different metal nitrates as precursors [18-22]. In our previous work, we successfully deposited different noble metal nanoparticles on CNT through hydrogen (H₂) reduction of metal- β -diketone complexes in scCO₂ [23-25]. Thus, scCO₂ technique described above is green and scalable, and has a bright future in integration of desirable nanoparticles into GCM.

After achievement in synthesis of Pt-based nanoparticle/GCM in scCO₂, we desire to further improve the electrochemical properties of such porous electrode material through controlling the structure of nanoparticles. The alloying Pt with a less noble late transition 3d metal such as Fe, Co, Ni, and Cu is a key strategy for creating Pt-based catalysts in all design categories [26]. The electronic structure of Pt can be modified, which prompts the significant enhancement in the electrocatalytic activity and durability. In our previous work, we deposited the PtRu alloys on the surfaces of CNT via H₂ reduction of precursors in scCO₂/methanol solution at 200 °C [27]. However, the reducing activity of H₂ is not strong enough to alloy Pt with Fe, Co, Ni metal, and high temperature is necessary.

Herein, we develop the scCO₂ technique as a green and efficient method to directly deposit alloyed Pt nanoparticles into GCM. Especially, we choose graphene hydrogel as the porous graphene to demonstrate this concept. By controlling the temperature of scCO₂ system and decompression rate, the graphene hydrogel can be dried to aerogel; at the same time, Pt or PtFe (Co) nanoparticles can be deposited into GCM through borane tetrahydrofuran complex solution

(borane-THF) reduction of precursors. Due to the strong reducing activity, borane-THF is able to reduce the precursors into alloys and multimetallic Pt-based nanoparticles can be obtained easily. Furthermore, no more extra drying process is needed to turn graphene hydrogel into aerogel. The resultant PtFe/GCM and PtFeCo/GCM catalysts exhibit enhanced electrocatalytic activity and durability toward oxygen reduction reaction (ORR), which has high potentials for fuel cell applications as the porous electrode material. Furthermore, the successful PtFe(Co)/GCM materials demonstrated in this manuscript indicate that our modified SCF method has great potential in synthesis more 3D graphene-based materials through depositing the different kinds of nanoparticles.

2. Experimental section

2.1 Synthesis of GCM alcohol gel

A 5 mL of homogeneous GO aqueous dispersion (2 mg mL^{-1}) was prepared and stored in a 10 mL cylindrical sampler vial. The 10 mg of ascorbic acid was added into the GO aqueous dispersion with 2-min sonication. Then, this vial was placed in an oil bath for 4 h at 90°C without stirring. After that, the 3D GCM hydrogel was obtained, and washed with distilled water for 5 times. Finally, the distilled water stored in hydrogel was replaced by absolute alcohol to form the GCM alcohol gel.

2.2 Functionalized GCM by multimetallic nanoparticles with $sc\text{CO}_2$ technique

The supercritical apparatus for this experiment is shown in Fig. S1. In a typical synthesis of PtFeCo/GCM catalyst, GCM alcohol gel, Pt(hfa)_2 (7.1 mg), $\text{Co(hfa)}_2 \cdot x\text{H}_2\text{O}$ (5.4 mg), and Fe(acac)_2 (2.9 mg) (hfa=hexafluoroacetylacetonate, acac=acetylacetonate) were loaded into a glass cell. The glass cell with metal precursors was put into a high-pressure stainless steel reactor R1 (10 mL) located on a heater. Valves V2, V4 were closed, and V1, V3 were opened to purge

the 20 mL CO₂ (pre-pumped to 150 atm) into the R1. Then, the reactor was heated to and maintained at 323 K; meanwhile, the pressure of reactor increased to 250 atm because of increasing temperature. After 2 h of waiting for the precursors to uniformly adsorb onto the surface of graphene, the reactor was cooled to 313 K, and vented out the CO₂ and excess precursors slowly by opening V4 at the vent rate of $\sim 0.1 \text{ mL min}^{-1}$. After that, valves V1, V3, V4 were closed, and 0.7 mL of the borane-THF was injected into reactor R2. Valves V1, V2 were then opened to purge the 20 mL of CO₂ (pre-pumped to 150 atm) into the R2. Closed valve V1, V2. The borane-THF can be completely dissolute into the CO₂ to form a single phase after 10 min at 333 K. Then, borane-THF and CO₂ mixture was pumped into the R1 and rapidly diffused into the precursors after V2, V3 opened. R1 was heated to 333 K and maintained for 1 h. After that, the system was cooled down to 313 K, and was depressurized by releasing CO₂ at the vent rate of $\sim 0.1 \text{ mL min}^{-1}$. The excess borane-THF and possible unreacted precursors were then removed by a continuous feed of 80 mL of CO₂ and released at a rate of $\sim 0.1 \text{ mL min}^{-1}$. Finally, the washed product was collected when all the CO₂ is released. For the comparisons, the Pt/GCM and PtFe/GCM samples were also prepared with the same technique.

2.3 Characterization

FEI Sirion field emission gun scanning electron microscope with the through-the-lens (TLD) detector was employed to characterize the 3D porous structure and morphology of as-prepared electrocatalysts. Transmission electron microscopy (FEI/Philips CM-200, USA) was used to further characterize the morphologies of electrocatalysts. Scanning transmission electron microscope (STEM) images and electron diffraction pattern (EDP) were obtained using Titan 80-300 S/TEM equipped with a probe spherical aberration corrector (FEI Company) operated at 300 kV. Nitrogen (N₂) adsorption/desorption measurement was performed on a Quantachrome

autosorb-6 automated gas sorption system. The chemical compositions and elemental analysis of electrocatalysts were performed by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS-165 with a monochromatized AlK α X-ray anode (1486.6 eV). X-ray diffraction (XRD) analyses were performed on a Siemens D5000 powder X-ray diffractometer with Cu KR radiation at 40 kV and 30 mA. The actual metal loading was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on Thermo-Fisher iCAP 6300. During the preparation of ICP samples, all the catalysts are treated with aqua regia (3:1 v/v HCl (37%) : HNO₃ (65%)) for 24 h, and make sure that all the metals can be dissolved to ions completely. (**Caution!** *It is necessary to take extreme care when using aqua regia solutions and it must never be stored in hermetically-sealed containers*)

2.4 Electrochemical measurements

2.4.1 Catalyst preparation for electrochemical measurements. The electrochemical measurements were performed by the three-electrode system controlled with a CHI 630E station (CH Instruments, Inc., USA). The Pt wire and Ag/AgCl (3 M KCl) were used as the counter electrode and reference electrode, respectively. A glassy carbon (GC) rotating disk electrode (RDE) (5 mm in diameter) was served as the working electrode. All potentials in this work were relative to hydrogen electrode (RHE). The preparation of working electrodes was processed by applying as-prepared catalyst inks onto the republished GC disk electrodes. First of all, as-prepared catalysts were dispersed in the mixed solutions of isopropanol (99.5%), Nafion (5%), water (V/V/V: 2/0.05/8). After 2 h sonication, the mixed solutions can form uniform catalytic inks (2 mg mL⁻¹). Then, a total of 10 μ L of each catalytic ink was applied onto the pre-polished GC disk electrode. The target catalyst loading on the GC disk electrodes are 2.2 μ g_{Pt} for PtFeCo/GCM, 2.4 μ g_{Pt} for PtFe/GCM, 3.9 μ g_{Pt} for Pt/GCM, and 4 μ g_{Pt} for commercial Pt/C (20

wt%). The well-prepared electrodes were dried at 60 °C for 30 min, and then the catalyst ink can form the uniform film on the surface GC disk electrode.

2.4.2 Electrochemical dissolution process. As-prepared catalysts were electrochemically etched to leach out Fe by cycling the potential between 0.05 and 1.2 V (vs. RHE) at a sweep rate of 100 mV s⁻¹ for 200 cycles in N₂-saturated HClO₄ solutions.

2.4.3 Electrochemical measurements for ORR. Cyclic voltammograms (CV) measurements were obtained in N₂-saturated 0.1 M HClO₄ solutions with a scan rate of 50 mV s⁻¹. From the CVs, the electrochemically active surface areas (ECSAs) of the catalysts were determined by integrating the area surrounded by the hydrogen desorption curve and the CV baseline (see Supporting Information). The ORR polarization curve measurements were performed in O₂-saturated 0.1 M HClO₄ solutions by using a RDE at room temperature with a sweep rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. The ORR kinetic currents were calculated from the Levich-Koutecky equation and normalized to the amount of Pt and to ECSA to get mass and specific activities of the catalysts, respectively (see Supporting Information).

2.4.4 Accelerated durability test (ADT) for catalysts. The catalysts were first pretreated using 200 cycles CV scans by potential sweeping from 0.05 to 1.0 V (vs. RHE) at a scan rate of 200 mV s⁻¹ in O₂-saturated 0.1 M HClO₄ solution at the room temperature. Thereafter, the durability of the catalysts is studied by an ADT at a room temperature by cycling the potential between 0.6 and 1.0 V for a duration of 20,000 potential cycles at sweep rates of 200 mV s⁻¹. The CVs before and after ADT were recorded at a scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ solution at the room temperature. And then, ORR polarization curves of the catalysts before and after ADT were also conducted at room temperature in O₂-saturated 0.1 M HClO₄ with a sweep rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm.

3. Results and discussion

Graphene hydrogel was prepared through gelatinization of GO sheets by ascorbic acid according to the previous work. As shown in Fig. S1 (see Supporting Information), the homogeneous GO aqueous dispersion was obtained to form the well-defined 3D hydrogel at 90 °C after 4 hours. Usually, the GCM can be obtained after drying process of graphene hydrogel using the scCO₂ method or freeze drying. In the present paper, we investigate that the graphene hydrogel is turned into to aerogel using modified scCO₂ technique while being deposited with the multimetallic Pt-based nanoparticles. In order to achieve this goal, three crucial issues should be addressed: (a) efficient drying the graphene hydrogel in scCO₂; (b) uniformly deposition of nanoparticles into GCM; and (c) synthesis of Pt alloyed with Fe (Co) metal by reduction of precursors. Nowadays, scCO₂ has been used for preparation of GCM. However, due to the low solubility of CO₂ in aqueous solution, longer time is needed to dry the graphene hydrogel. Here, the graphene hydrogel was first dialyzed in alcohol solution, and then graphene alcohol gel would be obtained. This treatment is crucial in constructing Pt-based/GCM materials on the basis of two reasons: (a) promotion of drying process in scCO₂. The graphene alcohol gel can be dried to GCM easily in scCO₂ because of the high solubility of CO₂ in alcohol; (b) the alcohol stored in the graphene gel can be used as a modifier to enable dissolution of the precursors in the scCO₂.²³

The rational synthesis of Pt-based/GCM material is schematically illustrated in Fig. 1. And the supercritical apparatus for this experiment is shown in Fig. S2. In a typical synthesis of PtFeCo/GCM, graphene alcohol gel, Pt(hfa)₂, Fe(acac)₂ and Co(hfa)₂ were loaded into the reactor cell R1 (Fig. 1A and Fig. S2). CO₂ was compressed to 150 atm by pump, and then 20 mL of CO₂ was injected into the reactor cell R1. When the temperature of the cell increased to 323 K,

scCO₂ can be obtained. Meanwhile the ethanol and metal precursors started to dissolve into the scCO₂ and formed a uniform mixture (Fig. 1B). Due to the low viscosity, high diffusivity, excellent wetting of surface, and zero surface tension properties of scCO₂, the precursors can be diffused into the porous structure of GCM with scCO₂, and then absorbed uniformly on the single graphene sheets (Fig. 1B). After 2 h, unabsorbed precursors have to be removed with the releasing of CO₂ by decompression, which is crucial for improving the particle dispersion in GCM (Fig. 1C). Note that the temperature should be kept at 323 K and the vent rate of CO₂ should be slower than 0.1 mL min⁻¹, otherwise, the GCM might collapse due to the fast releasing of ethanol from the cellular structure. Then, borane-THF was injected into the reactor cell R2, and 20 mL of CO₂ was pumped into reactor cell R2 (Fig. 1D and Fig. S2). The borane-THF and CO₂ will mix together and form the single supercritical phase. After that, this mixture was injected into reactor cell R1, and at the same time, the temperature was increased to 333 K (Fig. 1D). Compared to the reductant of H₂, borane-THF used here has much stronger reducing activity, which can be employed to reduce the precursors to PtFeCo nanoparticles at short time and low temperature. During the reduction process, the porous structure of GCM can be maintained. The reduction process was finished within 1 h, and PtFeCo/GCM can be obtained after washing process by extra CO₂. The washing process not only can remove the excess reductant, but also can further dry GCM.

Fig. 1. Schematic showing the synthesis mechanism of trimetallic PtFeCo nanoparticles supported by GCM using scCO₂ technique. (A) GCM alcohol gel with metal precursors of Pt(hfa)₂, Fe(acac)₃ and Co(hfa)₂ were loaded in reaction cell. (B) Uniform dispersion of Metal precursors in GCM and drying process of GCM gel in scCO₂ environment. (C) Remove the extra metal precursors by venting CO₂. (D) Borane-THF reduction of metal precursors to PtFeCo nanoparticle in scCO₂ environment. (E) Washing of PtFeCo/GCM product by extra CO₂ and further drying process of GCM gel.

The structures of products were characterized by XRD. Fig. 2a shows the XRD patterns of the Pt/GCM, PtFe/GCM and PtFeCo/GCM porous electrocatalysts. There are four main XRD peaks can be clearly seen for the Pt/GCM product. The peaks at $2\theta=39.9^\circ$, 46.6° , 67.8° , and 81.9° can be assigned to (111), (200), (220), and (311) crystalline planes of Pt, respectively. The XRD result is in agreement with those of standard Pt (JCPDSICDD card No. 01-1194). The result shows the Pt nanoparticles with the face-centered cubic (fcc) structure were deposited into the GCM using the scCO₂ technique. For PtFe (Co)/GCM catalysts, four main XRD peaks for each catalyst-(111), (200), (220), and (311)-are located between those for Pt and Fe (Co), which indicating that PtFe (Co) in catalysts are fcc structure. Fig. 2b shows the magnified view of XRD patterns. Compared to the Pt/GCM product, the XRD peaks for PtFe/GCM and PtFeCo/GCM

samples can be observed to shift toward higher angle (decreased d spacing), which indicate that the lattice contraction induced by Fe (Co) [28]. The XRD results prove that the fcc structured PtFe and PtFeCo alloys have been successful obtained using the scCO₂ technique.

Fig. 2. (a) XRD patterns of Pt/GCM, PtFe/GCM, and PtFeCo/GCM samples, (b) magnified view of XRD patterns.

The structure and composition of PtFeCo/GCM were further characterized by XPS, and ICP-AES. Fig. 3a shows the high-resolution C 1s XPS of GO, indicating a remarkable oxidation degree. The atomic ratio between C and O is 1.3 for GO. Fig. 3b is the C 1s core level spectrum of PtFeCo/GCM product. Compared with the GO, the majority of the oxygen functional groups in PtFeCo/GCM have been removed, and the “C-C” bonds became dominant. The atomic ratio of C/O increased to 9.0 compared with GO. XPS studies reveal that initial GO was transformed to reduced graphene oxide. Fig. 3c shows the Pt 4f XPS spectrum of PtFeCo/GCM, which indicates the metallic Pt are the predominant species in product. At the same time, we also found the existing Fe (Fig. 3d) and Co elements (Fig. 3e) in the GCM, which further proves that the PtFeCo nanoparticles have been deposited into GCM. Fig. 3f shows the Pt 4f core level spectra of Pt/GCM, PtFe/GCM and PtFeCo/GCM products. Compared to the Pt/GCM, the Pt 4f_{5/2} peak in PtFe/GCM has 0.3 eV shift to higher binding energy with introduce of Fe. By introducing Co, the Pt 4f_{7/2} peak in trimetallic PtFeCo/GCM has 0.3 eV shift compared with that of PtFe/GCM.

The XRS result, together with XRD data have proven that the PtFe and PtFeCo in GCM have alloying structure using scCO₂ technique. The element composition and nanoparticles loading for the products were analysed by ICP, and summarized in Table S1 (see Supporting Information). The Pt loadings are ~25.0 wt%, ~12.2 wt% and ~11.0 wt% for Pt/GCM, PtFe/GCM, and PtFeCo/GCM catalysts. The nominal atomic ratio of Pt/Fe/Co in PtFeCo/GCM product is 36 : 60 : 4, while it is 40 : 60 of Pt/Fe for bimetallic PtFe/GCM product. We also find that the initial Co precursor has very limited influence on the compositions of PtFeCo nanoparticle, implying that the Fe is easier to be alloyed with Pt compared with Co using the scCO₂ technique. However, the principle of this phenomenon is still not clear.

Fig. 3. The C 1s XPS spectra of (a) GO and (b) PtFeCo/GCM. The high-resolution XPS spectra of (c) Pt 4f, (d) Fe 2p, and (e) Co 2p for PtFeCo/GCM product. (f) Comparison of Pt 4f XPS spectra among Pt/GCM, PtFe/GCM and PtFeCo/GCM products.

The macroscopic view of the PtFeCo/GCM is shown in Fig. 1. Its cylindrical morphology and size conform to the morphology of GCM alcohol gel. The interior microstructures of this monolith were characterized by the SEM. Fig. 4 shows the typical cross-sectional scanning electron microscopy (SEM) images of PtFeCo/GCM product. In the low-magnification SEM image (Fig. 4a), the well-defined 3D network consists of interconnected micron-scale voids can

be observed. In the high-magnification SEM image (Fig. 4b), we can see that the porous structure was formed by 2D graphene sheets, and the pore size is in the range of 500 nm to 2 μm . Moreover, the Pt/GCM and PtFe/GCM samples have the similar microstructures with the PtFeCo/GCM. The SEM results show that the 3D porous structure of GCM can be protected during the drying process in scCO_2 environment.

Fig. 4. SEM images of PtFeCo/GCM with (a) low magnification, and (b) high magnification.

The detailed microstructures of PtFeCo/GCM were further studied by transmission electron microscopy (TEM), which can be seen in Fig. 5(a-d). With the low resolution (Fig. 5a), it is clearly seen that the typical wrinkled and fibrous structures of GCM formed by folding of few layers of graphene [29]. Due to the small size, the information of particles in GCM cannot be observed. But, there is no any particle aggregation can be found in the low resolution TEM image, implying the high dispersion of particles in the GCM. Fig. 5b and Fig. 5c show the higher resolution TEM image of PtFeCo/GCM. The nanoparticles are scattered uniformly onto the surface of graphene sheet with the ultrafine size. We found that many nanoparticles also disperse into the folded and fibrous structures of GCM (Fig. 5c), indicating that the ultrahigh dispersion of nanoparticles in GCM is achieved with this scCO_2 technique. As well as PtFeCo trimetallic nanoparticles, highly-dispersive Pt or PtFe bimetallic nanoparticles can be obtained easily (Fig.

S3 and Fig. S4, see Supporting Information). The average sizes of nanoparticles in GCM depend on the particle composition. These sizes were calculated from TEM images using the interactive imaging software from Matrox Electronic Systems. A minimum of 100 nanoparticles were counted, and the average size and standard deviation can be seen in Fig. S5. Specifically, the average particles sizes are 2.7 ± 0.5 nm for Pt/GCM (Fig. S5a), 2.0 ± 0.8 nm for PtFe/GCM (Fig. S5b), and 1.9 ± 0.2 nm for PtFeCo/GCM (Fig. S5c). The results show that the PtFe and PtFeCo nanoparticles are smaller than that of Pt in GCM. Previous work showed a similar phenomenon: that the metal nanoparticle size decreases by introducing the second metal [30]. In supercritical systems, the reducing reaction(s) of Pt and Fe (Co) precursors might be so fast that they can be reduced almost completely before nanoparticle nucleation due to the strong reducing activity of borane-THF, high pressure and the $s\text{CO}_2$ medium. Thus the size of PtFe (Co) nanoparticles would be determined by the number of the nuclei formed at the very beginning of reaction. The number of atoms required to form a nucleus would be dependent on the composition and was lower except at high Pt contents, which would cause the particle size decrease with the introduction of Fe (Co). The alloying structure of PtFeCo nanoparticle was further evidenced by electron diffraction pattern (EDP) (inset in Fig. 5b), and atomic resolution STEM (Fig. 5d), acquired using high-angle annular dark field detector (HAADF). Both EDP and HAADF-STEM results indicate that the PtFeCo nanoparticles are nanocrystals with fcc structure as evidenced by the lattice spacing and angles. The measured lattice constant of PtFeCo nanocrystal (~ 3.76 Å) is smaller than the Pt (~ 3.92 Å). The extremely low surface tension and excellent wetting of surface of SCF are not only important for uniform scattering of nanoparticles into GCM, but also crucial for formation of nanocrystals [10]. Furthermore, borane-THF, a powerful reductant, is another key to reduce the transition metal precursors to metallic nanoparticles, which is

impossible to be achieved by common reductant of H_2 at modest temperature. Besides metal nanoparticles, metal oxide and metal nitride nanoparticles can also be dispersed in porous graphene by performing oxidation, nitriding, thermolysis, or hydrolysis of metal precursors with $scCO_2$, indicating the powerful and versatile approach for constructing complicated graphene monolith-based materials [19].

Fig. 5. (a-c) TEM images of PtFeCo/GCM with different resolutions. Inset in b is EDP image. (d) STEM image of PtFeCo/GCM sample. Inset in d is the HR-STEM image of single particle.

The aforementioned results show that the PtFeCo/GCM porous electrocatalyst has been successfully obtained using the scCO_2 method. The N_2 adsorption/desorption measurement was employed to further characterize the porous structure of PtFeCo/GCM catalyst. Fig. 6a shows the N_2 adsorption/desorption isotherm of PtFeCo/GCM catalyst. The isotherm exhibits the IUPAC type-IV adsorption/desorption behaviours. According to the isotherm, PtFeCo/GCM porous catalyst has hierarchical porous structures, including micro-, meso- and macro-porous structures, which are in agreement with reported graphene-based aerogels in previous work [3]. We also measured the pore distribution on the basis of the Barret-Joyner-Halenda (BJH) theory, which can be seen in Fig. 6b. The abundant mesoporous structures can be found in PtFeCo/GCM catalyst, and the mesopore size distribution is centered at 5.6 nm. The mesoporous structures contribute most to the large specific surface area of $728.7 \text{ m}^2 \text{ g}^{-1}$ and high total pore volume of $0.65 \text{ cm}^3 \text{ g}^{-1}$ for PtFeCo/GCM porous catalyst. On the one hand, the PtFeCo nanoparticles with ultrafine size and ultra-high dispersion in GCM result in abundant mesoporous structures; on the other hand, the SCF can not only protect the porous structure of PtFeCo/GCM, but also can prevent the graphene sheets from stacking, resulting in benefits to the formation of mesopores and large specific surface area according to our previous work [4].

Fig. 6. (a) N_2 Adsorption/Desorption Isotherm and (b) Pore Size Distribution of PtFeCo/GCM porous catalyst.

The electrocatalytic properties of PtFeCo/GCM catalyst were evaluated and compared to the PtFe/GCM and the commercial Pt/C catalysts. The catalysts were first pre-treated using an electrochemical dissolution process to leach out Fe (Co) to form the de-alloying structure through 200 cycles scans by potential sweeping from 0.05 to 1.2 V at a scan rate of 100 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ according to the previous work [31]. It is a common de-alloying process to improve the electrocatalytic activities [32-34]. Fig. S6 shows the EDP image of de-alloying PtFeCo/GCM catalyst (Fig. S6, see Supporting Information). It shows two sets of fcc lattices comparing with the one set of fcc lattice of catalyst without de-alloying process (inset in Fig. 5b). The measured lattice constant is ~ 3.76 Å for fcc1 and ~ 4.08 Å for fcc2, which should be corresponding to the alloyed and de-alloyed phases. And the PtFeCo composition changes from 36 : 60 : 4 to 74 : 24 : 2 by ICP analysis.

First of all, CVs were measured to evaluate the electrocatalytic performance of as-prepared porous catalysts. The ECSAs of catalysts were calculated from the hydrogen adsorption/desorption in CV curves (Fig. 7a). The PtFe/GCM and PtFeCo/GCM catalysts exhibit high ECSA of 78.0 m² g_{Pt}⁻¹ and 71.0 m² g_{Pt}⁻¹, respectively, which are comparable to that of the commercial Pt/C catalyst (69.0 m² g_{Pt}⁻¹) (Table S2, see Supporting Information). The higher ECSA suggests that more electrochemical active sites exist in PtFe/GCM and PtFeCo/GCM catalysts.

We then evaluated the electrocatalytic performance of the PtFe/GCM and PtFeCo/GCM catalysts for ORR. The ORR measurements were performed in O₂-saturated 0.1 M HClO₄ solutions using a GC RDE at room temperature with a sweep rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. Fig. 7b shows the ORR polarization curves of the PtFeCo/GCM, PtFe/GCM and commercial Pt/C catalysts. We can see that the polarization curves display two

distinguishable potential regions: the diffusion-limiting current region below 0.6 V and the mixed kinetic diffusion control region between 0.6 and 1.1 V. Compared to commercial Pt/C catalyst, the ORR polarization curve of PtFe/GCM catalyst has the obvious shift to the higher potential, indicating that PtFe/GCM catalysts exhibit substantially enhanced ORR activities, including the higher onset and half-wave potentials. By introducing the second transition metal of Co, the trimetallic PtFeCo/GCM catalyst has further shift to the higher potential compared to the bimetallic PtFe/GCM catalyst. Specifically, the half-wave potential of PtFeCo/GCM is 0.916 V, which is higher than that of PtFe/GCM catalyst (0.885 V), indicates the significant enhancement in ORR performance for PtFeCo/GCM catalyst. The intrinsic electrocatalytic activities of catalysts can be represented by the kinetic current densities calculated using the Koutecky-Levich equation (for details, shown in Supporting Information). The mass and specific activities were calculated using the well-known mass-transport correction and normalized with the Pt-loading and the ECSA, respectively. ORR specific activities of three catalysts increase in the following order: PtFeCo/GCM $\geq$ PtFe/GCM > commercial Pt/C in the potential range of 0.88-0.98 V (Fig. 7c and 7d). The calculated mass activity and specific activity of PtFe/GCM and PtFeCo/GCM at 0.9 V were shown in Fig. 7e and 7f, respectively. For PtFe/GCM, the mass activity and specific activity are 0.72 A mg_{Pt}⁻¹ and 0.92 mA cm⁻², respectively, which are 8.47 times and 7.67 times those of commercial Pt/C catalyst (0.085 A mg_{Pt}⁻¹, 0.12 mA cm⁻²). The trimetallic PtFeCo/GCM catalyst shows even better electrocatalytic activity towards ORR. The trimetallic PtFeCo/GCM catalyst has an ORR mass activity of 1.28 A mg_{Pt}⁻¹ calculated at 0.9 V, which are 15.1 times that of commercial Pt/C catalyst (Table S2, see Supporting Information). This mass activity is also much higher than that of U.S. Department of Energy's 2017 target (0.44 A mg_{Pt}⁻¹). The specific activity of trimetallic PtFeCo/GCM catalyst shows the similar

trends to the mass activity (Fig. 7f). The specific activity of PtFeCo/GCM catalyst is 1.80 mA cm⁻² calculated at 0.9 V, which is 15.0 times that of commercial Pt/C catalyst (Table S2, see Supporting Information). The electrochemical results reveal that the SCF technique can be a powerful method to prepare the excellent electrocatalysts by high deposition of trimetallic Pt-based nanoparticles in porous graphene.

Fig. 7. Electrochemical properties of catalysts. (a) CVs of the commercial Pt/C, PtFe/GCM, and PtFeCo/GCM catalysts in N₂-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves recorded at a scan rate of 10 mV s⁻¹ and an electrode rotation speed of 1600 rpm. (c, d) The corresponding Tafel plots; (e) Mass activities and (f) Specific activities of catalysts obtained at 0.9 V.

The enhancement in electrochemical performances for the ORR described in PtFeCo/GCM catalyst can be demonstrated on basis of our experiment and the previous investigations. First, GCM as support has the porous architectures that not only maximizing the availability of catalyst surface area for electron transfer, but also providing better mass transport of reactants. The CV of Pt/GCM can be seen in Fig. S7(a). The ECSA is $67.0 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$, which is comparable with that of commercial Pt/C catalyst. Fig. S7 (b) shows the ORR polarization curves of Pt/GCM catalyst. Compared to commercial Pt/C catalyst, the half-wave potential of the Pt/GCM catalyst shifts 19 mV to a higher potential, suggesting enhanced electrocatalytic activity for ORR. In addition, the Pt/GCM catalyst has the higher mass and specific activities ($0.093 \text{ A mg}_{\text{Pt}}^{-1}$ and 0.14 mA cm^{-2}) than those of commercial Pt/C catalyst, which further proves the superior catalyst support of GCM. Second, alloying structure of Pt-based nanoparticle is the main reasons for high ORR activities. Numerous investigations have proven that the alloying Pt catalysts have significant enhancement in ORR because the modified electronic structure of Pt [26]. For example: Huang reported the PtNi/C catalyst that has 17.6 times enhancement in ORR activity ($1.62 \text{ A mg}_{\text{Pt}}^{-1}$, 2.53 mA cm^{-2}) compared with commercial Pt/C catalyst [35]. Importantly, after introducing the second less-noble metal of Co, the ORR activity of PtNiCo/C ($2.33 \text{ A mg}_{\text{Pt}}^{-1}$, 3.88 mA cm^{-2}) is 25-30 times that of commercial Pt/C catalyst. The reason for the high ORR activities described in that work is probably introduced to explain our catalysts that the d-band center of Pt is fine-tuned by Fe on basis of electronic effect of the second transition metal Co, which results in facilitating O_2 adsorption, activation, and weakening the reaction intermediates on the surface of Pt. Therefore, the electrocatalytic activities of PtFeCo/GCM are further improved by introducing Co into PtFe/GCM [35,36]. Third, some investigations have been carried out to determine the role of particle size and particle dispersion in the electrocatalytic activity of catalyst for the ORR

[26]. Through decreasing Pt-based nanoparticle size to a desirable range, the improved mass activity of catalyst can be obtained. For the effect of particle dispersion, improvement of nanoparticle dispersion in support can increase the number of active sites of catalyst, and enhance the electrocatalytic activity for the ORR, especially in terms of specific activity. In our experiments, the PtFeCo nanoparticles in porous catalysts have ultrafine size and ultra-high dispersion, which is beneficial to improve electrocatalytic activity for ORR. In summary, the highly efficient electrocatalytic activities of PtFe(Co)/GCM catalysts toward ORR could be attributed to the alloying structure, ultrafine size, highly dispersive, well-defined, and a better interface with 3D porous graphene support derived from the superior scCO₂ approach.

Besides the electrocatalytic activities toward ORR, the electrochemical durability of the trimetallic PtFeCo/GCM catalyst was also performed using the ADT, compared with that of commercial Pt/C catalyst. The commercial Pt/C catalyst exhibits the substantial ECSA loss (~50.7%) and electrocatalytic activity decrease toward ORR (Fig. S9, see Supporting Information). Only 0.038 A mg_{Pt}⁻¹ of mass activity and 0.05 mA cm⁻² of specific activity are maintained for the commercial Pt/C catalyst after the ADT. The CVs and ORR polarization curves of PtFeCo/GCM catalyst before and after ADT are shown in Fig. 8a and 8b, respectively. After the ADT, only ~15.5% ECSA loss, and slight fluctuation in ORR polarization can be seen in PtFeCo/GCM catalyst. The mass activity and the specific activity of the trimetallic PtFeCo/GCM before and after ADT can be seen in Fig. 8c and Fig. S8. After ADT, in detail, such trimetallic PtFeCo/GCM still has high mass activity of 0.69 A mg_{Pt}⁻¹ and high specific activity of 0.96 mA cm⁻², respectively, indicating the higher electrochemical durability of this catalyst compared with commercial Pt/C catalyst (Fig. 8c and Table S3). Previous work reported that graphene is a superior support that can significantly improve the Pt stability [37,38]. Fig.

S10 shows the ORR polarization curves of Pt/GCM before and after ADT. After ADT, the half-wave potential in ORR polarization for Pt/GCM is lowered by 25 mV, while there is a 50 mV lowering for the commercial Pt/C catalyst. Specifically, the mass and specific activities of Pt/GCM after ADT are $0.066 \text{ A mg}_{\text{Pt}}^{-1}$ and 0.099 mA cm^{-2} , respectively. The result proves that the GCM is a stable catalyst support. Previous work has also proven that the alloyed structure is not only beneficial for enhancement of ORR activity, but also good for improvement in durability. Huang reported that the PtNiCo/C catalyst also has excellent durability toward ORR (only 4% of Co) [35]. After ADT, Pt/Ni/Co composition changes from 71 : 25 : 4 to 83 : 16.5 : 0.5, however, the mass activity of PtNiCo/C is still as high as $1.01 \text{ A mg}_{\text{Pt}}^{-1}$. In this work, the PtNiCo nanoparticles in catalysts are typical fcc structure, and the Co content (~4%) is the similar with PtNiCo catalyst. Thus, the effect of Co is attributed to the electronic effect of Co to PtFe, which further downshifts the *d*-band center of Pt, facilitating O₂ and reaction intermediates adsorption. Guo's work also supports this point [39]. Moreover, we did the de-alloying treatment for the as-prepared catalysts before the electrochemical performance tests. After de-alloying treatment, PtFeCo composition changes from 36 : 60 : 4 to 74 : 24 : 2. During the dissolution of Fe and Co, the Pt covering the alloy can provide kinetic stability against the further dissolution of the Fe and Co [26,40]. After ADT, the PtFeCo composition changes from 74 : 24 : 2 to 82 : 17.5 : 0.5, which showed the good durability. Even though the PtFeCo/GCM exhibits the higher durability than commercial Pt/C, the PtFeCo/GCM still loses ~54.0% ORR activity. Fig. S11a shows the STEM image of PtFeCo nanoparticles after ADT. Some particle aggregations and particle shape change are observed. The particle size increases from 1.9 nm to 2.3 nm, and the particle size distribution becomes broader (Fig. S11b). The decrease of ORR activity likely comes from the change of shape and size of nanoparticle due to the transition metal loss after

ADT. However, we consider that the ORR durability of such trimetallic PtFeCo nanoparticle can be further enhanced by incorporating other stable elements, such as Au, Ir.

Fig. 8. Electrochemical durability of the trimetallic PtFeCo/GCM catalyst by ADT. (a) CVs and (b) ORR polarization curves before and after ADT, (c) the Tafel plots of catalyst before and after ADT, and (d) mass and specific activities at 0.9 V before and after ADT.

4. Conclusion

In summary, we have developed a green, highly-efficient, and large-scale manufacturing method for integrating highly dispersive and ultrafine-sized Pt-based nanoparticles into the porous graphene monoliths using the SCF technique. The organometallic precursors dissolved in scCO_2 can highly disperse onto the surface of the single graphene sheet in GCM because of the low viscosity and zero surface tension properties of scCO_2 . And then, the multimetallic Pt-based nanoparticles can be obtained by reduction reaction and highly dispersed into the GCM, which is impossible to be accomplished by traditional methods in liquid phase. The resultant PtFe/GCM

and PtFeCo/GCM catalysts show the significant enhancement in ORR activities. Specifically, the mass and specific activities are $0.72 \text{ A mg}_{\text{Pt}}^{-1}$ and 0.92 mA cm^{-2} for PtFe/GCM catalyst, $1.28 \text{ A mg}_{\text{Pt}}^{-1}$, 1.80 mA cm^{-2} for PtFeCo/GCM catalyst, which are 7.67-8.47 times and ~ 17.1 times those of commercial Pt/C catalyst ($0.085 \text{ A mg}_{\text{Pt}}^{-1}$, 0.12 mA cm^{-2}). The PtFeCo/GCM catalyst also shows a good durability. The successful synthesis of such attractive materials not only helps to encourage fuel cell commercialization, but also paves the way to explore new porous graphene materials functionalized by nanoparticles with widespread applications.

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