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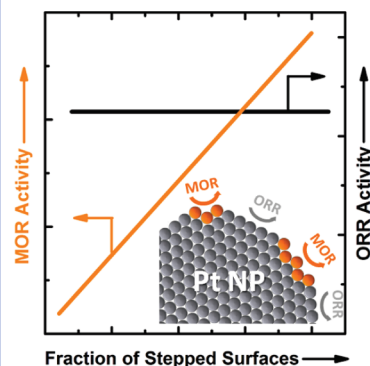
Role of Surface Steps of Pt Nanoparticles on the Electrochemical Activity for Oxygen Reduction

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ABSTRACT The design of highly active nanoscale catalysts for the oxygen reduction reaction (ORR) and oxidation of small molecules such as the methanol oxidation reaction (MOR) constitutes the grand scientific and technological challenge in fuel cells. Although increasing surface steps on Pt nanoparticles was shown recently to enhance the activity of electrochemical oxidation of carbon monoxide and methanol electro-oxidation, little is known about the role of surface steps of nanoparticles on ORR activity. Here, we report that the ORR activity of Pt nanoparticles of ~ 2 nm is not influenced by surface steps, in contrast to MOR activity. Further, CO annealing experiments and in situ X-ray adsorption measurements clearly compare the role of surface step for ORR and MOR on Pt nanoparticles. The findings provide new insights to design highly active catalysts for proton exchange membrane fuel cells and direct methanol fuel cells.

SECTION Energy Conversion and Storage



The oxygen reduction reaction (ORR)^{1,2} is kinetically sluggish, even on the surface of Pt, which limits the efficiency of fuel cells. One of the intensively debated issues over the last two decades is centered on whether and how nanoparticle activity for ORR should be dependent on nanoparticle size and/or surface atomic structure. As only recent high-resolution transmission electron microscopy allows the determination of surface steps on nanoparticles,³ researchers have traditionally related nanoparticle sizes to ORR activity. Kinoshita⁴ first showed that the intrinsic ORR activity in H₂SO₄ and H₃PO₄, having strong anion adsorption, decreases with increasing surface undercoordinated sites of smaller Pt nanoparticles (15–1.5 nm). Subsequently, it is noted that decreasing Pt particle sizes (30–1 nm) also lowers ORR activity in HClO₄,^{1,5,6} having minimal anion adsorption, which has been attributed to increasing surface oxygenated species with decreasing coordination of surface Pt atoms. As the particle terrace size and surface steps present on the terrace influence surface coordination of Pt nanoparticles, it is not clear if these two could cause reduced ORR activity in HClO₄. In order to investigate the influence of surface steps on ORR activity, Feliu and co-workers have employed model stepped single-crystal Pt surfaces, where transforming the (111) surface to 100% stepped surfaces with (111) or (100) terraces^{7,8} increases the ORR activity in 0.1 M HClO₄ by ~ 3 times. If this finding could be applied to nanoparticle surfaces, one would expect that decreasing terrace sizes of smaller Pt nanoparticles is the cause for reduced ORR activity. However, there is no evidence to show that the influence of surface steps on single-crystal surfaces can be translated directly to nanoparticle

surfaces. Our recent work⁹ has shown that increasing surface steps on Pt nanoparticles of comparable sizes can significantly increase the intrinsic activity for CO and methanol oxidation reactions (MOR), which is in good agreement with findings of these two reactions on stepped single-crystal surfaces.^{10–12} In this study, we examine the influence of surface steps on Pt nanoparticles on intrinsic ORR activities and compare the role of surface steps on intrinsic activity for ORR and MOR, where the number of surface steps can be controlled by the heat treatment temperature and CO annealing process.¹³ We show that ORR activity is not influenced by surface steps on Pt nanoparticles of ~ 2 nm, unlike MOR and CO oxidation.⁹

Pt nanoparticles supported on multiwall carbon nanotubes (MWNTs) were prepared by the single atom to cluster (SAC) approach.¹⁴ Four Pt/MWNT samples having the weight fraction of Pt of 20 wt % were obtained from different heat treatment temperatures in the range of 548–773 K. Our previous work⁹ has shown that surface steps on the (111) and (100) surfaces decrease with increasing heat treatment temperature (23–16% from 548 to 773 K), while they have comparable particle sizes (1.9 ± 0.6 – 2.6 ± 1.0 nm) (Figure S1, Supporting Information (SI)) using high-resolution transmission electron microscopy (HRTEM).

ORR activity of Pt/MWNT samples was measured using a rotating disk electrode (RDE) and linear sweep voltammetry in 0.1 M O₂-saturated HClO₄ electrolyte (Figure 1a). The electrochemical surface area (ESA) of Pt nanoparticles was obtained

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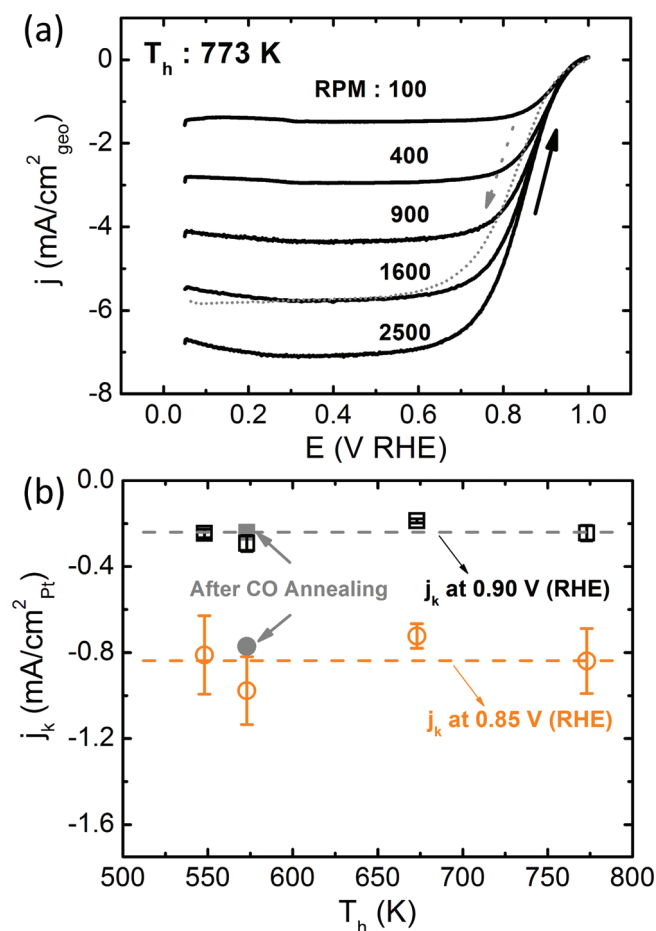


Figure 1. (a) ORR polarization curves of a Pt/MWNT sample heat-treated at 773 K (denoted as Pt/MWNT-773 K). Experiments were conducted in O₂-saturated 0.1 M HClO₄ with a scan rate of 10 mV/s. (b) Specific ORR activity of Pt/MWNT samples at 0.85 and 0.9 V versus RHE as a function of heat treatment temperature, which was obtained from the positive-going scan at 1600 rotation per minute (rpm).

from integrating the charge associated with hydrogen desorption in the O₂-free electrolyte (SI and Figure S2). Specific ORR activity normalized to the Pt ESA is independent of the heat treatment temperature in Figure 1b, which indicates that surface steps on Pt nanoparticles do not greatly influence intrinsic ORR activity. Specific ORR activity of Pt nanoparticles at 0.9 V versus RHE is $\sim 200 \mu\text{A}/\text{cm}^2_{\text{Pt}}$, which is in good accordance with the reported specific activity for Pt nanoparticles of comparable sizes in HClO₄.^{1,5,6} In addition, projecting the reported activity of stepped single-crystal surfaces^{7,8} (Table S1, SI) onto nanoparticle surfaces of Pt/MWNT samples (Figure S3a, SI), no noticeable ORR activity difference was found for Pt/MWNT samples (Figure S3b, SI). As previous work⁶ has shown, the ORR activity of Pt particles of 1 and 2 nm is very comparable (no difference considering experimental uncertainty). Therefore, considering the overlap in the particle size histograms of our samples, it is postulated that the change in the ORR activity as a result of particle size from 1.9 (± 0.6) to 2.6 nm (± 1 nm) is negligible. Considering transforming the (111) surface to 100% stepped surfaces with (111) or (100) terraces^{7,8} with only an

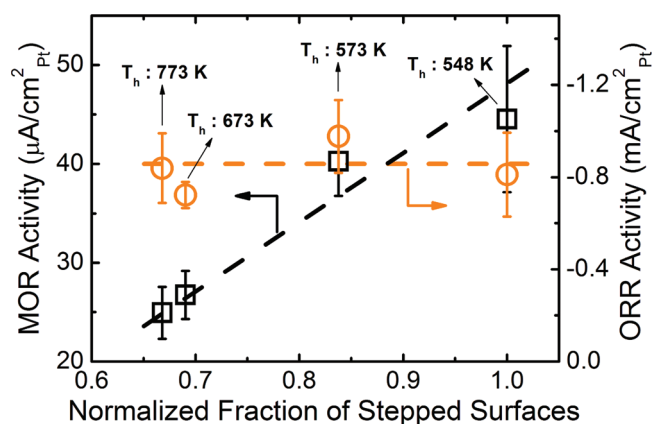


Figure 2. Specific MOR (left axis) and ORR activity (right axis) as a function of area fraction of stepped surfaces normalized to the 548 K sample. Specific MOR activity was measured at 0.5 V versus RHE after subtraction of the double-layer current.⁹ Specific ORR activity was measured at 0.85 V versus RHE at 1600 rpm.

ORR activity increase of ~ 3 times, the changes in the amount of surface steps in Pt/MWNT samples might not be enough to show a measurable ORR activity difference.

It is interesting to compare the role of surface steps on Pt nanoparticles on the intrinsic activity of ORR with that of MOR. Specific ORR activity at 0.85 V and specific MOR activity at 0.5 V (current density in the positive-going cyclic voltammetry) reported previously⁹ is plotted as a function of the area fraction of surface steps normalized to that of 548 K (Figure 2). Specific ORR activity at 0.85 V is independent of the normalized area fraction of stepped surfaces, while MOR activity linearly increases with the amount of stepped surfaces on Pt nanoparticles.

Conducting a CO annealing experiment can further contrast the role of surface steps on the ORR and MOR activity of Pt nanoparticles as CO annealing¹³ is shown to reduce adislands and stepped surfaces on Pt single crystals¹⁵ and Pt nanoparticles.⁹ Cyclic voltammetry of Pt/MWNT-573 K was cycled in a CO-saturated solution (CO annealing) from 0.1 to 1.1 V versus RHE at a scan rate of 50 mV/s for 10 min (Figure S4, SI), which was shown to reduce surface steps on Pt nanoparticles.⁹ There was a negligible change in the specific ORR activity of Pt/MWNT-573 K after CO annealing (Figures 1b and 3a), further confirming that the intrinsic ORR activity on Pt nanoparticles is not influenced greatly by surface steps. On the other hand, a considerable decrease in MOR activity after CO annealing was noted (Figure 3b), clearly showing strong dependence of intrinsic MOR activity on the surface steps. This result can be explained by previous single-crystal studies,^{11,12} where surface steps are shown to promote the MOR activity by providing active sites for the dissociative chemisorption of methanol to form adsorbed CO, further assisting the Langmuir–Hinshelwood-type reaction¹⁶ between adsorbed CO and oxygenated species and enhancing direct oxidation of various intermediates of methanol.¹¹ Moreover, a significant decrease in CO electro-oxidation activity after CO annealing on Pt/MWNT samples shown by our previous work⁹ supports this explanation. Therefore, a small increase in the number of surface steps on Pt

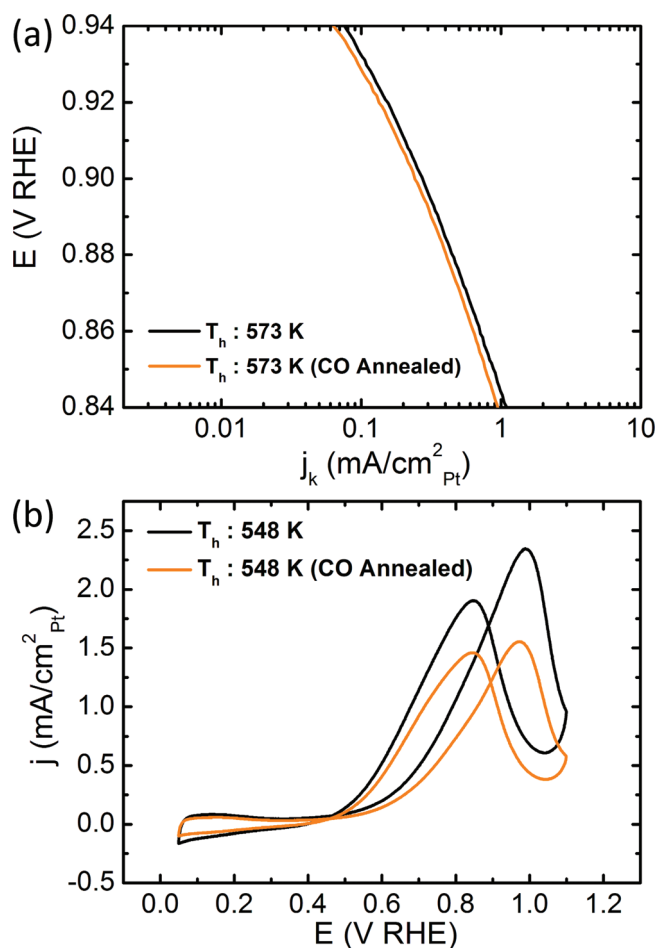


Figure 3. (a) Comparison of Tafel plots of ORR specific activity on Pt/MWNT-573 K before and after CO annealing at room temperature. Tafel plots were obtained from the polarization curves in the positive-going scans at 1600 rpm, which was normalized to the Pt electrochemical surface area (Figure S2, SI). (b) Comparison of cyclic voltammograms for methanol oxidation activity on Pt/MWNT-548 K before and after CO annealing at room temperature. The potential cycles were recorded at a scan rate of 50 mV/s from 0.05 to 1.1 V (RHE) in a N_2 -saturated solution of 1 M CH_3OH in 0.1 M HClO_4 at room temperature.

nanoparticles can considerably enhance MOR activity but not ORR activity.

Previous work has suggested that increasing the coverage of surface oxygenated species on Pt nanoparticles can reduce ORR activity⁵ at high potentials but increase MOR activity^{11,12} at low potentials. First-principle studies have shown stronger binding of oxygenated species¹⁷ on the surface steps (with an upshifted d band center relative to the Fermi level^{18,19}). Ultraviolet photoemission spectroscopy (UPS) experiments⁹ show oxygen-induced d-band broadening^{20,21} of these Pt/MWNT samples due to preferential adsorption of oxygenated species on stepped surfaces. To provide further insights into the surface coverage of oxygenated species on Pt nanoparticles with different numbers of surface steps, we examine normalized Pt L_3 -edge X-ray absorption near-edge structure (XANES) spectra of Pt/MWNT-573 and -773 K, which were collected in situ in an electrochemical cell²² as a function of

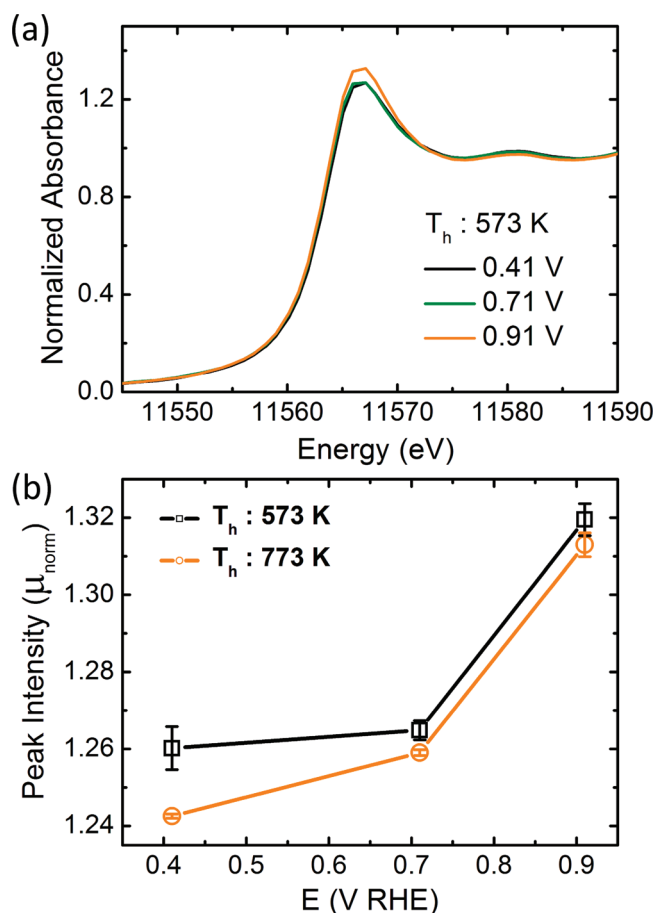
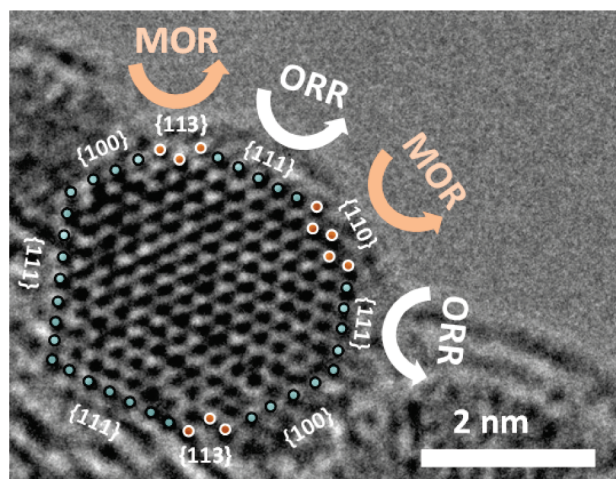


Figure 4. (a) XANES spectra obtained with the Pt/MWNT-573 K at the Pt L_3 edge at three different potentials. (b) Comparison of values extracted from the XANES spectra for Pt/MWNT-573 and -773 K as a function of potential in 1 M HClO_4 .

potential (Figures 4a and S5a, SI). First to note is that the white line intensity increases with electrode potential. Chemical adsorption of oxygenated species such as OH and $\text{O}^{23,24}$ on Pt can lead to the appearance of unoccupied antibonding states above the Fermi level, and thus, an increase in the L_3 X-ray absorption edge can be attributed to higher coverage of adsorbed oxygenated species on nanoparticle surfaces. Second, the difference in the μ values of Pt L_3 edges of the Pt/MWNT-573 and -773 K diminishes with increasing potential, as shown in Figure 4b. Higher μ value of Pt/MWNT-573 K compared to that of -773 K at lower potential region ($< \sim 0.5$ versus RHE, Figure S5b, SI) can be contributed to preferential adsorption of oxygenated species on surface steps, which can explain higher MOR activity of Pt/MWNT samples with more step sites. Arenz et al.¹³ show that nanoparticles with more surface irregularities can initiate adsorbed CO oxidation at lower potentials having a preignition region (0.35–0.6 versus RHE) using in situ CO adsorption spectra experiments, thus indicating preferential adsorption of oxygenated species on the surface irregularities at potentials as low as 0.35 V versus RHE. This trend further supports the difference in μ value of Pt/MWNT samples at the lower potential region. On the other hand, similar μ values for Pt/MWNT-573 and -773 K at high

Scheme 1. Schematic Illustration of the Sites That Govern the Activity of ORR and MOR on a Pt Nanoparticle in Pt/MWNT-673 K^a



^a Active sites on the nanoparticle terraces dominate ORR activity, while active sites involving surface steps govern MOR activity at low potentials.

potential region ($> \sim 0.8$ V versus RHE) reflect comparable coverage of oxygenated species (per Pt atom) on Pt nanoparticles. As the fraction of atoms on the terrace sites is much greater than that associated with stepped surfaces ($< \sim 25\%$, Figure S3a, SI) for all Pt/MWNT samples, coverage of oxygenated species on major surface sites (terrace sites) would dominate the μ values from XANES measurements. Comparable μ values of Pt/MWNT-573 and -773 K at high potentials suggest that the coverage of surface oxygenated species associated with surface steps were not markedly higher than those of terrace sites.

We found surface steps not to govern the ORR activity of nanoparticles of ~ 2 nm. This can be explained by the fact that major surfaces of Pt nanoparticles are (111) and (100) terraces (Figure S3, SI), and surface steps do not cause a significant change in ORR activity shown on stepped single-crystal surfaces.^{7,8} Considering experimental findings^{1,6} of an order of magnitude drop in ORR activity from bulk to nanoparticle (~ 2 nm) surfaces and computational results of a four-time reduction in ORR activity from 10 to 2 nm,²⁵ we hypothesize that the (111) and (100) terrace sizes greatly influence the ORR activity. Further studies are needed to test this hypothesis and understand by what mechanism terrace sizes can change ORR activity. In contrast, minority sites involving surface steps, which have higher oxygenated species at low potentials (Figure 4b) and markedly enhanced activity for MOR, dominate the intrinsic MOR activity of nanoparticles. Consequently, we schematically illustrate active sites that govern the activity of ORR [the (111) and (100) terraces] and MOR (involving surface steps) on the surface of a Pt nanoparticle from the Pt/MWNT-673 K (Scheme 1).

In summary, we show that the ORR activity of Pt/MWNTs is insensitive to changes in the number of surface steps on Pt nanoparticles of ~ 2 nm. This is in contrast to a linear relationship between the fraction of surface steps on nanoparticles and MOR activity, which highlights the significant role of

surface steps in enhancing the intrinsic activity of MOR. This study, for the first time, contrasts the influence of surface steps on Pt nanoparticles for ORR and MOR by extending the insights from previous single-crystal studies^{7,8,11,12} onto nanoparticles. The understanding can be utilized to design highly active ORR and MOR novel electrocatalysts^{26–30} for energy conversion and storage devices.

EXPERIMENTAL SECTION

High-resolution transmission electron microscopy (HRTM) was used to determine the histogram, terraces and surface steps of Pt nanoparticles (SI). In-situ X-ray absorption near-edge structure measurements were carried out at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), using beamline X-19A. The electrochemical cell designed for passing the X-ray beam was used for data collection in fluorescence mode, in which working and counterelectrodes were separated by a Nafion membrane.²² Data were collected at different electrode potentials in 1.0 M HClO₄ at room temperature.

All electrochemical measurements were performed in a three-electrode cell at room temperature. A saturated calomel electrode (SCE) (Analytical Sensor, Inc.) and a Pt wire were used as the reference and counterelectrodes, respectively. Details of electrode preparation can be found in SI. The specific ORR kinetic activity ($j_k/\text{mA cm}^{-2}_{\text{Pt}}$) of Pt/MWNT samples was calculated from RDE data (like those shown in Figure 1a) using the Koutecky–Levich equation⁶ and Pt ESA. The activity of methanol electro-oxidation was measured by cyclic voltammetry in N₂-saturated 1 M CH₃OH in 0.1 M HClO₄ at 50 mV/s. At least four experimental data sets were collected to generate the error bars in Figures 1 and 2, which were defined as the standard deviations of specific current (normalized to Pt ESA).

SUPPORTING INFORMATION AVAILABLE Experimental details, the reported activity of stepped single-crystal surfaces (Table S1), number-averaged diameter and average area fractions of all stepped surfaces of Pt/MWNTs as a function of heat treatment temperature (Figure S1), cyclic voltammograms of Pt/MWNT samples (Figure S2), the fractions of surface facets of Pt/MWNT samples and the estimated ORR activity from reported values of Pt single-crystal surfaces (Figure S3), cyclic voltammograms during potential cycling in a CO-saturated solution (CO annealing) (Figure S4), XANES spectra obtained with the Pt/MWNT-773 K at the Pt L₃ edge, and comparison of XANES spectra for Pt/MWNT-573 and -773 K at 0.41 V versus RHE (Figure S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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