Size effects of platinum particles@CNT on HER and ORR performance

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ABSTRACT Platinum (Pt) is an efficient catalyst for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), but the debate of the relevance between the Pt particle size and its electrocatalytic activity still exist. The strong metal-support interaction (SMSI) between the metal and carrier causes the charge transfer and mass transport from the support to the metal. Herein, Pt species (0.5 wt.%) with various particle sizes supported on carbon nanotubes (CNTs) have been synthesized by a photo-reduction method. The ~1.5 nm-sized Pt catalyst shows much higher HER performance than the counterparts in all pH solutions, and the mass activity of it is even 23–36 times that of Pt/C. While for ORR, the ~3 nm-sized Pt catalyst exhibits the optimal performance, and the mass activity is 3 times and even 16 times that of Pt/C in acidic and alkaline media, respectively. The high HER and ORR performances of the ~1.5 nm- and ~3 nm-sized Pt catalysts benefit from the SMSI between Pt and the CNTs matrix and the higher ratio of face sites to edge sites, which is meaningful for the design of efficient electrocatalysts for renewable energy application.

Keywords: size effect, HER, ORR, platinum, strong metal-support interaction

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) with hydrogen as anode fuel is a kind of clean energy transport system with water as the only product ($\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$) [1–3], which can avoid the environmental pollution. The cathodic oxygen reduction reaction (ORR) is sluggish because of the 4e reaction process, which is the rate

controlling step for the cell performance. On the other hand, high-purity hydrogen as anode fuel is necessary to avoid the CO “poisoning” phenomenon of Pt in the anode chamber of PEMFCs. Hydrogen evolution reaction (HER) is a desirable approach to obtain high-purity hydrogen [4,5]. At present, Pt is still the efficient ORR and HER catalysts because of its high electrocatalytic performance. But the amounts of Pt need to reach 20 wt.% and even 20–40 wt.% for using as HER and ORR catalysts, respectively, which limits the practical application due to its limited reserve and high price [6,7]. Although Pt-free electrocatalysts, such as phosphides [8], chalcogenides [9], oxides [10,11], nitrides [12] and carbon based materials [13], have shown promising HER and/or ORR activities, it is rather difficult to completely replace Pt with these catalysts due to the significant gap in performance between the present state-of-the-art Pt-based catalysts and the Pt-free catalysts. Therefore, the challenge is to develop efficient platinum-group-metal-free electrocatalysts, or to greatly decrease the Pt loading amount by enhancing the specific activity of Pt or improving the utilization efficiency of Pt atoms.

To overcome the challenges associated with Pt-based HER/ORR catalysts, it is critical to increase the utilization efficiency of Pt species. Though significant efforts have been made to enhance the catalytic activity of Pt and reduce the amount of Pt in industrial applications, particle size and size distribution are even important factors affecting the electrochemical activity of Pt in ORR and HER [14,15]. Generally, the electronic or geometric structures of Pt will be altered when the particle size of Pt

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nanoparticles is tuned. With the Pt particle size decreasing, the proportion of the low-coordinated surface sites (corner or edge) increases, which leads to enhanced catalytic activity [16]. Yan *et al.* [17] investigated the size effect of Pt nanoparticles supported on S-doped carbon material on HER, and found that ~1.5 nm Pt clusters had better HER activity than Pt single atoms, indicating the electron transfer played an important role in HER. Garryev *et al.* [18] studied the effect of different Pt particle sizes on ORR activity by using a metal-organic framework (MOF) to regulate the particle size, and pointed out that Pt particles with size of 1.1 nm exhibited better ORR activity. Though lots of efforts have been made to enhance the HER and/or ORR catalytic activities of Pt species by modulating the particle size, the debates of what sized Pt particle determining the main role during the electrochemical reaction still exist.

Strong metal-support interaction (SMSI) plays an important role in the catalytic process. Factors such as the composition, morphology, doping and surface modification of the support, as well as changes in the size or composition of the nanoparticles, can affect the SMSI, thereby affecting the catalytic performance [19]. Carbon nanotubes (CNTs), as a typical one-dimensional material, have a unique pore structure with good mechanical, thermal and electrical properties. Due to the large specific surface area of CNTs, Pt species can be effectively anchored homogeneously. In addition, the confinement of metal into CNTs has been of great interest for electronic properties in recent years [20–22]. Interaction between the encapsulated nanoparticles and the CNT surface could be strengthened because the planarity deviation of CNTs causes the π -electron density to shift from a concave to a convex surface, leading to an electron potential difference between the inner and outer walls of CNTs. Such synergic interactions could enhance the electronic properties of the resultant confinement of metal into CNTs [23,24].

Herein, small amount of Pt species (0.5 wt.%) with various particle sizes dispersed on the polydopamine modified CNTs (CNTs@PDA) have been designed and prepared by a light-irradiated reduction method, and the effects of Pt particle size on the performance of HER and ORR in different pH electrolytes have been systemically studied. It was found that Pt nanoparticles with size of ~1.5 nm exhibited much higher HER catalytic activity from acidic to alkaline conditions because of the SMSI between the Pt nanoparticles and CNTs matrix, while the size of ~3 nm was desirable for ORR in acidic and alkaline media.

EXPERIMENTAL SECTION

Materials

Graphitized multi-walled CNTs (>99.9%, inner diameter: 5–10 nm, outer diameter: 10–20 nm, length: 10–30 μm) were purchased from Shanghai Macklin Biochemical Co., Ltd. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%) was purchased from Adamas reagent Co., Ltd. Dopamine hydrochloride ($\text{C}_8\text{H}_{11}\text{NO}_2 \cdot \text{HCl}$, 98%) was purchased from Aladdin Chemistry Co., Ltd. Ethylene glycol (AR), potassium permanganate (KMnO_4 , AR) and sodium hydroxide (NaOH , AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion D-520 dispersion (5 wt.%) was purchased from Dupont China Holding Co., Ltd. Commercial 20 wt.% Pt/C was purchased from Shanghai HEPHAS Energy Equipment Co., Ltd. All materials were used as received without further purification.

Synthesis of Pt/CNTs

CNTs (40 mg) dispersed in 36 mL of deionized (DI) water were added in three conical flasks (named 1#, 2#, 3#), and then 8 mg of dopamine hydrochloride and 4 mL of 1.58 mg mL^{-1} potassium permanganate were added, and the obtained suspensions were stirred continuously for 6 h. After being centrifuged and washed three times with DI water, the surface modified CNTs with polydopamine (CNTs@PDA) were obtained. The surface modified CNTs were then dispersed into 60 mL of ethylene glycol in flasks (1#, 2#, 3#) and sonicated for 30 min.

Pt catalyst with size of ~1.5 nm: 200 μL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ aqueous solution (25 mg mL^{-1}) and 5 mL of 0.1 mol L^{-1} NaOH were then injected into flask 1# under vigorous stirring. Subsequently, the mixture was subjected to light irradiation under continuous stirring for 1 h by a 300 W Xe lamp, and then washed with deionized (DI) water and ethanol, and dried at 60°C under vacuum. Then the Pt catalyst with size of ~1.5 nm was obtained.

Pt catalyst with size of ~3 nm: 200 μL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ aqueous solution (25 mg mL^{-1}) and 3 mL of 0.1 mol L^{-1} NaOH were injected into flask 2# under vigorous stirring. Subsequently, the mixture was subjected to light irradiation under continuous stirring for 2 h by a 300 W Xe lamp, and then washed with DI water and ethanol, and dried at 60°C under vacuum. Then the Pt catalyst with size of ~3 nm was obtained.

Pt catalyst with size of ~6 nm: 200 μL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ aqueous solution (25 mg mL^{-1}) and 1 mL of 0.1 mol L^{-1}

NaOH were then injected into flask 3# under vigorous stirring. Subsequently, the mixture was refluxed at 120°C for 2 h, and washed with DI water and ethanol, and then dried at 60°C under vacuum. Then the Pt catalyst with size of ~6 nm was obtained.

Materials characterization

The powder X-ray diffraction (XRD) patterns were acquired on a Rigaku D/Max-2550 V X-ray diffractometer with a Cu K α radiation target (40 kV, 40 mA) at a scan rate of 4° min⁻¹. Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet iS10 FTIR spectrometer using the KBr technique. Raman spectrum was recorded on a Renishaw in Via-Reflex. X-ray photoelectron spectroscopy (XPS) signals were measured on a Thermo Fisher Scientific ESCALAB250 XPS instrument with monochromatic Mg K α X-rays, which was calibrated with carbon base. Scanning electron microscopy (SEM) imaging was carried out using an FEI Magellan-400 field emission scanning electron microscopy (5 kV). Transmission electron microscopy (TEM) patterns were collected using a JEM-2100F field emission transmission electron microscopy (200 kV). The Pt loading of Pt/CNTs was measured *via* an inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu).

Electrochemical measurements

The electrochemical measurements were carried out in 0.5 mol L⁻¹ H₂SO₄, 1.0 mol L⁻¹ Na₂SO₄ and 1.0 mol L⁻¹ KOH solutions by a CH Instruments 760E electrochemical workstation using a standard three-electrode setup. During HER and ORR tests, a glassy carbon electrode (GCE) coated with catalysts, an Ag/AgCl electrode which was stored in saturated KCl solution, and a graphite rod were employed as the working electrode, reference electrode and counter electrode, respectively. The potentials measured were calibrated to reversible hydrogen electrode (RHE) based on the equation: ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.1989 \text{ V}$), where $E_{\text{Ag/AgCl}}$ was the external potential measured against the Ag/AgCl reference electrode, which has been corrected with an RHE. The catalyst dispersion was prepared by mixing 5 mg of catalysts with 90 μL of DI water, 900 μL of isopropanol and 10 μL of Nafion solution followed by ultrasonication for 30 min. For the fabrication of working electrode, 7.9 μL of the as-prepared catalyst dispersion was loaded onto a glassy carbon electrode with the diameter of 0.5 cm (0.19625 cm²), and then dried at room temperature. The actual Pt mass loading were 0.220, 0.212, 0.203 and 7.9 μg for ~1.5 nm Pt, ~3 nm Pt, ~6 nm Pt and

commercial 20% Pt/C, respectively.

HER: Before electrochemical measurements, high-purity N₂ gas was bubbled into the solution for at least 30 min. Before recording the polarization curves, the working electrode was subjected to potential cycling between 0.2 and -0.2 V *vs.* RHE, between 0.2 and -0.5 V *vs.* RHE, and between 0.2 and -0.4 V *vs.* RHE at 100 mV s⁻¹ in 0.5 mol L⁻¹ H₂SO₄, 1.0 mol L⁻¹ Na₂SO₄, and 1.0 mol L⁻¹ KOH, respectively, until stable voltammogram curves were obtained. Linear sweep voltammogram (LSV) was carried out at 10 mV s⁻¹ for the polarization curves. Besides, the electrochemical impedance spectroscopy (EIS) measurements were conducted in a frequency range of 10⁻² Hz to 10⁵ Hz with an amplitude of 5 mV at a fixed voltage.

ORR: The cyclic voltammetric (CV) measurements were performed in 0.1 mol L⁻¹ O₂-saturated HClO₄ and 1.0 mol L⁻¹ O₂-saturated KOH solutions at a scan rate of 100 mV s⁻¹. Then, the LSV curves were measured at a scan rate of 5 mV s⁻¹ with a rotating speed of 1600 rpm.

The kinetic parameters of ORR on Pt/CNTs catalysts were investigated with a rotating disc electrode (RDE). Electron transfer number (n) and kinetic current density (j_k) were calculated by the Koutecky-Levich (K-L) equation [25,26]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{j_k} \quad (1)$$

$$B = 0.2nFC_0D_{\text{O}_2}^{\frac{2}{3}}\nu^{-\frac{1}{6}}, \quad (2)$$

$$j_k = nFkC_{\text{O}}, \quad (3)$$

where j refers to the current density obtained from the test, j_k and j_l are the kinetic current density and the diffusion limit current density, respectively. n is the electron transfer number during the oxygen reduction process, F is the Faraday constant (96,485 C mol⁻¹), C_{O} is the oxygen solubility (1.26 $\times 10^{-3}$ mol L⁻¹ in 0.1 mol L⁻¹ HClO₄, and 0.93 $\times 10^{-3}$ mol L⁻¹ in 1.0 mol L⁻¹ KOH), ν is the kinetic viscosity of the electrolyte (0.01 cm² s⁻¹), and D_{O_2} is the diffusion coefficient of O₂ in 0.1 mol L⁻¹ HClO₄ (1.93 $\times 10^{-5}$ cm² s⁻¹) and 1.0 mol L⁻¹ KOH solution (1.76 $\times 10^{-5}$ cm² s⁻¹), k is the electron transfer rate constant, and B is calculated from the slope of the K-L curve (j^{-1} *vs.* $\omega^{-1/2}$). When the speed is expressed in rpm, the coefficient is 0.2.

RESULTS

The preparation process of Pt particles by the photo-reduction method is schematically shown in Fig. 1a. Specifically, CNTs were first modified with PDA to form a negatively charged surface (Fig. S1a) and then uni-

Figure 1 (a) Schematic illustration of the synthetic route of Pt/CNTs by the photo-reduction method. (b) FTIR spectra of Pt/CNTs, CNTs@PDA and pristine CNTs. (c) Raman spectra of the corresponding samples.

formly dispersed in ethylene glycol. PDA with abundant catechol and amine functional groups, can chelate metal ions such as PtCl_6^{2-} . Eventually, the chelated PtCl_6^{2-} ions were reduced by the photoelectrons produced by PDA under Xenon lamp irradiation [24]. Due to the unique electronic structure and the surface characteristic of CNTs, the PDA can easily modify the surface of CNTs *via* π - π interactions [27]. Here, the surface PDA modification of CNTs plays dual roles to supply the photoelectron generator to reduce PtCl_6^{2-} species under irradiation due to the photosensitive property of PDA, and on the other hand to connect active sites such as Pt species in the whole CNT network simultaneously. XRD patterns of the obtained Pt/CNTs catalysts show no Pt-related diffraction peaks (Fig. S1b) because of the low amount of Pt loading (~0.5 wt.% in Table S1), implying no large-size Pt particles [28]. As shown in the FTIR spectra in Fig. 1b, the absorption peak at around 1625 cm^{-1} was assigned to the

N-H bending vibration, and the peak intensity increased after being modified with PDA, indicating the successful introduction of PDA. Besides, it can also be found that the vibrations at 1625 and 1650 cm^{-1} were inhibited after loading the Pt species on CNTs@PDA, which is due to the effect of anchoring Pt nanoparticles [28–30]. From the Raman spectra in Fig. 1c and the corresponding data in Table S2, the I_D/I_G ratio of CNTs@PDA increases slightly compared with that of CNTs, implying more defects and disordered structures introduced after the surface modification by PDA. While the I_D/I_G value of ~1.5 nm-sized Pt sample is lower than that of other catalysts, indicating that part of defect sites were anchored by small-sized Pt nanoparticles, while in contrast large-sized platinum particles would increase the structural disorder of the materials [31,32]. In addition, the positive shift of G and G' peaks was founded after coating with PDA, due to the increasing number of layers resulting in

a slight modification of the intra C–C bond in scrolling structures and a change of the phonon dispersion [32].

Fig. 2a–c show the SEM images of the prepared Pt/CNTs catalysts with different particle sizes of Pt species, with the Pt nanoparticles homogeneously dispersed on the CNTs, which was further proved by the SEM images with different magnifications in Figs S2–S4. TEM images in the insets of Fig. 2d–f consolidate the even dispersion of Pt particles, with the sizes of ~1.5, ~3 and ~6 nm shown in the high resolution TEM (HRTEM) images, respectively. PDA with a thickness of 0.38 nm was also observed by HRTEM (Fig. S5). The multi-circles selected area electron diffraction (SAED) patterns in the insets of Fig. 2d–f indicate the polycrystalline characteristics of the prepared Pt particles. Moreover, the histograms in Fig. 2g–i which are calculated by averaging the diameter of ~200 nanoparticles show the main particle size distributed at ~1.5 nm, ~3 nm and ~6 nm, respectively, in-

dicating the successful preparation of Pt particles with different sizes by the photo-reduction method. In addition, the high angle annular dark field (HAADF) (Fig. 2j) and the elemental mapping images (Fig. 2k–m) of the ~3 nm-sized Pt catalyst further verify the uniform dispersion of Pt nanoparticles, and the existence of N element further indicates the successful modification of PDA on the surface of CNTs.

The surface chemical states of the prepared samples were investigated by XPS, and all the calibrations were based on the standard binding energy of C–C at 284.8 eV. According to the full XPS spectra (Fig. S6), N and O signals were all detected for CNTs@PDA, indicating that the dopamine was successfully introduced on the CNTs surface since N and O were the typical elements in dopamine. To further explore the bonding configuration, high-resolution XPS spectra were collected and analyzed. As shown in Fig. 3a and the data in Table S3, the C 1s

Figure 2 SEM and HRTEM images of Pt/CNTs with sizes of (a, d) ~1.5 nm, (b, e) ~3 nm, and (c, f) ~6 nm. The TEM images of Pt/CNTs and the corresponding SAED patterns are in the insets of (d–f). Pt particle size distribution histograms: (g) ~1.5 nm, (h) ~3 nm, (i) ~6 nm. (j–m) HAADF and elemental mapping images of ~3 nm-sized Pt catalyst.

Figure 3 High-resolution XPS spectra of (a) C 1s, (b) O 1s, (c) N 1s and (d) Pt 4f for the prepared samples.

spectra were deconvoluted into five peaks at about 284.8, 285.4, 286.1, 287.4 and 288.6 eV, belonging to graphitic C, C–N, C–O, C=O and O–C=O, respectively, suggesting the interaction between N and the surrounding C atoms [33,34]. Especially, C=O and O–C=O peaks were found only after the deposition of Pt due to that the phenols of PDA can act as nucleation sites and self-reducing agents which convert catechol to quinone or O–C=O during the photo-reduction process [30]. The XPS spectra of O 1s for the catalysts are displayed in Fig. 3b, and the peaks of C=O, C–OH, and C–O can be found with the binding energies at 531.3, 532.2, and 533.6 eV, respectively. O 1s spectra have slightly changed after Pt particles are anchored, and the ~1.5 nm-sized Pt catalyst shifts negatively (0.18 eV) compared with CNTs@PDA. While the content of C–O increased obviously for the ~6 nm-sized Pt catalyst due to large Pt particle size (Table S3). The XPS N 1s spectra of the samples (Fig. 3c) were characterized by peaks at binding energies of 398.7, 400.3, 401.4, and 402.4 eV, assigned to pyridinic N, pyrrolic N, graphitic N and oxidized N, respectively, indicating that the Pt/CNTs catalysts have similar ratios of pyridinic nitrogen and

pyrrolic nitrogen (76.8% for ~1.5 nm Pt, 81% for ~3 nm Pt, 79.1% for ~6 nm Pt and 73.0% for CNTs@PDA). It has been reported that pyridinic nitrogen and pyrrolic nitrogen are beneficial to HER and ORR [35,36], which may lead to the excellent electrocatalytic performance of these catalysts. All N peaks of Pt/CNTs shift to a low binding energy compared with those of CNTs@PDA. The surface chemical states of Pt nanoparticles were also characterized by high-resolution Pt 4f XPS (Fig. 3d). Three sets of peaks located at Pt 4f_{7/2} and Pt 4f_{5/2} can be observed, attributed to metallic Pt⁰ and partially oxidized Pt^{δ+} (Pt²⁺ and Pt⁴⁺) species, respectively. Interestingly, with the decrease in Pt nanoparticle size, the binding energies of Pt 4f_{7/2} and Pt 4f_{5/2} shift positively, especially for the ~1.5 nm-sized Pt catalyst which shows a binding energy 0.53 and 0.05 eV higher than Pt/C and ~3 nm Pt catalyst, indicating more amount of Pt^{δ+} species produced. The contents of Pt²⁺ and Pt⁴⁺ in ~1.5 nm-sized Pt catalyst reach 34.62% and 18.40%, respectively (Table S3). The above results indicate that the charge transfers from Pt to CNTs matrix, suggesting the strong electronic interaction between the Pt nanoparticles and the support.

To investigate the size effect of Pt nanoparticles on the catalytic performance, HER activities of the Pt/CNTs catalysts were then evaluated using a three-electrode setup with graphite rod as the counter electrode in N_2 -saturated acidic ($0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, pH ~ 0.3), neutral ($1.0 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, pH ~ 7) and basic ($1.0 \text{ mol L}^{-1} \text{ KOH}$, pH ~ 14) media at room temperature. As shown in the LSV curves with iR correction (Fig. 4a–c), with the size of Pt nanoparticles decreasing, the overpotentials required to reach the current density of 10 mA cm^{-2} (η_{10}) become lower. Fig. 4a shows the HER performance of the catalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution with the specific performance comparison listed in Table S4. It can be seen that the $\sim 1.5 \text{ nm}$ -sized Pt catalyst shows the smallest onset potential of $\sim 1.3 \text{ mV}$ versus RHE. The η_{10} of $\sim 1.5 \text{ nm}$ -sized Pt catalyst is only 13.0 mV , which is much smaller than those of $\sim 3 \text{ nm}$ -sized Pt (33.7 mV) and $\sim 6 \text{ nm}$ -sized Pt (38.7 mV) samples and even 6 mV lower than that of Pt/C (19.5 mV), implying the superior electrocatalytic HER activity of the $\sim 1.5 \text{ nm}$ Pt catalyst. Moreover, the excellent HER catalytic activity makes the $\sim 1.5 \text{ nm}$ -sized Pt catalyst one of the most efficient Pt-based catalysts in acidic electrolytes (Fig. S7). In addition, the η_{10} of $\sim 1.5 \text{ nm}$ -sized Pt catalyst only decayed 10.0 mV after 10,000-cycles test, which was even more stable than that of Pt/C (10.2 mV), meaning the excellent long-term stability (Fig. 4d). In neutral solution, the $\sim 1.5 \text{ nm}$ -sized Pt catalyst still shows a higher HER activities with an onset potential of 236.7 mV (Table. S4) and a smaller η_{10} of 413.5 mV compared with $\sim 3 \text{ nm}$ Pt ($E_{\text{onset}} = 277.9 \text{ mV}$, $\eta_{10} = 482.9 \text{ mV}$) and $\sim 6 \text{ nm}$ Pt ($E_{\text{onset}} = 377.4 \text{ mV}$, $\eta_{10} = 651.8 \text{ mV}$) (Fig. 4b). Similar trends were observed in alkaline media that $\sim 1.5 \text{ nm}$ Pt catalyst showed superior activity ($E_{\text{onset}} = 10.0 \text{ mV}$, $\eta_{10} = 56.7 \text{ mV}$) to the other samples ($E_{\text{onset}} = 9.5 \text{ mV}$, $\eta_{10} = 65.4 \text{ mV}$ for $\sim 3 \text{ nm}$ Pt catalyst, and $E_{\text{onset}} = 60.0 \text{ mV}$, $\eta_{10} = 131.8 \text{ mV}$ for $\sim 6 \text{ nm}$ Pt catalyst). The stability of catalysts in neutral and alkaline solutions after 10,000 cycles were also tested as shown in Fig. 4e and f, respectively, and the η_{10} of $\sim 1.5 \text{ nm}$ -sized Pt catalyst reduced by 6.0 and 21.6 mV , respectively, which were comparable to 22.3 and 8.1 mV of Pt/C, demonstrating the excellent HER stability of the $\sim 1.5 \text{ nm}$ Pt catalyst in both neutral and alkaline solutions.

Tafel slopes of the prepared samples in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution were all below 30 mV dec^{-1} (Fig. 4g), indicating that the HER occurred through a Volmer–Tafel route [37]. While the $\sim 1.5 \text{ nm}$ -sized Pt catalyst exhibits the lowest Tafel value of 16.7 mV dec^{-1} , which is even lower than that of Pt/C (19.6 mV dec^{-1}), suggesting the much faster HER kinetics of the former [38]. In

neutral and alkaline electrolytes, the Tafel slopes for the samples exhibit the same trends with those in acidic solution (Fig. 4h and i), in which the $\sim 1.5 \text{ nm}$ -sized Pt catalyst shows much lower Tafel slopes than the $\sim 3 \text{ nm}$ - and $\sim 6 \text{ nm}$ -sized Pt catalysts, which is comparable to commercial Pt/C, meaning the faster HER kinetics for the $\sim 1.5 \text{ nm}$ Pt. However, the $\sim 1.5 \text{ nm}$ -sized Pt catalyst might have proceeded *via* a Volmer–Heyrovsky mechanism with the Heyrovsky step being the rate limiting step because the Tafel slopes were above 40 mV dec^{-1} [39–41]. In addition, the exchange current density (J_0) of $\sim 1.5 \text{ nm}$ -sized Pt catalyst is also higher than those of $\sim 3 \text{ nm}$ - and $\sim 6 \text{ nm}$ -sized Pt in all pH electrolytes (Table. S4), suggesting the abundant electrocatalytic active sites of the former, leading to its excellent HER performance [42]. The high HER performance of $\sim 1.5 \text{ nm}$ -sized Pt catalyst is related to its lower charge-transfer resistance (R_{ct}). The arc diameters in Nyquist plots are smaller than those of $\sim 3 \text{ nm}$ Pt and $\sim 6 \text{ nm}$ Pt under the same overpotentials especially in neutral and alkaline conditions (Fig. S8), suggesting the much lower charge-transfer resistance of $\sim 1.5 \text{ nm}$ -sized Pt catalyst during the HER process [43–45]. To further investigate the electrocatalytic sites, the electrochemical active surface areas (ECSA) of the three catalysts in the non-Faraday region were measured by calculating the electrochemical double-layer capacitance (C_{dl}), and the $\sim 1.5 \text{ nm}$ Pt catalyst possessed the C_{dl} values of 5.25 , 3.51 , and 3.95 mF cm^{-2} in acidic, neutral and alkaline solutions (Fig. S9), respectively, which were much higher than those of the counterparts. According to the equation ($\text{ECSA} = C_{dl}/C_s$) [46,47], the $\sim 1.5 \text{ nm}$ Pt exhibits the largest ECSA among the prepared samples (Table. S4), indicating more amount of active sites exposed on the $\sim 1.5 \text{ nm}$ -sized Pt catalyst [47].

It also can be seen from the histograms in Fig. 4j and the data in Fig. S10 that the mass current density of HER for the $\sim 1.5 \text{ nm}$ Pt catalyst reaches 1.959 A mg^{-1} at the overpotential of 10 mV in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, which is 2.24 and 2.43 times higher than those of $\sim 3 \text{ nm}$ Pt (0.875 A mg^{-1}) and $\sim 6 \text{ nm}$ Pt (0.806 A mg^{-1}), respectively. Similar trends also occur in neutral and alkaline conditions. In $1.0 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution, the mass activity of the $\sim 1.5 \text{ nm}$ Pt is 3.05 and even 14.45 times higher than those of the counterparts as shown in Fig. 4k and Fig. S10. Mass activity under alkaline conditions is also shown in Fig. 4l and Fig. S10. Similarly, the $\sim 1.5 \text{ nm}$ Pt shows much higher mass activity ($1.755 \text{ A mg}_{Pt}^{-1}$) than those of $\sim 3 \text{ nm}$ Pt ($1.451 \text{ A mg}_{Pt}^{-1}$) and $\sim 6 \text{ nm}$ Pt ($0.084 \text{ A mg}_{Pt}^{-1}$). Additionally, it is worth mentioning that the mass activities of $\sim 1.5 \text{ nm}$ Pt are 36.28 , 28.89 and

Figure 4 Polarization curves (iR compensated) and the curves before and after 10,000 cycles of the catalysts for HER in (a, d) 0.5 mol L⁻¹ H₂SO₄, (b, e) 1.0 mol L⁻¹ Na₂SO₄ and (c, f) 1.0 mol L⁻¹ KOH. Tafel slopes and mass activities of the catalysts in (g, j) 0.5 mol L⁻¹ H₂SO₄, (h, k) 1.0 mol L⁻¹ Na₂SO₄ and (i, l) 1.0 mol L⁻¹ KOH.

22.79 times higher than that of Pt/C in acidic, neutral and alkaline solutions, respectively, indicating the excellent HER performance of the ~1.5 nm Pt nanoparticles.

The effect of Pt particle size on the ORR activity was also investigated as shown in Fig. 5 and Table S4, and 20% Pt/C was also adopted for comparison. In contrast with HER, the smallest particles (~1.5 nm Pt) do not show the best ORR performance in O₂-saturated

0.1 mol L⁻¹ HClO₄ and 1.0 mol L⁻¹ KOH aqueous solution, while the ~3 nm-sized Pt catalyst displays the best performance both in acidic and alkaline conditions. Especially in alkaline electrolytes, the ~3 nm Pt catalyst ($E_{\text{onset}} = 0.953$ V, $E_{1/2} = 0.870$ V) shows comparable ORR performance to Pt/C ($E_{\text{onset}} = 0.989$ V, $E_{1/2} = 0.894$ V). Meanwhile, the smaller Tafel slopes (183.7 mV dec⁻¹ in 0.1 mol L⁻¹ HClO₄, 68.2 mV dec⁻¹ in 1.0 mol L⁻¹ KOH) of

Figure 5 Polarization curves and the corresponding Tafel slopes of the catalysts for ORR in (a, c) 0.1 mol L⁻¹ HClO₄ and (b, d) 1.0 mol L⁻¹ KOH. K-L plots and histograms of the mass activities of the catalysts in (e, g) 0.1 mol L⁻¹ HClO₄ and (f, h) 0.1 mol L⁻¹ KOH.

the ~3 nm Pt catalyst (Fig. 5c and d, Table S4) illustrate a higher electron transfer efficiency than those of ~1.5 nm Pt (260.9 mV dec⁻¹ in 0.1 mol L⁻¹ HClO₄, 88.3 mV dec⁻¹ in 1.0 mol L⁻¹ KOH), ~6 nm Pt (323.8 mV dec⁻¹ in 0.1 mol L⁻¹ HClO₄, 172.6 mV dec⁻¹ in 1.0 mol L⁻¹ KOH), and Pt/C (137.1 mV dec⁻¹ in 0.1 mol L⁻¹ HClO₄, 69.7 mV dec⁻¹ in 1.0 mol L⁻¹ KOH). To better understand the ORR kinetics of Pt/CNTs, the polarization curves (Figs S11 and S12) for ORR were recorded at varied rotation speeds in O₂-saturated 0.1 mol L⁻¹ HClO₄ and 1.0 mol L⁻¹ KOH, respectively. The electron transfer number (*n*) of Pt/CNTs for catalyzing ORR was calculated through the slopes of K-L plots (Fig. 5e and f), and it can be found that the *n* of ~3 nm-sized Pt catalyst is about 4 in both acidic and alkaline electrolyte, indicating a four-electron reaction process, consistent with the theoretical value [48]. Moreover, the ~3 nm-sized Pt catalyst still retains 84% of initial current at the end of

15,000 s test under alkaline conditions (Fig. S13), which is higher than Pt/C (83%), indicating the excellent stability of the ~3 nm Pt catalyst. In addition, the mass activity of ~3 nm-sized Pt catalyst in acid electrolyte is 30.5 mA mg_{Pt}⁻¹ at 0.9 V (Fig. 5g), which is much higher than those of ~1.5 nm Pt (14.1 mA mg_{Pt}⁻¹), ~6 nm Pt (5.9 mA mg_{Pt}⁻¹), and Pt/C (10.8 mA mg_{Pt}⁻¹). That is, the mass activity of ~3 nm Pt catalyst is 2.17, 5.21, and 2.82 times higher than those of the other three catalysts. In alkaline electrolyte, a similar trend was found that the ORR mass activity of ~3 nm Pt catalyst was optimal among all catalysts (Fig. 5h), and the mass activity was 489.4 mA mg_{Pt}⁻¹, which is 16 times higher than that of commercial Pt/C (30.6 mA mg_{Pt}⁻¹). Besides, almost all the prepared Pt/CNTs catalysts exhibit higher mass activity than Pt/C (Fig. S14), which is due to the high ECSA and the functional groups modified on CNTs protecting Pt nanoparticles from agglomeration [49].

DISCUSSION

The prepared Pt/CNTs electrocatalysts with different Pt particles size possess similar structure and similar mass transport behavior. In all pH electrolytes, the ~ 1.5 nm-sized Pt catalyst shows the best HER performance among the prepared catalysts, which may originate from the following reasons: (1) PDA plays dual roles of providing active sites and increasing hydrophilicity which facilitates the diffusion of active substances and evolution of H_2 and H_2O molecules, resulting in the enhancement of HER [50]; (2) the SMSI effect between the ~ 1.5 nm-sized Pt nanoparticles and the CNTs@PDA matrix results in the electron transfer from Pt to matrix, leading to the lean-electron area of Pt and the formation of $\text{Pt}^{\delta+}$ (Pt^{2+} and Pt^{4+}) species to some extent as well as the downshift of d-band center of Pt, which enhances the hydrogen evolution performance [51,52]; (3) the conductive carbon matrix can promote electron transfer and prevent active Pt NPs from agglomeration during the HER process. The corresponding HER catalytic mechanism of the ~ 1.5 nm-sized Pt catalyst in acidic solutions is shown in Fig. 6a. Firstly, the Pt nanoparticles with the downshift of d-band center resulting from the strong electronic interaction between them and the CNTs matrix can effectively capture H^+ to form Pt@H_{ad} , and then the hydrophilic CNTs surface modified by PDA accelerates the hydrogen desorption step, resulting in the enhancement of HER per-

formance. Under neutral or alkaline conditions, the presence of $\text{Pt}^{\delta+}$ species facilitates the dissociation of water because of the easy formation of Pt-H^* , and meanwhile the hydrophilic surface of CNTs due to the modification of PDA accelerates the H_2 molecule desorption, resulting in the enhancement of HER performance. (Fig. 6b) [53].

While for ORR, the ~ 3 nm-sized Pt catalyst possesses the most prominent ORR performance, which should be ascribed to the following aspects: (1) much more amount of ORR active sites such as Pt (111) crystal plane are exposed on ~ 3 nm sized Pt catalyst because of the easier formation of truncated octahedron when the size of Pt nanoparticles is smaller than 5.0 nm, and the proportion of terrace sites (Pt (111) and Pt (100)) increases with the increase in the size of Pt nanoparticles, providing the highest active site exposure for ~ 3 nm-sized Pt [16]; (2) the much higher ratio of pyridinic N (31.89%) would accelerate the ORR process of ~ 3 nm-sized Pt catalyst because the strong electron-accepting ability of pyridinic N can effectively facilitate the O_2 adsorption and reduction. The corresponding ORR catalytic mechanism on the ~ 3 nm-sized Pt catalyst is shown in Fig. 6c. In acidic solutions, the O-O bond breaks directly to form O^* intermediates, and then the as-formed O^* is reduced successively to H_2O . In alkaline solutions, The O^* cleaves from the O-O bond and combines with water to form

Figure 6 Schematic of PEMFC with ~ 1.5 nm-sized Pt/CNTs as cathode catalyst for HER in acidic (a) and alkaline solutions (b), and ~ 3 nm-sized Pt/CNTs as cathode catalyst for ORR (c).

OH^- [54].

By modulating the appropriate Pt particle size, effective HER and ORR catalysts with low Pt loadings can be successfully obtained, which realizes a cogeneration unit of PEMFC with high-purity hydrogen as anode fuel cell.

CONCLUSIONS

In summary, Pt particles with various sizes supported on nitrogen-doped CNTs were prepared by the photo-reduction method. It was found that the particle size of Pt species has great influence on the HER and ORR catalytic activity. The ~1.5 nm-sized Pt exhibits much higher catalytic activity for HER than ~3 nm- and ~6 nm-sized Pt catalysts in all-pH conditions, and moreover the mass activity of it is even 23–36 times that of Pt/C. While the ~3 nm-sized Pt catalyst shows the optimized ORR performance in acidic and alkaline electrolytes, and the mass activity is 3 times and even 16 times that of Pt/C in acidic and alkaline solutions, respectively. The SMSI between the Pt and CNTs matrix and the much more Pt (111) respectively endow the ~1.5 nm Pt with high HER and ~3 nm Pt with outstanding ORR activity. These results would be meaningful for the design of efficient electrocatalysts, which is promising in practical application of clean energy.

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Supplementary information Supporting data are available in the online version of the paper.

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Pt@CNT中铂晶粒尺寸对HER和ORR的影响

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摘要 铂(Pt)是析氢反应(HER)和氧还原反应(ORR)的高效催化剂, 然而, 关于铂颗粒粒径大小与其电催化活性之间相关性的争论仍然存在. 金属-载体强相互作用(SMSI)是导致金属与载体之间电荷转移和质量转移的相互作用. 本文采用光还原法合成了碳纳米管负载的不同粒径的Pt粒子(0.5 wt.%). 在所有pH溶液中, 尺寸约为1.5 nm的Pt催化剂的HER催化性能都明显高于同类催化剂, 其质量活性甚至是Pt/C的23–36倍. 而对于ORR, 约3 nm的Pt催化剂表现出最佳的催化性能, 在酸性和碱性条件下, 其质量活性分别是Pt/C的3倍和16倍. ~1.5和~3 nm大小的Pt催化剂分别表现出的较优异的HER和ORR性能, 主要与铂和碳纳米管之间的相互作用有关, 这为可再生能源电催化剂的设计提供了参考.