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Platinum Nanoparticles Dispersed on High-Surface-Area Roelike Nitrogen-Doped Mesoporous Carbon for Oxygen Reduction Reaction

Size Zhang,^{†,§} Tao Fu,^{†,§} Jiyang Li,[†] Yueying Peng,[†] and Jinbao Zhao^{*,†,‡}

[†]State Key Lab of Physical Chemistry of Solid Surfaces, Department of Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, People's Republic of China [‡]School of Energy Research, Xiamen University, Xiamen, 361005, People's Republic of China

Supporting Information

ABSTRACT: The high price of fuel cells is mainly attributed to the low catalytic efficiency and short working life of the state-of-the-art commercial catalysts for the oxygen reduction reaction. Hereon, a nitrogen-doped mesoporous carbon (NMC) with a roelike shape have been synthesized as the carbon support for the platinum (Pt) catalyst, which has a high specific surface area and pore volume. The doping with nitrogen creates many active sites on the NMC, which can enhance the catalytic activity of the supported Pt nanoparticles. The synthesis of the NMC is simple and reproducible, which uses polydopamine as the precursor and



can be conveniently accomplished at room temperature. The Pt nanoparticles loaded on the NMC (Pt/NMC) exhibit a high mass activity (0.9 V vs reversible hydrogen electrode) of 0.384 A mg_{Pt}⁻¹ in acidic media, which is 8.1 times of the catalyst using Vulcan XC-72R as the support (Pt/Vulcan) and prepared by the same synthetic process, and 5.9 times of the commercialized catalyst (Pt/C-com, 20 wt%). The Pt/NMC also exhibits a better electrochemical stability. Compared to the severe degradation of the Pt/Vulcan and the Pt/C-com after the accelerated durability test (5000 cycles), the Pt/NMC remained high catalytic activity and electrochemical active surface area, which may be due to the suitable morphology and the influence of nitrogen in the NMC.

KEYWORDS: Pt catalyst carbon support, nitrogen-doped, roelike shape, mesoporous structure, high specific surface area, oxygen reduction reaction

1. INTRODUCTION

Fuel cells have great potential in the energy applications of both military fields and daily life, which is due to their advantages of high energy efficiency and pollution-free. However, the application of the proton exchange membrane fuel cell (PEMFC) is still limited, to a certain extent. The foremost reason is that the reaction rate of the oxygen reduction reaction (ORR) in the cathode is low, because of the large overpotential of ORR on Pt catalyst; thus, a large amount of platinum (Pt) is needed to reduce it, which makes the PEMFC a costly device.¹ In order to obtain an inexpensive and efficient ORR catalyst, many studies have turned to the direction of structural transformation on Pt nanoparticles or alloying with other metallic elements.^{2,3} Nonetheless, the effect of carbon support on catalytic activity and stability of the catalyst is also a crucial problem that should not be ignored.

The existing studies have suggested that the catalyst support has great impact on the catalytic performance of the ORR catalyst.^{4,5} For now, various materials, such as carbon nanotubes (CNTs), hollow carbon spheres, reduced graphene oxide (rGo), and even metal oxide were applied to be the catalyst support. Wang et al. used CNTs as the catalyst support of PMFC and found that the durability of the catalyst was significantly improved.⁶ The study of Tesfu-Zeru et al. showed that the hollow mesoporous carbon support could distinctly advance the ORR performance of the catalyst in direct methanol fuel cell and improve its long-term stability, and the fuel cell also received an excellent ability to resist methanol." Kim et al. discussed the effect of extra treated TiO₂ as the support of Pt nanoparticles, which led to an increase of ORR activity.⁸ In our previous work, we also observed that the ORR performance of the catalyst could be further improved when the traditional carbon support was replaced by rGO.⁹ These studies demonstrate that the support of commercialized catalysts can be modified to improve the catalytic performance, and the key to optimize the catalyst is to choose a support with good morphology (favorable porosity and high specific surface area) and modified surface.

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Meanwhile, the heteroatom-doped carbon is considered to have an ORR catalytic activity that is comparable to the commercial catalyst under alkaline media; $^{10-12}$ the limited current density is approaching 7 mA cm^{-2} by the nitrogendoped graphene, which has been extensively studied.¹³⁻¹⁵ This novel characteristic has been proved to be attributed to the nitrogen doping on the surface of the graphitized carbon clusters, which contributes *p*-electrons to the π -sites of graphene and forms the Lewis basic sites.¹⁶ However, this type of nonmetallic catalyst has great limitations, such as the specific selectivity in alkaline, the catalytic performance still lagging behind the requirement of the commercial applicaand so on. Also, some works have indicated that the tion,¹ interference caused by the unremoved metal atoms in the synthesis process cannot be eliminated.¹⁷ At the same time, the nitrogen-doped carbon as a support of the platinum nano-particles has also attracted much attention.¹⁸⁻²⁰ Riccardo et al. used both experimental and theoretically calculating methods to construe the interaction in Pt-based, nitrogen-doped, or nitrogen/sulfur-codoped catalysts.^{21–23} Xie et al. synthesized a nitrogen-doped graphene aerogel and its unique structure brought out a better ORR performance.²⁴

Here, a facile route has been designed to synthesize a roelike nitrogen-doped mesoporous carbon (noted as NMC) as the support material of the Pt catalyst. By using polydopamine (PDA) as the precursor, which contains nitrogen, the synthetic procedures of the NMC do not need additional nitrogen source. Unlike the polyacrylonitrile (PAN), which is needed to be polymerized at low temperature, the reaction in our synthesis can spontaneously occur at room temperature. We used polyvinylpyrrolidone (PVP) as a surfactant to regulate the morphology of the NMC, and we used the silica micelle as a sacrificial template to control the pore size of the NMC. The platinum catalyst then was loaded onto the NMC (Pt/NMC) and the commercial carbon support Vulcan XC-72R (Pt/ Vulcan) using the same synthetic method. With the commercial catalyst (Pt/C-com with 20 wt % Pt, Johnson Matthey HiSPEC 3000, Vulcan XC-72R as the catalyst support) as the reference substance, a series of characterization have been performed for the above three samples. We have found that the nitrogen-doped carbon support with optimized morphology has significantly enhanced the ORR catalytic efficiency of Pt nanoparticles both in acid and alkaline media, and showing a mass activity of 5.9 times better than that of the Pt/C-com in acid media. In addition, the accelerated durability test (ADT) has showed that the Pt/NMC has better long-term electrochemical performance. Its electrochemical surface area (ECSA) has decreased by 23% (20% for the Pt/Vulcan and 37% for the Pt/C-com) after 5000 times potential cycling in O2-saturated acid media, and its mass activity has decreased by only 26% (37% for the Pt/Vulcan and 42% for the Pt/C-com).

2. EXPERIMENTAL SECTION

2.1. Synthesis of the Electrocatalyst. 2.1.1. Materials. We bought dopamine hydrochloride (DA·Cl) from Aladdin Co., Ltd. (Shanghai, China), and potassium tetrachloroplatinate (K_2PtCl_4 , 99.99%) was purchased from J&K Scientific Ltd. (Beijing, China). Hydrochloric acid (HCl), perchloric acid (HClO₄), potassium hydroxide (KOH), polyvinylpyrrolidone (PVP, K-30), trishydroxymethyl aminomethane (Tris), formaldehyde (37 wt %, stabilized with 10% methanol), and hydrofluoric acid (HF) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Colloidal silica micelle (Ludox TM-40, average grain diameter: 22.0 nm) was obtained from Sigma–Aldrich Trading Co., Ltd. (Shanghai,

China). Commercial 20 wt % Pt catalyst (Johnson Matthey), Nafion ionomer (5 wt %) and Vulcan XC-72R carbon (Cobalt Co., Ltd.) were supported by Shanghai Hesen Electrical, Ltd. (Shanghai, China). All reagents were used without further purification, except otherwise stated.

2.1.2. Synthesis of the NMC. The fabrication of the NMC was on the strength of hard-template method. We used the colloidal silica micelle as the template, and then the DA was coated on it with the help of PVP to reduce the conglutination. First, a mixture of 1.2 mL of colloidal silica, 50.0 mg of PVP, and 36.0 mg of Tris were dispersed in 26.8 mL of deionized water with ultrasonic treatment for 15 min. Subsequently, 200.0 mg DA (dissolved in 2.0 mL deionized water) was added dropwise into the mixture and stirred for 24 h. The product was washed for three times by deionized water and centrifuged at 11 000 rpm for 30 min. The product then was dried by a freeze dryer and ground in an agate mortar. After pyrolysis at 800 °C in argon for ~2 h, the carbonized product was immersed in 30.0 mL 10% HF to remove the silica template. After the purification by deionized water, the NMC was finally obtained by a freeze dryer.

2.1.3. Synthesis of the Pt/Vulcan and the Pt/NMC. The Pt/Vulcan and the Pt/NMC were prepared as follows: the mixture of 18.0 mg Carbon Vulcan (XC-72R) or NMC and desired amount of K_2 PtCl₄ was dispersed in 10.0 mL 37 wt % formaldehyde. Then, 0.4 mL HCl solution (0.2 mol L⁻¹) was injected into the mixture, followed by ultrasonic processing for 15 min. The treated samples were heated into 80 °C for 2 h under reflux condition. After washing the products three times with ethanol/deionized water, the target catalysts for further characterization were finally obtained.

2.2. Characterization. The images from transmission electron microscope (TEM) and the electron energy-dispersive X-ray analysis (EDX) results were acquired using JEOL Jem-1400 (100 kV) and FEI Tecnai G2 F30 (300 kV) equipment. The scanning electron microscopy (SEM) observation was performed by Hitachi S-4800 (15 kV). The size evaluations of Pt nanoparticles were performed by gathering size statistics of 200 particles in TEM images. The crystalline structure of the loaded Pt nanoparticles was measured by Rigaku Mini Flex 600 X-ray diffractometer, which use the Cu K α Xray source radiation with a scan rate of 2.0° min⁻¹. Chemical compositions of the samples were obtained by X-ray photoelectron spectroscopy (XPS) and the measuring instrument was PHI QUANTUM 2000, which use the Al K α source radiation. The energy distribution scale of XPS was revised by the C 1s peak maximum at 284.6 eV. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurement was used to determine the platinum content of each sample, the experiments were implemented by Plasma 1000 (NCS Testing Technology). The single-point Brunauer-Emmett-Teller (BET) method was used to measure the pore volume and the total specific surface area. This measurement was performed by using an ASAP 2020 (Micromeritics Instruments, Ltd., Shanghai, China).

2.3. Electrochemical Measurements. The electrochemical measurements were operated on the CHI 730E electrochemical workstation with a three-electrode cell. The Ag/AgCl electrode (in KCl-saturated solution) was used to be the reference electrode, and the graphite electrode was used to be the counter electrode.^{14,25} All potentials were referred to a reversible hydrogen electrode (RHE) based on the equation $E_{(vs RHE)} = E_{(vs Ag/AgCl)} + 0.1971 + 0.0592pH.$

The catalyst ink was obtained by using the following steps. First, 2.5 mg of catalyst was dispersed into 1.0 mL mixed solution of ethanol (980 μ L) and Nafion ionomer (5%, 20 μ L). The mixture then was sonicated for 2 h to prepare the homogeneous catalyst ink. Subsequently, the ink of 10 μ L was deposited dropwise onto the surface of the glassy carbon in a rotating disk working electrode (PINE Instrument, surface area = 0.247 cm²). The total catalyst loading is 25.0 μ g (101.2 μ g cm⁻²) for all samples. The total Pt loading is 2.3 μ g (9.3 μ g cm⁻²) for the Pt/NMC and the Pt/Vulcan. The total Pt loading of the Pt/C-com (20 wt %) is 5 μ g (20.2 μ g cm⁻²).

The cyclic voltammetry (CV) was measured in O_2 or N_2 -saturated 0.1 M KOH or $HClO_4$ solution (at a scan rate of 50 mV s⁻¹) and the

Scheme 1. Synthetic Process of NMC



Figure 1. (A) N₂ adsorption-desorption isotherms and (B) the pore size distribution.

gas flow was maintained during the test. The linear scanning voltammetry (LSV) curves were tested in O_2 -saturated 0.1 M KOH or HClO₄ with a rotating speed of 1600 rpm, and the scan rate is 10 mV s⁻¹. The potential window of CV and LSV tests is between -0.03 V and 1.17 V in alkaline electrolyte and 0.10-1.35 V in acid electrolyte (vs RHE). The electrolyte has been bubbled with oxygen or nitrogen for at least 15 min before the CV and LSV test. The accelerated durability test (ADT) was carried out in O_2 -saturated electrolyte and by a 5000 repeated potential cycling process at 0.6–.1 V with a scan rate of 50 mV s⁻¹.

The limiting diffusion currents were measured graphically in the diffusion-limited region (0.3-0.7 V). The ECSA was calculated based on the coulometry of H⁺ desorption region according to the equation

$$ECSA = \frac{Q}{0.21 \times [Pt] \times V}$$

where [Pt] is the Pt amount loading on the electrode (mg) and V is the scan rate. The constant 0.21 mC cm⁻² is the required coulomb electric charge with saturated adsorption of a single layer of H⁺ by the surface of Pt.

All the measurements were performed at room temperature, unless noted otherwise.

3. RESULTS AND DISCUSSION

3.1. Characterization of NMC, Pt/NMC, and Pt/Vulcan. As shown in Scheme 1, the precursor of the NMC is a PDA-coated silica micelles. Through the TEM images (Figure S1 in the Supporting Information), one can notice that, compared to the samples without PVP (Figure S1A in the Supporting Information), the PDA assisted by PVP is more evenly coated on the silica micelles (Figure S1B in the Supporting Information). The pyrolytic temperature of 800 °C is chosen for the heat treatment²⁶ after repeated comparison. After pyrolysis at 800 °C, the structure still maintains its integrity and uniformity. The silica templates are removed by HF etching. As shown in the SEM and TEM images (Figure S2 in the Supporting Information), many hollow and roelike units are formed, which are the aggregates of many hollow spheres.

The NMC structure obtained by PVP (Figure S1D in the Supporting Information) is more uniform than that of the samples synthesized without PVP (Figure S1C in the Supporting Information). This hollow structure reduces the number of ineffective positions inside the NMC that cannot load the Pt nanoparticles, which significantly increases the mass specific surface area of the NMC. Compared with the commercial carbon supports (Vulcan series), those supports with better morphology make the substrates better combine with the catalyst.

Figure 1A shows the nitrogen adsorption-desorption isotherms of Vulcan XC-72R and NMC. The BET surface area is 1060 m² g⁻¹ for NMC and 198 m² g⁻¹ for Vulcan. This result of NMC is higher than that of most catalyst supports prepared by hard-template method (The comparison can be seen in Table S1 in the Supporting Information, including common catalyst supports). There is a distinct hysteresis loop of NMC at the relative pressure (P/P_0) of 0.65–0.9, which stands as proof of the existence of mesopores.²⁷ Based on the Barrett-Joyner-Halenda (BJH) model, the pore size distribution of the NMC (Figure 1B) was obtained through nitrogen adsorption calculation. The average pore size is ~ 15.6 nm, which is close to the average size of the silica template (22 nm), so the pore size of the NMC should be controlled by changing the diameter of the silica micelle. Compared with the diameter of the template, the average pore size of the NMC is slightly reduced, which may be due to the thermal shrinkage that occurs²⁶ during the pyrolysis of the SiO₂@PDA precursor, and some smaller mesopores may be formed simultaneously.²⁵ The pore volume of NMC is as high as $3.57 \text{ cm}^3 \text{ g}^{-1}$, which exceeds the existing results of hard-template method (Table S1). It can be predicted that, by using the NMC as the catalyst support, the high pore volume and specific surface area of the NMC can improve the contact between the oxygen and the catalyst, which will optimize the three-phase boundary of the ORR reaction and therefore accelerate the mass transfer of

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Figure 2. TEM, HRTEM, and EDX images of (A, C, D) Pt/NMC and (B, E) Pt/Vulcan.

both reactants and reaction products to reduce the over-potential of ORR. $^{\rm 24,28}$

The TEM images (Figure 2) show the Pt/NMC and the Pt/ Vulcan synthesized under the same condition with different carbon supports. We can see that the Pt particles are welldispersed on the NMC without apparent agglomerations (Figure 2A), but several sites where Pt particles aggregate (Figure 2B) can be seen on the Pt/Vulcan sample (as indicated by the red circle), which may be because the untreated Vulcan lacks sufficient surface functional groups to anchor the Pt atoms.²⁹ The EDX analysis of the Pt/NMC (Figure 2C) shows that the sample contains N atoms that play a role of surface modification in the NMC, providing more active sites, so that Pt nanoparticles can be uniformly distributed on the support.³ The average Pt nanoparticle size of the Pt/NMC is ~3.41 nm, and 4.20 nm for the Pt/Vulcan. The image of the highresolution TEM (HRTEM) (Figure 2D) shows that the lattice fringes of Pt nanoparticles in the Pt/NMC have an interplanar distance of 0.23 nm, which can be confirmed as the (111) plane of Pt. The elemental mapping (Figure 2C) also proves that Pt is uniformly loaded on the NMC support. The mass ratio of Pt in these two samples is \sim 9.2 ± 0.2 wt % measured by the ICP-AES, which is basically consistent with the result of EDX.

The XRD results of the Pt/Vulcan and the Pt/NMC are presented in Figure 3. Several representative diffraction peaks such as Pt(111), Pt(200), and Pt(220) can be viewed on the



Figure 3. XRD patterns of Pt/NMC and Pt/Vulcan.

diagram. Compared with the peaks of the Pt/Vulcan, the full width at half-maximum (fwhm) of the Pt/NMC peaks is found to be widened, which means that the Pt particle size on the NMC is relatively smaller.³¹ Based on the Debye-Scherrer formula, only considering the diffraction peak of the (111) plane, the average Pt nanoparticle sizes of Pt/NMC and Pt/ Vulcan are \sim 3.0 and 3.9 nm, which are similar to that observed in the HRTEM. The average Pt nanoparticle size in the Pt/ Vulcan that was synthesized under the same condition is obviously larger than that of Pt nanoparticles in the Pt/NMC. The obtained results are also consistent with those reported in previous studies.^{32,33} Compared with the ordinary carbon support, the same synthesis method can obtain relatively smaller particle size and more uniform metal nanoparticles on the N-doped carbon support, which indicates that the doping of N atoms, as a method of surface modification, can rearrange the electronic structure on the surface of the NMC and create anchoring sites that enable more Pt atoms to be attached on it.^{34,35} Hence, the Pt nanoparticles can be more evenly distributed on the carbon support.

In order to explore the interaction between the Pt nanoparticles and the NMC and find the primary causes of the improved ORR catalytic performance, the XPS characterization of the NMC, Pt/NMC, and Pt/Vulcan have been performed. The full spectrum result (Figure S3) shows that the NMC synthesized by dopamine has high nitrogen content, and the atomic ratio of the nitrogen atom is \sim 3.23%. The precursor is pyrolyzed in the argon atmosphere, which means dopamine is used both as a carbon source and a nitrogen source for the NMC. The N 1s high-resolution spectrum (Figure 4A) can be deconvoluted into three different peaks, which correspond to quaternary N (401.4 eV), pyrrolic N (399.7 eV), and pyridinic N (398.7 eV). The relative content of pyridinic N is \sim 42.4%. From the previous studies, it is known that the pyridinic N is strongly associated with the generation of ORR active sites in N-doped carbon material.^{36,37} In the electrochemical performance test, although a negative shift of approximately -0.06 V exists in the half-wave potential, compared to the Pt/C-com, it can be seen that the NMC has a certain ORR catalytic performance under the alkaline media (Figure S4 in the Supporting Information, and the comparison to recent published work can be seen in Table S2 in the Supporting Information).³⁸ This is because the high content of pyridinic N



Figure 4. (A) N 1s spectrum of Pt/NMC; (B) Pt 4f spectra of Pt/NMC and Pt/Vulcan.



Figure 5. (A) CV tested at room temperature in N₂-saturated (black curves) or O₂-saturated (red curves) 0.1 M KOH aqueous solution; (B) LSV in O₂-saturated 0.1 M KOH aqueous solution; (C) CV in N₂-saturated 0.1 M HClO₄ aqueous solution; and (D) LSV in O₂-saturated 0.1 M HClO₄ aqueous solution.

creates Lewis basic sites, which improves the oxygen affinity of the NMC itself.¹⁶ Meanwhile, the pyridinic N also facilitates the adsorption of O_2 on the catalyst,^{39,40} and its lone pair electrons promotes the electron transfer.⁴¹ A low peak at 397.8 eV (Figure 4A) can be classified as a pyridinic N bonded to the Pt atom. The dangling bond on the edge of the carbon rings enhances the adsorption energy of the Pt atom on the carbon support, which allows the pyridinic N (which is also located at the edge of the carbon ring) to form the Pt–N bond with it.^{18,31} The overbinding between atomic O and Pt atoms, which means the relatively high binding energy of O and Pt, is the main reason for the sluggish reaction rate of ORR.⁴² According to the first-principles, Holmes et al. summarizes that the interaction between pyridinic N and Pt atoms can reduce the overbinding between the O atom and the Pt atom, thus weakens the adsorption energy of O atoms on Pt catalyst,⁴³ which would promote the ORR performance of the Pt catalyst. The Pt 4f spectrum of the Pt/NMC (Figure 4B) can be deconvoluted into two pairs of doublet. The first pair of doublet with higher intensity can be classified as the spin—orbit splitting of $4f_{5/2}$ (74.8 eV) and $4f_{7/2}$ (71.5 eV) regions of Pt, the other pair of doublet with lower intensity (72.9 and 76.6 eV) can be attributed to platinum oxide. Our observation indicates that the binding energies of Pt/NMC sample have a

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0.3 eV of positive shift, compared to the Pt/Vulcan sample (Figure 4B), which are 71.2 and 74.6 eV. This may be caused by the smaller size of Pt nanoparticles⁴⁴ and the doping of N atoms.⁴⁵ In fact, this slight positive shift has also appeared not only in platinum, but also many nitrogen-doped metal catalysts. The pyridinic N with lone pair electrons has a larger overlap with the d-orbital electrons of many metal atoms, such as Ag,³³ Co,⁴⁶ Au⁴⁷ and so on, which may leads to a higher electronic state. Pt becomes more stable on the nitrogen-doped carbon due to the interaction of Pt and N, for example, Pt–N bonding. This interaction brings about the electron transfer from N atoms to Pt atoms, which could be the reason for the improved ORR performance and its electrochemical stability.

3.2. Electrocatalytic Performance of Pt/NMC and Pt/ Vulcan for Oxygen Reduction Reaction (ORR). According to the previous report,^{10,25} the N-doped carbon itself has a certain ORR activity under alkaline media, which is close or even better than the commercialized Pt/C catalyst. Based on the series of characterization that has been mentioned in this paper, it is reasonable to come up that, once loaded with Pt, the synergistic effect would enhance the ORR catalytic performance both in acidic and alkaline media. Therefore, several electrochemical tests were executed to evaluate the ORR catalytic performance of Pt/Vulcan, Pt/C-com, and Pt/ NMC in acidic and alkaline media, respectively. Figure 5A is the CV curves tested at room temperature in N2-saturated (black curves) or O₂-saturated (red curves) 0.1 M KOH aqueous solution. Both the Pt/Vulcan and the Pt/C-com have a negative cathodic peak at 0.86 V (vs RHE) under the O_2 saturated condition. Although the cathodic peak of the Pt/ NMC has a slight negative shift of ~20 mV, the cathodic current is equal to that of the Pt/C-com and is far greater than the Pt/Vulcan, which is loaded with the same amount of Pt (9 wt %). Figure 5B is the polarization curves obtained in 0.1 M KOH of oxygen saturation. The Pt/NMC shows a 64 mV positive shift of half-wave potential, compared to the Pt/ Vulcan, and 42 mV to the Pt/C-com. The half-wave potential of Pt/NMC is much higher than bare NMC (from 0.78 V to 0.88 V). The limiting diffusion current (j_L) of the Pt/NMC is also larger than that of the Pt/Vulcan and the Pt/C-com. According to the data showed in Figure 5B, the mass activity of the Pt/NMC is 0.372 A mg_{Pt}^{-1} (at 0.9 V vs RHE), which is 6.7 times of the Pt/Vulcan (0.055 A mg_{Pt}^{-1}), and 5.6 times of the Pt/C-com (0.066 A mg_{Pt}^{-1}). From the polarization curve of the NMC (see Figure S4), the NMC possesses a certain ORR catalytic activity in O2-saturated alkaline media. Therefore, the ORR catalytic performance of the Pt/NMC in alkaline media is improved by the smaller Pt nanoparticles on the NMC and the synergistic effect between Pt and doped N.

Figure 5C shows the CV curves tested in 0.1 M HClO₄ solution of nitrogen saturation. Compared to the Pt/Vulcan and Pt/C-com, a larger double layer capacitance of the Pt/ NMC can be observed because of the high specific surface area of the carbon support. Also, the CV curve of the Pt/NMC indicates that its onset potential of Pt–O formation is 0.85 V, which is higher than that of Pt/C-com (0.82 V). It is worth mentioning that the Pt–O formation and its subsequent reduction are also attributed to the intrinsic ORR performance. Usually, the stability of Pt increases as the onset potential of Pt–O formation increases, which makes Pt less oxophilic, thereby improving its oxidation resistance and stability.^{48,49} Meanwhile, the enhanced charge generation of the Pt/NMC at 0.1–0.5 V (H⁺ absorption/desorption regions) can be seen

from the diagram, which indicates that, compared with the Pt/ Vulcan and the Pt/C-com, a large number of protons are adsorbed or desorbed on the surface of the Pt/NMC.³¹ This enhancement is directly related to the superficial area of Pt nanoparticles that were exposed to the reactants, usually named as electrochemical active surface area (ECSA). The ECSA of the Pt/NMC, the Pt/Vulcan, and the Pt/C-com are determined to be 195.2, 98.9, and 96.3 m² g⁻¹, based on the H⁺ desorption region in the voltammograms. The larger ECSA is mainly caused by the relatively small size of Pt nanoparticles and the mesoporous structure of the NMC. As mentioned above, the modification of the surface of carbon materials by N-doping indirectly leads to the smaller Pt particles. However, according to an ideal geometric model,⁵⁰ which assumes that the ECSA of spherical nanoparticles is equal to its "geometric" surface area (S_{σ}) , the average nanoparticle size of Pt (d_{Pt}) on the Pt/NMC should be close to ~1.5 nm from the equation

$$d_{\rm Pt} = \frac{6}{\rho S_{\rm g}}$$

where ρ is the density of platinum. Considering the parts that are inaccessible for electrochemical reaction, the calculated value is much smaller than the average particle size observed in the TEM images (3.4 nm). This may be because many small particles cannot be clearly seen in the TEM photomicrographs, and these tiny Pt clusters are ignored in the statistical process.⁵¹ The ECSA of each sample was calculated before and after 5000 CV cycles (Table 1; CV analyses can be found in

Table 1. Pt Particle Size and ECSA of Each Sample before and after 5000 Cycles of ADT

| | Pt Particle Size (nm) | | $ECSA (m^2 g_{Pt}^{-1})$ | |
|-----------|-----------------------|-------|--------------------------|-------|
| sample | before | after | before | after |
| Pt/Vulcan | 4.2 | 6.1 | 98.9 | 79.0 |
| Pt/C-com | 3.8 | 6.7 | 96.3 | 61.4 |
| Pt/NMC | 3.4 | 4.0 | 195.2 | 150.4 |

Figure S5 in the Supporting Information). The results show that the ECSA of all samples decreases to a certain extent after the ADT. The ECSA of the Pt/NMC has decreased by 23% (from 195.2 m² g⁻¹ to 150.4 m² g⁻¹), which is relatively higher than that of the Pt/Vulcan (20%, from 98.9 m² g⁻¹ to 79.0 m² g⁻¹). This is probably because some of the small Pt clusters have formed larger particles during the CV process, which may reduce the ECSA of the Pt/NMC in a comparatively high extent. This will be further discussed throughout the following paragraphs.

Figure 5D shows the polarization curves measured in O_2 saturated 0.1 M HClO₄ solution. The Pt/NMC has also showed better ORR activity over the control group in the acidic media. The half-wave potential of the Pt/NMC has a positive shift of ~100 mV, compared with that of the Pt/ Vulcan, and a 20 mV of positive shift, compared with the Pt/ C-com. The specific activity of each sample is obtained by the calculation based on limiting diffusion current and ECSA, and the values of the Pt/NMC, the Pt/Vulcan and the Pt/C-com are 0.197, 0.048, and 0.067 mA cm⁻², respectively. The specific activity of the Pt/NMC is 4.1 times higher than that of the Pt/ Vulcan with a relatively close loading of Pt. The mass activities of the Pt/NMC, the Pt/Vulcan, and the Pt/C-com are 0.384, 0.047, and 0.065 A mg_{Pt}⁻¹, respectively. The mass activity of



Figure 6. ADT of (A) Pt/NMC, (B) Pt/Vulcan, and (C) Pt/C-com in O_2 -saturated 0.1 M HClO₄ aqueous solution at a scan rate of 10 mV s⁻¹; (D) is the comparison of the mass activities of the samples at 0.9 V (vs RHE).

the Pt/NMC is the highest in these three samples, which is 8.1 times of the Pt/Vulcan and 5.9 times of the Pt/C-com. The summary of ORR performance of each sample can be seen in Table S3 in the Supporting Information, and the comparison between the samples of this work and other published research can be seen in Table S4 in the Supporting Information. It is necessary to mention that the acquired ORR activity of Pt/Ccom is relatively lower than the normal results reported by other researchers^{52,53} (see Table S5 in the Supporting Information for details). This may be caused by the contamination of Cl⁻ ions, which is inevitable by using Ag/ AgCl reference electrode, and the incomplete electrochemical cell cleanliness. However, this could be a systematic deviation, because of the fact that all of the samples were processed under the same conditions. It is undoubted that the ORR activity can be significantly enhanced by using NMC as the catalyst support. These excellent catalytic activity enhancements indicate that this novel carbon material can be an excellent support with ultrahigh specific area and high stability for Pt nanoparticles, because of its special roelike structure and the N-doping.

The accelerated durability test of the samples has been processed in O_2 -saturated 0.1 M HClO₄ solution for 5000 cycles between 0.6–1.1 V (vs RHE). Figure 6 and Table 2 show the polarization curves and the mass activities of each sample before and after ADT. The polarization curve of the Pt/NMC (Figure 6A) only changes slightly after ADT, and its half-wave potential decreases only by 7 mV. However, the half-wave potential of the Pt/Vulcan and the Pt/C-com shows a negative shift of 35 and 30 mV, respectively. The retention rates of the mass activities of Pt/NMC, Pt/Vulcan, and Pt/C-com are 74%, 63%, and 58%, respectively. The above data indicate that the NMC can enhance the long-term ORR activity of loaded Pt nanoparticles. Meanwhile, the ECSA of

Table 2. Mass Activities and the Half-Wave Potential of the Samples before and after ADT

| | | $\begin{array}{c} \text{Mass Activity} \\ \text{(A } \text{mg}_{\text{Pt}}^{-1} \text{)} \end{array}$ | | |
|-----------|----------------------------|---|-------|-----------------------|
| sample | half-wave potential (V) | before | after | retention rate (%) |
| Pt/Vulcan | 0.778 | 0.047 | 0.030 | 63 |
| Pt/C-com | 0.859 | 0.065 | 0.038 | 58 |
| Pt/NMC | 0.879 | 0.384 | 0.282 | 74 |

Pt/NMC after ADT is still more than two times of Pt/C-com. The N-doped carbon and its high specific area can effectively retard the degradation of ECSA.

After a long period of cycling, the agglomeration of the nanoparticles loaded on the surface of the support and the spoil of the crystal structure lead to the degradation of ORR catalysts. Further exploration has been made to prove the excellent long-term electrochemical performance of the Pt/ NMC. HRTEM was used to characterize the particle size and the morphology of Pt nanoparticles on the surface of three samples before and after ADT. As shown in Figure 7 and Table 1, after 5000 potential cycles of ADT, the Pt particles on the NMC remain uniform, but a slight increase in average particle size also exists, while both the Pt/Vulcan (Figure 7A) and the Pt/C-com (Figure 7B) have obvious agglomeration and their particle size distribution becomes much broader. Several larger Pt nanoparticles can also be observed in the TEM picture of the Pt/NMC (Figure 7C), because some small Pt clusters have a tendency to dissolve and redeposit on the adjacent Pt nanoparticles, which could form an appropriate size to reduce the surface energy during the cycling process.^{31,54} This is also the main reason for the previously mentioned decline in ECSA. However, most of the platinum nanoparticles keep their original size, which is due to the interaction between the Pt

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Figure 7. TEM images and particle size distribution of (A) Pt/Vulcan, (B) Pt/C-com, and (C) Pt/NMC.

and N that stabilizes the Pt nanoparticles loaded on the NMC. This comparison strongly indicates that using the NMC as a stable catalyst support is beneficial to the long-term electrochemical performance of the catalyst. Notably, some published research has shown that the ultrahigh specific surface area of the carbon support (>1800 m² g⁻¹) may cause electrochemical corrosion, such as the structural damage, the loss of ORR activity, and the loss of Pt catalyst.^{20,55–57} However, this corrosive effect has not been observed from the ADT results and the TEM images mentioned above. The retention rate (Table 2) of the Pt/NMC after ADT is higher than Pt/Vulcan and Pt/C-com, and the structure of Pt/NMC remains unchanged after ADT (Figure 7), which indicates that the effects of high specific surface area of the NMC on the catalyst are positive. The high and appropriate specific surface area provides a more uniform distribution of Pt nanoparticles.

4. CONCLUSION

The nitrogen-doped carbon with a mesoporous structure and high nitrogen content has been synthesized by a simple synthesis procedure. Through a series of characterizations, we have confirmed that using the NMC as a catalyst support brings higher specific surface area and the regulation in the electronic structure of the carbon by the doping of N atoms, which makes the Pt nanoparticles distribute in a more uniform way on the support, and then promotes the ORR activity of the Pt nanoparticles by synergistic effect. The electrochemical tests show that the Pt/NMC exhibits higher ORR activity at a lower platinum loading (9.2 wt %), in both acidic and alkaline media. As a modified carbon support, the NMC has significantly improved the ORR activity of pure platinum catalyst and greatly enhanced the utilization rate of platinum. At the same time, according to the ADT result and the HRTEM images of the cycled samples, the NMC can reduce the agglomeration of Pt nanoparticles, which further improves the cycle life of the Pt catalyst. In summary, the NMC with Pt nanoparticles could be an excellent ORR catalyst with lower cost, which may have potential in application as the cathode catalyst in fuel cells.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b01242.

CV/LSV, XPS, TEM/SEM, and summary tables to replenish the properties of NMC and Pt/NMC (PDF)

AUTHOR INFORMATION

Corresponding Author

*Tel./Fax: 0086-592-2186935. E-mail: jbzhao@xmu.edu.cn. ORCID [©]

Jinbao Zhao: 0000-0002-2753-7508

Author Contributions

[§]These authors made equal contributions and share the first authorship.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Bezerra, C. W. B.; Zhang, L.; Liu, H.; Lee, K.; Marques, A. L. B.; Marques, E. P.; Wang, H.; Zhang, J. A review of heat-treatment effects on activity and stability of PEM fuel cell catalysts for oxygen reduction reaction. *J. Power Sources* **2007**, *173*, 891–908.

(2) Li, M.; Zhao, Z.; Cheng, T.; Fortunelli, A.; Chen, C. Y.; Yu, R.; Zhang, Q.; Gu, L.; Merinov, B. V.; Lin, Z.; et al. Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction. *Science* **2016**, *354*, 1414.

(3) Fu, T.; Fang, J.; Wang, C.; Zhao, J. Hollow porous nanoparticles with Pt skin on Ag-Pt alloy structure as highly active electrocatalyst for oxygen reduction reaction. *J. Mater. Chem. A* **2016**, *4*, 8803–8811.

(4) Sharma, S.; Pollet, B. G. Support materials for PEMFC and DMFC electrocatalysts-A review. *J. Power Sources* **2012**, *208*, 96–119.

(5) Galeano, C.; Meier, J. C.; Peinecke, V.; Bongard, H.; Katsounaros, I.; Topalov, A. A.; Lu, A.; Mayrhofer, K. J.; Schuth, F. Toward highly stable electrocatalysts via nanoparticle pore confinement. J. Am. Chem. Soc. **2012**, 134, 20457–65.

(6) Wang, X.; Li, W.; Chen, Z.; Waje, M.; Yan, Y. Durability investigation of carbon nanotube as catalyst support for proton exchange membrane fuel cell. *J. Power Sources* **2006**, *158*, 154–159.

(7) Tesfu-Zeru, T.; Sakthivel, M.; Drillet, J. F. Investigation of mesoporous carbon hollow spheres as catalyst support in DMFC cathode. *Appl. Catal., B* **2017**, *204*, 173–184.

(8) Kim, D.-S.; Zeid, E. F. A.; Kim, Y.-T. Additive treatment effect of TiO_2 as supports for Pt-based electrocatalysts on oxygen reduction reaction activity. *Electrochim. Acta* **2010**, *55*, 3628–3633.

(9) Fu, T.; Huang, J.; Lai, S.; Zhang, S.; Fang, J.; Zhao, J. Pt skin coated hollow Ag-Pt bimetallic nanoparticles with high catalytic activity for oxygen reduction reaction. *J. Power Sources* **2017**, 365, 17–25.

(10) Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. *Science* **2009**, *323*, 760.

(11) Li, W.; Yang, D.; Chen, H.; Gao, Y.; Li, H. Sulfur-doped carbon nanotubes as catalysts for the oxygen reduction reaction in alkaline medium. *Electrochim. Acta* **2015**, *165*, 191–197.

(12) Yu, D.; Xue, Y.; Dai, L. Vertically Aligned carbon nanotube arrays co-doped with phosphorus and nitrogen as efficient metal-free electrocatalysts for oxygen reduction. *J. Phys. Chem. Lett.* **2012**, *3*, 2863.

(13) Qu, L.; Liu, Y.; Baek, J.; Dai, L. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells. *ACS Nano* **2010**, *4*, 1321.

(14) Wei, W.; Liang, H.; Parvez, K.; Zhuang, X.; Feng, X.; Müllen, K. Nitrogen-doped carbon nanosheets with size-defined mesopores as highly efficient metal-free catalyst for the oxygen reduction reaction †. *Angew. Chem., Int. Ed.* **2014**, *53*, 1570.

(15) Zhou, X.; Bai, Z.; Wu, M.; Qiao, J.; Chen, Z. 3-Dimensional porous N-doped graphene foam as a non-precious catalyst for the oxygen reduction reaction. *J. Mater. Chem. A* **2015**, *3*, 3343–3350.

(16) Guo, D.; Shibuya, R.; Akiba, C.; Saji, S.; Kondo, T.; Nakamura, J. Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science* **2016**, *351*, 361–365.

(17) Niu, W.; Li, L.; Wang, N.; Zeng, S.; Liu, J.; Zhao, D.; Chen, S. Volatilizable templates-assisted scalable preparation of honeycomblike porous carbons for efficient oxygen electroreduction. *J. Mater. Chem. A* **2016**, *4*, 10820.

(18) Kong, K. J.; Choi, Y.; Ryu, B. H.; Lee, J. O.; Chang, H. Investigation of metal/carbon-related materials for fuel cell

applications by electronic structure calculations. *Mater. Sci. Eng., C* 2006, 26, 1207–1210.

(19) Gao, S.; Fan, H.; Wei, X.; Li, L.; Bando, Y.; Golberg, D. Nitrogen-doped carbon with mesopore confinement efficiently enhances the tolerance, sensitivity, and stability of a Pt catalyst for the oxygen reduction reaction. *Part. Part. Syst. Charact.* **2013**, *30*, 864–872.

(20) Wang, Y.-J.; Fang, B.; Li, H.; Bi, X. T.; Wang, H. Progress in modified carbon support materials for Pt and Pt-alloy cathode catalysts in polymer electrolyte membrane fuel cells. *Prog. Mater. Sci.* **2016**, *82*, 445–498.

(21) Perazzolo, V.; Brandiele, R.; Durante, C.; Zerbetto, M.; Causin, V.; Rizzi, G. A.; Cerri, I.; Granozzi, G.; Gennaro, A. Density functional theory (DFT) and experimental evidences of metal-support interaction in platinum nanoparticles supported on nitrogen- and sulfur-doped mesoporous carbons: synthesis, activity, and stability. *ACS Catal.* **2018**, *8*, 1122–1137.

(22) Brandiele, R.; Durante, C.; Zerbetto, M.; Vicentini, N.; Kosmala, T.; Badocco, D.; Pastore, P.; Rizzi, G. A.; Isse, A. A.; Gennaro, A. Probing the correlation between Pt-support interaction and oxygen reduction reaction activity in mesoporous carbon materials modified with Pt-N active sites. *Electrochim. Acta* **2018**, 277, 287–300.

(23) Perini, L.; Durante, C.; Favaro, M.; Perazzolo, V.; Agnoli, S.; Schneider, O.; Granozzi, G.; Gennaro, A. Metal-support interaction in platinum and palladium nanoparticles loaded on nitrogen-doped mesoporous carbon for oxygen reduction reaction. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1170–1179.

(24) Xie, B.; Zhang, Y.; Zhang, R. Coassembly and high ORR performance of monodisperse Pt nanocrystals with a mesopore-rich nitrogen-doped graphene aerogel. *J. Mater. Chem. A* **2017**, *S*, 17544–17548.

(25) Liang, H. W.; Zhuang, X.; Brüller, S.; Feng, X.; Müllen, K. Hierarchically porous carbons with optimized nitrogen doping as highly active electrocatalysts for oxygen reduction. *Nat. Commun.* **2014**, *5*, 4973.

(26) Tang, J.; Liu, J.; Li, C.; Li, Y.; Tade, M. O.; Dai, S.; Yamauchi, Y. Synthesis of nitrogen-doped mesoporous carbon spheres with extra-large pores through assembly of diblock copolymer micelles. *Angew. Chem., Int. Ed.* **2014**, *54*, 588.

(27) Guo, X.; Li, L.; Zhang, X.; Chen, J. Platinum nanoparticles encapsulated in nitrogen-doped mesoporous carbons as methanol-tolerant oxygen reduction electrocatalysts. *ChemElectroChem* **2015**, *2*, 404–411.

(28) Cao, J.; Chen, Z.; Xu, J.; Wang, W.; Chen, Z. Mesoporous carbon synthesized from dual colloidal silica/block copolymer template approach as the support of platinum nanoparticles for direct methanol fuel cells. *Electrochim. Acta* **2013**, *88*, 184–192.

(29) Eguizabal, A.; Uson, L.; Sebastian, V.; Hueso, J. L.; Pina, M. P. Efficient and facile tuning of Vulcan XC72 with ultra-small Pt nanoparticles for electrocatalytic applications. *RSC Adv.* **2015**, *5*, 90691–90697.

(30) Vinayan, B. P.; Nagar, R.; Rajalakshmi, N.; Ramaprabhu, S. Novel platinum–cobalt alloy nanoparticles dispersed on nitrogendoped graphene as a cathode electrocatalyst for PEMFC applications. *Adv. Funct. Mater.* **2012**, *22*, 3519–3526.

(31) Peera, S. G.; Arunchander, A.; Sahu, A. K. Platinum nanoparticles supported on nitrogen and fluorine co-doped graphite nanofibers as an excellent and durable oxygen reduction catalyst for polymer electrolyte fuel cells. *Carbon* **2016**, *107*, 667–679.

(32) He, C.; Meng, H.; Yao, X.; Shen, P. K. Rapid formation of nanoscale tungsten carbide on graphitized carbon for electrocatalysis. *Int. J. Hydrogen Energy* **2012**, *37*, 8154–8160.

(33) Hu, M.; Yan, Y.; Duan, X.; Ye, L.; Zhou, J.; Lin, H.; Yuan, Y. Effective anchoring of silver nanoparticles onto N-doped carbon with enhanced catalytic performance for the hydrogenation of dimethyl oxalate to methyl glycolate. *Catal. Commun.* **2017**, *100*, 148.

(34) Zhao, Y.; Zhou, Y.; O'Hayre, R.; Shao, Z. Electrocatalytic oxidation of methanol on Pt catalyst supported on nitrogen-doped

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graphene induced by hydrazine reduction. J. Phys. Chem. Solids 2013, 74, 1608-1614.

(35) Stambula, S.; Gauquelin, N.; Bugnet, M.; Gorantla, S.; Turner, S.; Sun, S.; Liu, J.; Zhang, G.; Sun, X.; Botton, G. A. Chemical structure of nitrogen-doped graphene with single platinum atoms and atomic clusters as a platform for the PEMFC electrode. *J. Phys. Chem. C* **2014**, *118*, 3890–3900.

(36) Lv, Q.; Si, W.; Yang, Z.; Wang, N.; Tu, Z.; Yi, Y.; Huang, C.; Jiang, L.; Zhang, M.; He, J.; Long, Y. Nitrogen-doped porous graphdiyne: a highly efficient metal-free electrocatalyst for oxygen reduction reaction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 29744.

(37) Yang, H. B.; Miao, J.; Hung, S.-F.; Chen, J.; Tao, H. B.; Wang, X.; Zhang, L.; Chen, R.; Gao, J.; Chen, H. M.; Dai, L.; Liu, B. Identification of catalytic sites for oxygen reduction and oxygen evolution in N-doped graphene materials: Development of highly efficient metal-free bifunctional electrocatalyst. *Sci. Adv.* **2016**, *2*, e1501122.

(38) Ratso, S.; Kruusenberg, I.; Vikkisk, M.; Joost, U.; Shulga, E.; Kink, I.; Kallio, T.; Tammeveski, K. Highly active nitrogen-doped fewlayer graphene/carbon nanotube composite electrocatalyst for oxygen reduction reaction in alkaline media. *Carbon* **2014**, *73*, 361–370.

(39) Matter, P. H.; Zhang, L.; Ozkan, U. S. The role of nanostructure in nitrogen-containing carbon catalysts for the oxygen reduction reaction. *J. Catal.* **2006**, *239*, 83–96.

(40) Maldonado, S.; Stevenson, K. J. Influence of nitrogen doping on oxygen reduction electrocatalysis at carbon nanofiber electrodes. *J. Phys. Chem. B* **2005**, *109*, 4707–16.

(41) Yang, S.; Feng, X.; Wang, X.; Mullen, K. Graphene-based carbon nitride nanosheets as efficient metal-free electrocatalysts for oxygen reduction reactions. *Angew. Chem., Int. Ed.* **2011**, *50*, 5339–43.

(42) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.

(43) Holme, T.; Zhou, Y.; Pasquarelli, R.; O'Hayre, R. First principles study of doped carbon supports for enhanced platinum catalysts. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9461–8.

(44) Cheung, T. T. P. X-ray photoemission of small platinum and palladium clusters. *Surf. Sci.* **1984**, *140*, 151–164.

(45) Zhang, L. M.; Wang, Z. B.; Zhang, J. J.; Sui, X. L.; Zhao, L.; Gu, D. M. Honeycomb-like mesoporous nitrogen-doped carbon supported Pt catalyst for methanol electrooxidation. *Carbon* **2015**, *93*, 1050–1058.

(46) Zhou, W.; Zhou, J.; Zhou, Y.; Lu, J.; Zhou, K.; Yang, L.; Tang, Z.; Li, L.; Chen, S. N-doped carbon-wrapped cobalt nanoparticles on N-doped graphene nanosheets for high-efficiency hydrogen production. *Chem. Mater.* **2015**, *27*, 2026–2032.

(47) Zhou, W.; Xiong, T.; Shi, C.; Zhou, J.; Zhou, K.; Zhu, N.; Li, L.; Tang, Z.; Chen, S. Bioreduction of precious metals by microorganism: efficient gold@N-doped carbon electrocatalysts for the hydrogen evolution reaction. *Angew. Chem.* **2016**, *128*, 8556–8560.

(48) Li, L.; Chen, S. G.; Wei, Z. D.; Qi, X. Q.; Xia, M. R.; Wang, Y. Q. Experimental and DFT study of thiol-stabilized Pt/CNTs catalysts. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16581–16587.

(49) Takahashi, I.; Kocha, S. S. Examination of the activity and durability of PEMFC catalysts in liquid electrolytes. *J. Power Sources* **2010**, *195*, 6312–6322.

(50) Guterman, V. E.; Pakharev, A. Y.; Tabachkova, N. Y. Microstructure and size effects in Pt/C and Pt3Ni/C electrocatalysts synthesized in solutions based on binary organic solvents. *Appl. Catal., A* **2013**, 453, 113–120.

(51) Galeano, C.; Meier, J. C.; Soorholtz, M.; Bongard, H. J.; Baldizzone, C.; Mayrhofer, K. J. J.; Schueth, F. Nitrogen-Doped Hollow Carbon Spheres as a Support for Platinum-Based Electrocatalysts. *ACS Catal.* **2014**, *4*, 3856–3868. (52) Zhang, S.; Chen, S. Enhanced-electrocatalytic activity of Pt nanoparticles supported onnitrogen-doped carbon for the oxygen reduction reaction. *J. Power Sources* **2013**, *240*, 60–65.

(53) Huang, X.; Zhao, Z.; Cao, L.; Chen, Y.; Zhu, E.; Lin, Z.; Li, M.; Yan, A.; Zettl, A.; Wang, Y. M.; Duan, X.; Mueller, T.; Huang, Y. High-performance transition metal-doped Pt3Ni octahedra for oxygen reduction reaction. *Science* **2015**, *348*, 1230–1234.

(54) Shao-Horn, Y.; Sheng, W. C.; Chen, S.; Ferreira, P. J.; Holby, E. F.; Morgan, D. Instability of supported platinum nanoparticles in low-temperature fuel cells. *Top. Catal.* **2007**, *46*, 285–305.

(55) Li, Y.; Li, Z.; Shen, P. K. Simultaneous formation of ultrahigh surface area and three-dimensional hierarchical porous graphene-like networks for fast and highly stable supercapacitors. *Adv. Mater.* **2013**, 25, 2474–2480.

(56) Lust, E.; Vaarmets, K.; Nerut, J.; Tallo, I.; Valk, P.; Sepp, S.; Härk, E. Influence of specific surface area and microporositymesoporosity of pristine and Pt-nanoclusters modified carbide derived carbon electrodes on the oxygen electroreduction. *Electrochim. Acta* **2014**, *140*, 294–303.

(57) Takasu, Y.; Kawaguchi, T.; Sugimoto, W.; Murakami, Y. Effects of the surface area of carbon support on the characteristics of highlydispersed Pt-Ru particles as catalysts for methanol oxidation. *Electrochim. Acta* **2003**, *48*, 3861–3868.