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Mechanistic Understanding of Size-dependent Oxygen Reduction Activity and Selectivity over Pt/CNT Nanocatalysts

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Abstract: Identifying the underlying nature of the structure sensitivity of oxygen reduction reaction (ORR) over carbon supported Pt catalysts is an important but challenging issue in electrochemical system. In this work, we combine experiments, density functional theory calculations with model calculations to clarify the sizedependent ORR activity and selectivity over differently sized Pt/CNT catalysts. HAADF-STEM, HRTEM and XPS measurements show that the Pt nanoparticles supported on CNT possess a well-defined truncated octahedron shape in most cases and similar electronic properties. The observed size-insensitive TOF_{active site} based on the number of Pt(111) atoms suggests the Pt(111) surface as the dominant active site. Moreover, the Pt(111) surface is also suggested as the dominant active sites for the formation of H_2O_2 , and the catalyst with the higher Pt binding energy facilitates the oxygen reduction to H₂O. The insights revealed here could shed new light on the design and optimization of Pt-based ORR catalysts.

Introduction

Green electrochemical technologies like fuel cells hold a crucial place in renewable energy conversion systems, and their large-scale commercialization is predominantly limited by the cathodic oxygen reduction reaction (ORR) due to its sluggish kinetics.^[1-4] Carbon supported Pt-based catalysts have been recognized as the state-of-the-art ORR catalysts especially in acidic medium.^[5-13] In previous studies, strongly adsorbed acidic electrolytes such as H₂SO₄ and H₃PO₄ are found to be unfavorable for the reaction, while HClO₄ solution is believed to be a promising non-adsorbing electrolyte.^[14-19] In addition, tremendous efforts have been devoted to fine-tuning Pt geometric and electronic properties toward enhanced ORR performance.^[1,4,11-14]

The ORR over Pt nanoparticles supported on carbon materials is a typical structure-sensitive reaction.^[12,13,19-23] Optimal Pt particle sizes were observed in the range of 2-3 nm.^[18-21] To date, understanding the nature of the Pt particle size effects has been a longstanding scientific question. On the other hand, the ORR selectivity is another important factor to evaluate

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the Pt ORR catalysts. The atomically dispersed Pt species were reported to possess a high selectivity for the H₂O₂ formation through a 2e⁻ pathway ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) rather than H_2O_2 through a 4e⁻ pathway (O₂ + 4H⁺ + 4e⁻ \rightarrow 2H₂O),^[24] while the Pt particle size effects on the ORR selectivity have not been understood very much. Notably, the Pt nanoparticles with differently geometric structure usually exhibit different Pt electronic properties that would influence the ORR performance.^[19,25-29] However, limited work has been dedicated to the Pt particle size effects under excluding the Pt electronic effects. Considering the characteristic of such catalytic system, it is highly favorable to disentangle the Pt size effects from the electronic effects and identify the underlying nature of the Pt size effects from the perspective of active site.

Herein, we focus our attention on mechanistic understanding of the structure sensitivity of carbon nanotubes (CNT) supported Pt catalyzed ORR. The CNT supported Pt catalysts with different particle sizes but similar electronic properties are employed to examine the ORR performance in HCIO₄ solution. A methodology by combining experiments, density functional theory (DFT) calculations with model calculations is proposed to clarify the size-dependent ORR activity and selectivity over the Pt/CNT catalysts. The insights here might open up a new avenue for the design of Pt-based ORR catalysts.

Results and Discussion

Mechanistic understanding of size-dependent ORR activity

The end-close carbon nanotubes support with the highly crystalline and mesoporous characteristics reflected in Figure S1 by scanning electron microscope (SEM), transmission electron microscope (TEM) and N₂ physisorption measurements was used to load differently sized Pt nanoparticles by incipient wetness impregnation. Figure 1a-1c give high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images and the corresponding particle size distributions of 2, 8 and 10 wt% Pt/CNT catalysts. Their average particle sizes are determined to be 1.7, 2.2 and 2.7 nm, respectively. Core-level XPS measurements in Figure 1d show that these three catalysts exhibit similar Pt⁰ 4f_{7/2} binding energy of ca. 71.70 eV, indicating similar Pt electronic properties. Valenceband XPS measurements in Figure 1e are also carried out, because they can provide the information about Fermi levels and density of state.^[30] Clearly, the densities of Pt 5d states gradually increase with the Pt loading, being in consistent with previous observations of metal loading effects, [31] while the positions of Fermi levels are similar, further supporting the three catalysts with similar Pt electronic properties.

ORR measurements of the three Pt/CNT catalysts and pure CNT support were performed in O_2 -saturated 0.1 M HClO₄ solutions, and the cyclic voltammetry (CV) curves and the linear

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Figure 1. (a-c) Typical HAADF-STEM images, (d) core-level Pt 4f XPS spectra and (e) valence-band XPS spectra, (f) CV curves at a scan rate of 100 mV s⁻¹ and (g) mass activities at 0.7 V of 2, 8 and 10 wt% Pt/CNT catalysts. The insets in (a), (b) and (c) indicate the corresponding Pt particle size distributions of the three catalysts. The CV curve of pure CNT is also shown in (f). (h) Free energy profiles of ORR via the dissociative mechanism on the Pt(111), Pt(100) and Pt(211) surfaces. The inset in (h) indicates a comparison for the reaction free energies at 1.23 V of the protonation of O* and OH* on the three Pt surfaces.

sweep voltammetry (LSV) curves are shown in Figure 1f and Figure S2, respectively. Compared to the pure CNT support, these CNT supported Pt catalysts exhibit distinct reduction peaks in the range of 0.6-0.7 V, indicating that the Pt dominates the ORR process. Moreover, the kinetic control is mostly observed in Figure S2 at potentials above 0.7 V over the three catalysts by rotating electrode techniques. According to the Koutecky-Levich equation presented in the experimental section, the kinetic current densities of the three catalysts at 0.7 V at the typical rotating speed of 1600 rpm were obtained to calculate their mass activities. Figure 1g shows the mass activity of the three catalysts as a function of the Pt particle size. Obviously, there are size-dependent ORR activities over the three catalysts.

To gain mechanistic insights into the size-dependent ORR activity, we employ DFT calculations to understand the ORR

mechanism on three typical Pt surfaces, i.e., Pt (111), Pt (100) and Pt (211) surfaces. To model the interaction with the solvent, we placed 1/3 ML adsorbates and 1/3 ML water molecules layer on the three Pt surfaces as suggested by previous studies.^[32,33] As shown in Scheme 1, the ORR process to form water in acidic medium might proceed by means of a dissociative mechanism (I), associative mechanism (II) and/or hydrogen peroxide mechanism (III) with a four-electron pathway. With DFT structural optimization calculations, the calculated energy profiles of ORR on the three Pt surfaces for the three reaction mechanisms were plotted, and the results are shown in Figure 1h and Figure S3. At the ORR equilibrium potential, the formation of O* on the three Pt surfaces for the Mechanism I is observed to be exothermic and thus thermodynamically favorable, while the protonation of O₂* and OOH* on the three Pt surfaces

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is highly endothermic and thus thermodynamically unfavorable for the Mechanism II and Mechanism III. These indicate that under the acidic reaction conditions, the ORR mainly proceeds via the Mechanism I, i.e., the dissociative mechanism, which is consistent with previous studies.^[4,33,,34]



Scheme 1. Three kinds of ORR mechanisms: (I) dissociative mechanism, (II) associative mechanism and (III) hydrogen peroxide mechanism.

Furthermore, Table 1 presents the most stable adsorption configurations and the corresponding Pt-O bond lengths as well as the adsorption free energies (ΔG_{ads}) of the key intermediates in the Mechanism I, e.g., O* and OH* species. Clearly, the most stable adsorption site of the O* species is the fcc site on the Pt(111) surface, while the bridge site on the Pt(100) and Pt(211) surfaces; that of the OH* species is the top site on the Pt(111) and Pt(100) surfaces, while the bridge site on the Pt(211) surface. As also seen in Figure 1h, at the ORR equilibrium potential, the formation of O* on the Pt(111) surface compared

Table 1. Structural and energetic parameters of O^* and OH^* species on Pt(111), Pt(100) and Pt(211) surfaces.

		Stable co	onfiguration	Bond length of Pt-O	ΔG _{ads} *
		top view	side view		
B+ (111)	0*			2.062 Å	1.71 eV
F((11))	OH*			2.117 Å	0.92 eV
	0*			2.005 Å	1.48 eV
Pt (100)	OH*			2.105 Å	0.76 eV
D4 (014)	0*		bood	1.957 Å	1.23 eV
Pt (211)	OH*			2.154 Å	0.78 eV

* The higher is the ΔG_{ads} value, the weaker is the adsorption of the intermediates on the Pt surfaces.

to the other two surfaces is lowly exothermic, which can be reflected by the trend of the ΔG_{ads} values of O^{*} on the three Pt surfaces in Table 1. It is also observed that the protonation of O^{*} and OH^{*} are endothermic, suggesting non-spontaneous occurrence of these steps; the protonation of O^{*} is more endothermic than that of OH^{*}. All of these results suggest that the protonation of O^{*} is most likely the rate-determining step.

Since the onset potential (i.e., Uonset) is an important measure of the ORR activity, the theoretical Uonset values of the three Pt surfaces were obtained from the correlated free energy profiles at equilibrium potential, i.e., 0.78, 0.72 and 0.41 eV for the Pt(111), Pt(100) and Pt(211) surfaces, respectively, and the corresponding free energy profiles at the calculated Uonset are shown in Figure 1h. Based on the calculated U_{onset} values, the Pt(111) and Pt(100) surfaces have much higher U_{onset} values than the Pt(211) surface. This indicates that the Pt(211) surface provides a negligible contribution to the ORR activity, which is in coincident with some previous studies.[22] It is noted that in our DFT studies, the Uonset value on the Pt(111) surface is slightly higher than that on the Pt(100) surface, while in the DFT studies of Norskov and coworkers, the Uonset value on the Pt(100) surface (i.e., 0.80 eV) is slightly higher than that on the Pt(111) surface (i.e., 0.78 eV).[22] In other words, it is difficult to identify which one is the dominant active sites for the ORR on the Pt(111) and Pt(100) surfaces only based on the thermodynamic stability of reaction intermediates without the consideration of reaction barrier. However, it remains a big challenge to accurately calculate the reaction barriers due to the ORR reaction characteristics, such as the occurrence of ORR in the liquid phase, the presence of charge on the catalyst surfaces, the electric double layers on the electrode surfaces.[35] In addition, some recent theoretical studies on the Pt(111) surface showed that the ORR activity and mechanism also highly depend on the reaction conditions, e.g., potential.^[36] All of these theoretical studies suggest that the identification of clear ORR catalyst active sites and reaction mechanism is limited by the current theoretical methods and studies. More advanced and detailed theoretical calculations would be needed in the future studies.

Recently, we have developed a simple yet effective method of model calculations to discriminate the dominant active sites for the Pt/CNT and Ru/CNT catalyzed hydrolytic dehydrogenation of ammonia borane [37,38] as well as Pd/CNT catalyzed selective hydrogenation of acetylene.[39] As a consecutive effort, we further employed this method to discriminate the dominant active sites for the ORR over Pt/CNT catalysts. For this method, high transmission electron microscopy resolution (HRTEM) measurements were first carried out to analyze the Pt particle shape and the type of the surfaces. As observed in Figure 2a-2c, the Pt nanoparticles in most cases for the 2-10 wt% Pt/CNT catalysts are prone to exist as the top slice of truncated cuboctahedron, which is consistent with the previous studies.^[37,40] To determine the type of the top surface of the above shape, we further carried out the fast Fourier transform (FFT) to find a mixture of (100) and (111) surfaces with the top surface of (100) based on the 70.5° angle between (111) surfaces as well as 54.8° angle between (111) and (100) surfaces. As schematically shown in Figure 2d, a representative shape of CNT supported Pt nanoparticle consists of (111), (100), edge and corner atoms. Moreover, the numbers of (111), (100),

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Figure 2. (a-c) Typical HRTEM images and the corresponding FFT analyses of 2-10 wt% Pt/CNT nanocatalysts. (d) Schematic diagram of truncated cuboctahedron for CNT supported Pt nanoparticle. (e) Number of atoms per mole of Pt for the specific sites and normalized TOFs of the catalysts as a function of Pt particle size.

edge and corner atoms over the differently sized Pt/CNT catalysts per mole of Pt could be estimated by the number of specific sites of each particle times the number of particles. The corresponding results are presented in Figure 2e.

It is further assumed that the activity of each specific type of active site is the same regardless of the Pt particle size, because the three Pt/CNT catalysts exhibit similar Pt electronic properties mentioned above. In other words, the difference in the Pt catalyzed ORR activity mainly originates from the difference in the number and type of the active sites. If one type of Pt active site is responsible for the ORR activity, the kinetic current of catalysts would increase linearly with the number of the specific Pt active sites. In this regard, turnover frequency (TOF) and normalized one of each type of active site, calculated from the data in Figure 1g and 2e, should be constant. It can be seen in Figure S4 and 2e that only when the Pt(111) surface acts as the active sites, the corresponding $\mathsf{TOF}_{\mathsf{active site}}$ and normalized one appear to be almost constant. This suggests that the Pt(111) surface is the dominating active sites for the ORR over the Pt/CNT catalysts.

Mechanistic understanding of size-dependent ORR selectivity

In addition to the electrocatalytic ORR activity, the ORR selectivity is another important factor in the evaluation of the Pt/CNT ORR electrocatalysts. Figure 3a shows rotating ring-disk electrode (RRDE) polarization curves of the three Pt/CNT catalysts by the rotating ring and disk electrode testing. Based on the data in Figure 3a, the average number of electron transferred (n per O_2) and the average yield of H_2O_2 (%) for the three Pt/CNT catalysts were obtained. As shown in Figure 3b, the average numbers of electron transferred of the 2, 8 and 10 wt% Pt/CNT catalysts are 3.64, 3.91 and 3.94, respectively. This

indicates that the ORR on the last two catalysts predominately produces water via the four-electron pathway, while that on the first one partially proceeds via the two-electron pathway. Correspondingly, the 2 wt% Pt/CNT ORR catalyst gives rise to much higher H_2O_2 yield (i.e., 18.13%) than the other two catalysts, which are 4.44% and 3.01%, respectively. Combining these results with the three catalysts with different Pt particle sizes, it is suggested that there is size-dependent ORR selectivity over the three catalysts.

It is well-known that the equilibrium potential for the ORR via a four-electron pathway is 1.23 V, while that for the formation of hydrogen peroxide via a two-electron pathway is 0.70 V.[41] Considering that the OOH* has been demonstrated to be the key decisive intermediate for the formation of hydrogen peroxide via the two-electron pathway,^[41] DFT calculations were employed to understand the size-dependent ORR selectivity over the three catalysts. Figure 3c shows the most stable adsorption configurations of OOH* as well as the corresponding lengths of the Pt-O and O-O bonds on the Pt(111), Pt(100) and Pt(211) surfaces. Specifically, the most stable adsorption site of the OOH* species is the top site on the Pt(111) and Pt(100) surfaces, while the bridge site on the Pt(211) surface. As seen in Figure 3d, the adsorption free energies of the OOH^{*} (ΔG_{OOH^*}) on the Pt(111) surface is observed to be higher than those on the Pt(100) and Pt(211) surfaces, which suggests that the formation of OOH* is lowly exothermic on the Pt(111) surface compared to the other two surfaces.

Furthermore, Figure 3e presents the calculated energy profiles on the Pt(111), Pt(100) and Pt(211) surfaces at 0.7 V. Clearly, the Pt(111) surface is more close to the ideal catalytically active sites for the oxygen reduction to hydrogen peroxide than the Pt(100) and Pt(211) surfaces. This suggests that the Pt(111) surface is more likely for the formation of H_2O_2 compared to the Pt(100) and Pt(211) surfaces.

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Figure 3. (a) RRDE polarization curves, (b) the average n per O₂ and the average yield of H_2O_2 (%) of the three Pt/CNT catalysts. (c) Stable adsorption configurations of OOH^{*}, (d) the corresponding ΔG_{OOH^*} and (e) the free energy profiles for hydrogen peroxide mechanism at 0.7 V on Pt(111), Pt(100) and Pt(211) surfaces.

Based on all the above analyses, the size-dependent ORR activity and selectivity over the Pt/CNT catalysts were understood in detail by a combination of the experiments, model calculations and DFT calculations. The Pt(111) surface is suggested as the dominant active sites not only for the oxygen reduction to water, but also for the oxygen reduction to hydrogen peroxide. It is noted that for the 2 wt% Pt/CNT catalyst, it exhibits much higher H₂O₂ yield than the other two catalysts with the high Pt loadings in Figure 3. Although the three catalysts show similar Pt electronic properties, they have different Pt particle size distributions. Especially for the catalyst with the low Pt loading, there exist relatively more small-sized Pt nanoparticles immobilized on the carbon nanotubes support in Figure 1. Our previous studies have demonstrated that when using Pt loading to change the Pt particle size for the Pt/CNT catalysts, the smaller-sized Pt nanoparticles exhibit much lower Pt binding energy.^[42] These Pt nanoparticles with the lower Pt binding energy might be favorable for the formation of hydrogen peroxide.

Along this line, we further probed the effects of the Pt electronic properties in Figure S5 over the three catalysts on the average number of electron transferred and the average yield of H_2O_2 of the ORR, where these three catalysts exhibit similar Pt particles sizes in Figure S6 (i.e., 2.1 ± 0.3 , 2.2 ± 0.4 and 2.0 ± 0.4 nm) and their more preparation and characterization details are presented in Supporting Information. As clearly seen in Figure 4 and S7, increasing the Pt⁰ 4f_{7/2} binding energy gives rise to higher average number of electron transferred and lower H_2O_2 yield. This could be because the higher Pt binding energy is favorable for the oxygen adsorption and thus its dissociation,

while the lower Pt binding energy for the formation of OOH* and thus the formation of hydrogen peroxide. These results could support the above deduction that the Pt catalyst with the lower Pt binding energy would facilitate the formation of hydrogen peroxide.



Figure 4. The average n per O_2 and average yield of H_2O_2 (%) of the three catalysts with different Pt^0 4f_{7/2} binding energy.

Notably, although in our work the Pt(111) surface is found to act as the dominant active sites for both the oxygen reduction to water (main reaction) and that to hydrogen peroxide (side reaction), their reaction rates are remarkably different. According to our above DFT and experimental studies, on the Pt catalysts, the ORR process to form water in acidic medium have been shown to mainly proceed by means of the dissociative mechanism. In other words, it is much easier to dissociate the oxygen molecule to O* species rather than to form the OOH* species.

Conclusions

In summary, we have clarified the underlying nature of the sizedependent ORR activity and selectivity over the Pt/CNT catalysts from the catalyst active site point of view by combining the experiments, DFT calculations with model calculations. With employing the model of truncated octahedron for Pt nanoparticle, the observed size-insensitive TOF_{active site} based on the number of Pt(111) atoms suggests Pt(111) as the dominant active sites for the ORR. The origin of the size-dependent ORR activity is mainly attributed to the difference in the Pt geometric properties rather than the Pt electronic properties. Moreover, the Pt(111) surface is also suggested as the dominant active sites for the formation of H_2O_2 . The difference in the H_2O_2 selectivity mainly originates from the difference in the Pt binding energy. These results could be valuable for the design and optimization of Ptbased electrocatalysts for the ORR.

Experimental Section

Catalyst preparation: Multi-walled carbon nanotubes (CNT, purchased from Beijing Cnano Technology Limited) were used to support Pt catalysts with different Pt contents (i.e., 2, 8 and 10 wt%) by incipient wetness impregnation with an aqueous solution of H₂PtCl₆ (Sinopharm Chemical Reagent Co. Ltd). The precursors of Pt/CNT catalysts were dried in stagnant air at room temperature for 12 h, then at 80 °C for 12 h, followed by reducing in 10% H₂/N₂ at 250 °C for 3 h, and passivating in 1% O₂/Ar at room temperature for 30 min. The as-prepared catalysts were denoted as 2 wt% Pt/CNT, 8 wt% Pt/CNT and 10 wt% Pt/CNT. The pristine CNT were treated by acid oxidation of 8 M HNO₃ (65%, Shanghai Lingfeng Chemicals) mixed with 8 M H₂SO₄ (98%, Shanghai Lingfeng Chemicals) in an ultrasonic bath of 60 °C for 2 h, and acid oxidation followed by high temperature, respectively. The as-obtained samples were labelled as CNT-O and CNT-D. The Pt/CNT-D catalysts were prepared using the same procedure mentioned above.

Catalyst characterization: The morphology of CNT was characterized by Field emission scanning electron microscope (SEM, Nova NanoSEM 450, US) and transmission electron microscope (TEM, JEOL JEM-1400, Japan). The size distribution and the mean particle size of all catalysts were calculated on the basis of the sizes of at least 300 random particles by HAADF-STEM (Tecnai G2 F20 S-Twin) images. The shape of Pt particles was observed by HRTEM (JEOL JEM-2100, Japan). Nitrogen adsorption/desorption isotherms were measured at 77 K with a Quadrasorb SI analyzer. The pore size distributions were derived from the desorption branch by using the Barrett-Joyner-Halenda (BJH) model. The High-resolution core-level (CL) and valence-band (VB) X-ray photoelectron spectroscopy (XPS) data were collected with a ThermoFisher ESCALAB250Xi equipped with an AI Ka X-ray (1486.6 eV, excitation source working at 15 kV). The analyzer was in the constant analyzer energy (CAE) mode at a pass energy of 30 eV for all the valence-band XPS measurements. The binding energies were measured with an accuracy of 0.05 eV. The C 1s peak at 284.6 eV was taken as an internal standard to correct the shift in the binding energy caused by sample charging. The elements of the samples were analyzed by inductively coupled plasma atomic emission spectrometer (Agilent 725-ES ICP-AES).

Catalytic measurements: The as-obtained Pt/CNT catalysts were evaluated in a single-compartment conventional three-electrode cell at room temperature and ambient pressure using electrochemical measurements (RRDE-3A, Japan) on a computer controlled bipotentiostat CHI 760E (Shanghai Chenhua Co., China). A rotating glassy carbon disk electrode of 5 nm diameter (0.196 cm²) coated by a catalyst film was used as the working electrode. Pt wire and saturated calomel electrode (AGCL) were used as the counter electrode and reference electrode respectively, with 0.1 M HClO₄ solution aqueous solution used as electrolyte. The catalyst ink was prepared by ultrasonically dispersing 5 mg fine catalyst powder in 1 mL absolute ethanol and 50 μ L 5 wt% Nafion solution for 20 min. 10 μ L of this ink was deposited onto the surface of glassy carbon disk electrode followed by air drying to gain a Pt/CNT catalyst loading of ca. 240 μ g cm⁻².

The ORR activity was evaluated by CV at a scan rate of 100 mV s⁻¹ and LSV at a scan rate of 5 mV s⁻¹ in O₂-saturated 0.1 M HClO₄. The potential scan range was set between -0.25 and 0.95 V referred to that of the Ag/AgCl potential, and the potentials reported in this study were all normalized to that of the reversible hydrogen electrode (RHE) according to the following equation:

$$\frac{1}{i} = \frac{1}{i_{k}} + \frac{1}{i_{k}} = \frac{1}{i_{k}} + \frac{1}{B\omega^{0.5}}$$
(1)

$$B = 0.2nFC_{\rho}(D_{\rho})^{\frac{2}{3}} \upsilon^{-\frac{1}{6}}$$
(2)

where j is the measured current density, j_k and j_d are the kinetic current density and the diffusion current density, respectively. ω is the rotating rate of rotating disk electrode (400, 625, 900, 1225, 1600, 2025 rpm). n is transferred electron number, F is the Faraday constant (96485 C mol⁻¹), C₀ is the bulk concentration of O₂ (C₀ = 1.26x10⁻³ mol/L), D₀ is the O₂ diffusion coefficient (D₀ = 1.93x10⁻⁵ cm²/s), v is the kinematic viscosity of the electrolyte (v = 1.009x10⁻² cm²/s). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

The TOF of the active site,^[8] e.g., Pt(111) site, is calculated by normalizing cathode kinetic current to the number of Pt(111) atoms over differently sized Pt/CNT catalysts, as following:

$$TOF_{\text{active site}}(\text{e-site}^{-1} \cdot \text{s}^{-1}) = j_k \times S_{disk} / (1.6 \times 10^{-19}) / N_{\text{active site}}$$
(3)

Where j_k is the kinetic current density at 0.7 V, S_{disk} is the area of glassy carbon disk electrode of 5 nm diameter.

The TOF_{active site} is normalized to the highest TOF_{max} for each Pt/CNT catalyst, which can be expressed by

Normalized
$$TOF_{active site} = TOF_{active site} / TOF_{max}$$
 (4)

For the calculation of electron transfer number (n per O₂) and yield of H₂O₂ on different catalysts, based on both ring and disk currents from rotating ring-disk electrode (RRDE) of 4 nm diameter, they were estimated by the following equations:

$$n = \frac{4 \times i_d}{i_s + i_s / N} \tag{5}$$

$$H_2 O_2 \% = 200 \times \frac{i_r / N}{i_d + i_r / N}$$
 (6)

where i_d is the disk current density, i_r is the ring current density and N is the current collection efficiency of the Pt ring disk determined using a solution of Fe(CN)_3^- (N=0.42).

Computational details

Method: The density functional theory (DFT) simulations of the adsorption and reaction process involved in ORR on Pt surfaces were performed by using the Vienna ab initio simulation package (VASP).^[43-46] The ion-electron interaction was described with the projector augmented wave (PAW) method.^[47,48] Electron exchange-correlation was represented by the functional of Revised Perdew, Burke, and Ernzerhof (RPBE) of generalized gradient approximation (GGA).^[49,50] A cutoff energy of 400 eV was used for the plane-wave basis set. The Hellman-Feynman forces on each ion was minimized to be less than 0.03 eV/Å.

Models: The Pt(111), Pt(100) were respectively modelled using a $p(3 \times 3)$ supercell slab model, containing four atomic layers slabs, with a relaxation of the top two layers. The Brillouin-zone integration has been performed with a 3 x 3 x 1 Monkhorst-Pack k-point mesh^[51,52] for the above models. For Pt(211), a $p(1 \times 3)$ supercell with ten atomic layers was chosen as the step model, including a relaxation of the top six layers. The Brillouin-zone integration has been performed with a 4 x 3 x 1 Monkhorst-Pack k-point mesh for Pt(211) model. For all surfaces, a vacuum thickness of 12 Å was used to avoid the interaction from the top supercells. All of the surface models were constructed based on bulk fcc Pt crystal whose lattice constant was 3.98 Å.

Free energy calculations: The overpotential during the ORR process can be determined by examining the reaction free energies of the different elementary steps.^[53] In order to obtain the reaction free energy of each elementary step of ORR, we calculated the adsorption free energy of O^{*}, OH^{*} and OOH^{*}. Since it is difficult to obtain the exact free energy of O, OH and OOH radicals in the electrolyte solution, the adsorption free energy of stoichiometrically appropriate amounts of H₂O (g) and H₂ (g), defined as follows:

$$\Delta G_{O^*} = \Delta G(H_2O(g) + * \to O^* + H_2(g)) = \mu_{O^*} + \mu_{H_2} - \mu_{H_2O} - \mu_*$$

$$= (E_{O^*} + E_{H_2} - E_{H_2O} - E_*) - T \times (S_{O^*} + S_{H_2} - S_{H_2O} - S_*)$$

$$+ (E_{ZPE(O^*)} + E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(*)})$$
(7)

 $\Delta G_{OH^*} = \Delta G(H_2O(g) + * \to OH^* + 1/2H_2(g)) = \mu_{OH^*} + 0.5 \times \mu_{H_2} - \mu_{H_2O} - \mu_*$ $= (E_{OH^*} + 0.5 \times E_{H_2} - E_{H_2O} - E_*) - T \times (S_{OH^*} + 0.5 \times S_{H_2} - S_{H_2O} - S_*)$ $+ (E_{ZPE(OH^*)} + 0.5 \times E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(^*)})$ (8)

$$\Delta G_{OOH^*} = \Delta G(2H_2O(g) + * \to OOH^* + 3/2H_2(g))$$

$$= \mu_{OOH^*} + 1.5 \times \mu_{H_2} - 2 \times \mu_{H_2O} - \mu_*$$

$$= (E_{OOH^*} + 1.5 \times E_{H_2} - 2 \times E_{H_2O} - E_*)$$

$$-T \times (S_{OOH^*} + 1.5 \times S_{H_2} - 2 \times S_{H_2O} - S_*)$$

$$+ (E_{ZPE(OOH^*)} + 1.5 \times E_{ZPE(H_2)} - 2 \times E_{ZPE(H_2O)} - E_{ZPE(*)})$$
(9)

For each elementary step, the reaction free energy was defined as the difference between free energies of the final and initial states and was given by the following expression:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_{field}$$
(10)

Where ΔE is the difference of adsorption energy between product and reactant molecules adsorbed on catalyst surface, obtained from DFT calculations. ΔG_U = eU, where U is the electrode potential relative to the standard hydrogen electrode. T is the temperature, and e is the charge transferred. ΔZPE is the change of zero-point energy computed by DFT calculations. ΔS is the entropy change from the DFT calculations. ΔG_{pH} is the correction of the H⁺ free energy by the concentration dependence of the entropy: $\Delta G_{pH=-k_B}Tln[H^+]$. k_B is Boltzmann constant. ΔG_{field} is the electric field in the double layer. We neglect this in the work. The free energy of H⁺ + e⁻ is calculated by 1/2 G_{H2}-eU+k_BTln[H^+].

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Keywords: Sustainable chemistry • Catalysis • Platinum • Active site • Density functional calculations

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FULL PAPER

The size-dependent ORR activity and selectivity over Pt/CNT catalysts have been clarified by combining the experiments, DFT calculations and model calculations. The Pt(111) surface, especially for the catalyst with the higher Pt binding energy, is favourable for the oxygen reduction to H_2O .



*one or two words that highlight the emphasis of the paper or the field of the study

Oxygen Reduction*

Jie Gan, Wei Luo, Wenyao Chen, Jianing Guo, Zhonghua Xiang, Bingxu Chen, Fan Yang, Yunjun Cao, Fei Song, Xuezhi Duan,* Xinggui Zhou

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Mechanistic Understanding of Sizedependent Oxygen Reduction Activity and Selectivity over Pt/CNT Nanocatalysts