Single-Atomic Ruthenium Catalytic Sites on Nitrogen-Doped Graphene for Oxygen Reduction Reaction in Acidic Medium

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Supporting Information

ABSTRACT: The cathodic oxygen reduction reaction (ORR) is essential in the electrochemical energy conversion of fuel cells. Here, through the NH3 atmosphere annealing of a graphene oxide (GO) precursor containing trace amounts of Ru, we have synthesized atomically dispersed Ru on nitrogen-doped graphene that performs as an electrocatalyst for the ORR in acidic medium. The Ru/nitrogen-doped GO catalyst exhibits excellent four-electron ORR activity, offering onset and half-wave potentials of 0.89 and 0.75 V, respectively, vs a reversible hydrogen electrode (RHE) in 0.1 M HClO4, together with better durability and tolerance toward methanol and carbon monoxide poisoning than seen in commercial Pt/C catalysts. X-ray adsorption fine structure analysis and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy are performed and indicate that the chemical structure of Ru is predominantly composed of isolated Ru atoms coordinated with nitrogen atoms on the graphene substrate. Furthermore, a density function theory study of the ORR mechanism suggests that a Ru-oxo-N4 structure appears to be responsible for the ORR catalytic activity in the acidic medium. These findings provide a route for the design of efficient ORR single-atom catalysts.

KEYWORDS: oxygen reduction reaction, nitrogen-doped graphene oxide, atomically dispersed ruthenium, electrocatalysts

Fuel cells, which directly convert the chemical energy from fuel into electricity, have been recognized as promising candidates for efficient and clean energy conversion.3 A problem is that the sluggish four-electron oxygen reduction reaction (ORR) at the cathode in fuel cell systems remains a major technical challenge and severely limits its widespread commercialization.4,5 Currently, expensive and chemically sensitive Pt-based alloys are the most effective ORR electrocatalyst in proton exchange membrane fuel cells (PEMFCs), which are commonly a reliable system for practical application.7 But due to the harsh acidic environment and high oxidation potential required for PEMFC cathode operation, few materials are stable enough to be considered as ORR electrocatalysts for PEMFCs.8 Several approaches have been implemented to reduce the usage of Pt, such as dispersing the Pt catalyst in the form of small nanoparticles or by alloying Pt nanoparticles with more abundant metals.9−11 However, the Pt nanoparticles tend to agglomerate into larger particles that can be more easily poisoned during long-term practical operation, leading to considerable degradation of performance. Hence much effort has been devoted to replacing the Pt-based

Received: March 28, 2017
Accepted: June 15, 2017
electrocatalysts for ORR, and especially for use in acid media which is a required condition of PEMFCs. As the limit in downsizing metal morphology, the concept of single-atom catalysts (SACs) has emerged since it maximizes the exposed atom efficiency. However, the preparation of SACs remains challenging because the high free energy of individual metal atoms leads to metal aggregation, affording nanoclusters or nanoparticles, particularly under harsh acidic reaction conditions. An effective strategy to overcome this obstacle is to lower the free energy by anchoring the metal atoms in their isolated form on the supporting substrate through a strong metal–support interaction. Recent advances have reported a series of SACs prepared by co-precipitation, atomic layer deposition, galvanic replacement reaction, and incipient wetness impregnation on various metals or metal oxide surfaces. An essential component for electrochemical applications is a conductive and redox-inert supporting material. Graphene has a combination of a large specific area, high electrical conductivity, and excellent chemical stability, making it a promising candidate for a catalyst support material in PEMFCs. While there has been much progress in metal nanoparticles loaded on graphene-based catalysts for ORR, the SAC systems are far less explored.

We recently demonstrated that the individual Co atoms could be incorporated with nitrogen-doped (N-doped) graphene through heat-treating graphene oxide (GO) and small amounts of Co salts in a gaseous NH3 atmosphere. Materials characterization showed that the Co atoms were highly dispersed and embedded into the lattice of the N-doped graphene layer, acting as the active sites for the hydrogen evolution reaction (HER). This facile protocol provides a route to reach the atomic level of metal dispersion on the surface of graphene as well as the formation of nitrogen-coordinated transition-metal centers (M-Nx). Related systems have been investigated as potential alternatives for ORR active site in electrocatalysts. However, to date, only Fe and Co with nitrogen coordination sites (Fe-Nx, Co-Nx) are generally found to possess activity and durability toward ORR in acidic media. While several improvements were recently attained by modified synthesis strategies, including maximizing the
specific surface area or increasing the density of active sites, the ORR catalytic performance is still largely hampered by the intrinsic electrochemical properties of the Fe-N\textsubscript{x} or Co-N\textsubscript{x} moieties.\textsuperscript{35−39} Thus, there is a drive to discover other ORR active sites with improved catalytic activity. Ru complexes were extensively investigated in hydrogenation, olefin metathesis, and water oxidation, however they have seldom been explored for ORR.\textsuperscript{40−43} Here, we report the synthesis of atomically dispersed Ru species embedded on a N-doped graphene matrix (Ru-N/G) via a facile technique using GO containing trace amounts of Ru salts as the precursor. The isolated atomic Ru-N\textsubscript{4} moieties in Ru-N/G have been confirmed and characterized by X-ray adsorption fine structure analysis (XAFS) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). This Ru and N-doped graphene-based catalyst exhibits high performance and stability toward ORR in an acidic media with extraordinarily low overpotential. Computational studies suggest that a Ru-oxo species with nitrogen coordination contributes favorably to the origin of oxygen reduction activity.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ru-N/G Electro-catalyst. As shown in Figure 1a, the first step for synthesis of Ru-N/G involves the dispersion of GO (prepared by the improved Hummers’ method)\textsuperscript{44} in deionized water, and a solution of hexaamineruthenium(III) chloride (Ru(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{3}) was then added into the dispersed GO solution, followed by bath sonication. With abundant oxygen-containing functional groups such as hydroxyl, carboxyl, and carbonyl moieties, GO possesses a strong interaction and sorption capacity of metal cations in aqueous solution.\textsuperscript{45,46} The Ru content loading was carefully controlled to 0.62 wt % in GO to ensure that sufficient isolation between Ru atoms could be achieved. In order to remove the water and minimize the restacking of GO, a lyophilization process was performed on the homogeneous solution to obtain a GO foam with distributed Ru ions. Subsequently, upon annealing the GO foam at high temperature in the presence of NH\textsubscript{3}, nitrogen doping and reduction of GO were carried out simultaneously, producing both the conductive skeleton and nitrogen binding sites for Ru atom incorporation onto the graphene surface.\textsuperscript{47} Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that the Ru loading in the Ru-N/G catalyst annealed at 750 °C (Ru-N/G-750) was 1.7 wt % Ru after the annealing procedure. The surface morphology of Ru-N/G-750 was probed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images show that for the Ru-N/G-750, a graphene flake-like structure was preserved after high-temperature annealing under NH\textsubscript{3} (Figures 1b and S1). High-resolution TEM images clearly resolve the thin wrinkled morphology of Ru-N/G-750 and the absence of metal nanoparticles on graphene sheets (Figure 1c, d). The presence of Ru atoms on the graphene was further confirmed by aberration-corrected HAADF-STEM images (Figure 1e). For a small number of Ru aggregates with sizes of 1−2 nm (Figure S2), the majority of Ru was observed as uniformly distributed bright dots in the subangstrom-resolution HAADF-STEM image; the bright dots are heavy element atoms on the graphene surface. The small size (∼1 Å) and homogeneous dispersion of these bright dots in the carbon matrix indicated that each bright dot corresponds to a single individual Ru atom.
In addition, energy-dispersive X-ray spectroscopy (EDS) and elemental mapping analysis also confirmed a coherent existence of Ru and N doping throughout the material (Figure S3). In Raman spectroscopy measurements, the typical graphitic D and G bands are at \( \sim 1350 \) and \( 1580 \) cm\(^{-1} \), and a 2D band is at \( \sim 2700 \) cm\(^{-1} \). The absence of a hexagonal diffraction pattern in the selected area electron diffraction (SAED) pattern implies that most of the support consists of turbostratic or defective multilayer graphene (Figure S4). X-ray photoelectron spectroscopy (XPS) characterization was performed to investigate the elemental composition of the catalyst. The N 1s spectrum was deconvoluted into peaks at 398.4, 400.2, and 401.4 eV, which are associated with pyridinic N (58.6%), pyrrolic N (22.9%), and graphitic N (18.5%), respectively (Figure 1f). In agreement with previous studies, the nitrogen species of Ru-N/G-750 was dominated by the pyridinic nitrogen, which are generally considered potential metal-coordination sites.\(^{27,39,48}\) Furthermore, detailed XPS analysis of Ru-N/G-750 showed the Ru 3p\(_{3/2}\) peaks at 463.0 eV (Figure S5). Compared to the 3p\(_{3/2}\) peaks at 461.2 eV for Ru metal and 463.2 for RuO\(_2\),\(^{49}\) the Ru in the Ru-N/G-750 catalyst is likely to be present in an oxidation state close to Ru(III) or Ru(IV).

**Electrochemical Measurement of ORR Activity.** To evaluate the ORR electrocatalytic performance of the Ru-N/G catalyst, rotating disk electrode (RDE) measurements were carried out in acidic electrolyte (0.1 M HClO\(_4\)) at a rotation speed of 1600 rpm. The Ru-N/G catalysts were prepared at various annealing temperatures (T\(_{\text{annealing}}\)) under NH\(_3\) in the range from 550 to 800 °C to find an optimum nitrogen-doping condition. These products are designated as Ru-N/G-550, Ru-N/G-650, Ru-N/G-750, and Ru-N/G-800, respectively. The RDE polarization curves of Ru-N/G catalysts are depicted in Figure 2a. As can be seen, for the Ru-N/G-750 catalyst, the appearance of a reduction current started at +0.89 V vs reversible hydrogen electrode (RHE), reflecting its exceptionally low overpotential. However, for Ru-N/G-650, the onset potential was much more negative at +0.76 V, and for Ru-N/G-550, it was even more negatively shifted to +0.62 V. The polarization curves of the reduction currents also differ among the samples. For instance, at +0.45 V vs RHE, the reduction current densities were 0.86 mA/cm\(^2\) for Ru-N/G-550, 2.34 mA/cm\(^2\) for Ru-N/G-650, 4.89 mA/cm\(^2\) for Ru-N/G-750, and 6.24 mA/cm\(^2\) for Ru-N/G-800 (Figure 2b).
mA/cm² for Ru-N/G-650, and 4.81 mA/cm² for Ru-N/G-750, values that correlate with $T_{\text{annealing}}$ from 550 to 750 °C. With the annealing temperature elevated to 800 °C, a significant decrease of both the limiting current and slope of Ru-N/G catalyst occurred in the RDE voltammogram. When the annealing temperature rose above 850 °C in NH₃, a striking shrinkage and weight loss of graphene could be observed during thermal treatment, accompanied by appearance of large Ru particles on the edges (Figure S6). The collapse of the graphene skeleton and emergence of Ru particles could be ascribed to the agglomeration of Ru species under high temperature and simultaneous decomposition of NH₃ and graphene etching induced by Ru particles. Thus, far, Ru-N/G-750 stands out as the best ORR catalyst among the series. Figure 2b illustrates the comparison of Ru-N/G-750 with other benchmark catalysts, including a commercial Pt/C (20 wt % Pt on Vulcan carbon black, Alfa Aesar) catalyst and Fe/N-doped graphene (Fe-N/G-750),52 which was prepared under a similar protocol (see Experimental Methods for details). It can be seen that Ru-N/G-750 exhibited extraordinary ORR activity with an onset potential at 0.89 V and half-wave potential ($E_{1/2}$) at 0.75 V, and its onset potential is $\sim$70 mV more positive than that of the Fe-N/G-750 catalyst, even comparable with that of Pt/C (20 wt %) catalyst in acidic electrolyte. In cyclic voltammetry (CV) measurements, the Ru-N/G-750 catalyst exhibits a well-defined irreversible reduction wave starting at $\sim$0.81 V with the peak potential of 0.58 V (vs RHE) in O₂-saturated solution, and a quasi-rectangular double-layer capacity current in Ar-saturated electrolyte is observed (Figure 2c). The electrochemically active surface areas were also measured by double-layer capacitance measurement as 475 cm²ECSA (Figure S7 and Supporting Note S1). When plotting the current density on a logarithmic scale vs working potential, the ORR Tafel slope of Ru-N/G-750 catalyst was determined to be 134 mV/decade, in sharp contrast with that of Pt/C and Fe-N/G-750 at $\sim$85 mV/decade (Figure 2d), which is closest to the theoretical 120 mV/decade while assuming that the electron-transfer number based on the Koutecky–Levich plot (K-L plot), showing that the four-electron pathway directly to H₂O is dominant in the ORR process catalyzed by Ru-N/G-750 in acidic media.

Normalized to the metal loading, the mass activity of the ORR for the Ru-N/G-750 catalysts at the 0.70 V vs RHE was 7.5 times greater than the commercial Pt/C (Figure 3c), suggesting that the single Ru atoms can notably increase the utilization of metal, with the additional benefit of lowering the cost of the catalyst for the ORR. Furthermore, cycling durability tests in O₂-saturated electrolytes were carried out to examine the long-term stability of the Ru-N/G-750 catalyst under working conditions. After 10,000 cycles between 0.6 and 1.0 V (vs RHE) at a scan rate of 100 mV s⁻¹, the catalyst retains up to 93% of its initial saturated current and only undergoes an 18 mV negative shift of the half-wave potential after cycling, along with a retention of 90% activity and well-preserved Ru moieties on the graphene substrate after a 10,000 s chronoamperometric measurement at 0.70 V, indicating its remarkable durability (Figures 3d, S8, and S9). In addition, the resistance of the catalyst to methanol crossover, which is essential for the application of this catalyst in a direct methanol fuel cell (DMFC), was assessed by adding 1 M methanol during the chronoamperometric measurements on ORR (Figure 3e). As shown in Figure 3e, compared to the dramatic change of current caused by oxidation of methanol on Pt/C, no noticeable current change was observed for Ru-N/G-750 after the addition of methanol in electrolyte. Moreover, as the major factor responsible for degradation of Pt-based electrocatalysts in practical applications, the carbon monoxide (CO) poisoning effect on the Ru-N/G-750 catalyst was evaluated by injecting CO during the ORR measurement (Figure S10). Similarly, there was no significant current loss with Ru-N/G-750, whereas ORR current on the labile Pt/C catalyst was completely quenched by CO. It is noteworthy that the Ru-N/G-750
Catalyst also exhibited apparent ORR activity in alkaline media (Figure S11a). Taken together, the above durability testing results demonstrate that Ru-N/G-750 is an effective electro-catalyst for ORR with a four-electron pathway and is free from both methanol crossover and CO poisoning effects.

As control samples, Ru-containing graphene without N-doping (Ru-G-750) and pure N-doped graphene (N/G-750) were prepared to elucidate the role of Ru and N doping toward the ORR activity (see Experimental Methods for details). The results show that the absence of Ru or N doping both lead to a marked decrease of ORR currents in the voltammograms (Figure 4a). On introducing thiocyanate ions (SCN\(^{-}\)) into the acidic electrolyte (10 mM), the increased overpotential and the significantly decreased current density also suggest the existence of metal-centered catalytic sites for ORR in the Ru-N/G-750 catalyst (Figure S11b).\(^{57}\) The catalyst with the Ru loading doubled in the precursor (2Ru-N/G-750) was also synthesized with a similar protocol in an attempt to increase active sites in the catalyst. Unexpectedly, the 2Ru-N/G-750 exhibited an even lower reduction current than Ru-N/G-750. The morphology of these catalyst was examined by TEM imaging (Figure 4b–e). In contrast to nanoparticle-free Ru-N/G-750 catalyst, Ru-based nanoparticles on graphene sheets were observed both in Ru-G-750 and 2Ru-N/G-750. This phenomenon is presumed to be the result of Ru agglomeration on the graphene sheets during thermal treatment. As discussed above, the defective GO precursor will react with NH\(_3\) to produce N-doped graphene, which provides a C–N lattice that serves as ligands to coordinate with a limited number of Ru atoms. Without the N-doping, Ru atoms are likely not incorporated into the graphene lattice; instead they would aggregate due to the high free energy of individual atoms (Figure 4b,c).\(^{14}\) The higher loading of Ru also leads to the generation of Ru-based nanoparticles that are observed in TEM images of 2Ru-N/G-750, potentially due to the limited graphene substrate N binding sites (Figure 4d,e).\(^{58}\) The detailed C 1s, O 1s, and N 1s XPS spectra of control samples are shown in Figure S12. A set of Ru-N/G catalysts with various relative Ru loading were also prepared, and their detailed ORR performances were evaluated by RDE measurements (Figure S13). In combination with the HAADF-STEM images and electrochemical characterization, these results

Figure 5. (a) Fourier transform magnitudes of the experimental Ru K-edge EXAFS spectra of the Ru-N/G samples prepared under different conditions along with reference materials. The Fourier transforms are not corrected for phase shift. (b) WT for the k\(^3\)-weighted EXAFS signal of sample Ru-N/G-750. The maximum at 5.5 Å\(^{-1}\) is associated with the Ru-N(O) contributions. (c) The normalized Ru K-edge XANES spectra and first derivative curves (the inset) of different samples and references. (d–f) Comparison between the experimental Ru K-edge XANES spectrum of Ru-N/G-750 and the theoretical spectrum calculated from the depicted structures using the full-potential FDM. The vertical dashed lines are provided to guide the eye.
provide reasonable evidence that catalytic ORR activity of Ru-N/G-750 in acidic condition originates from the presence of both N and atomic Ru species and excludes the contribution of Ru-based nanoparticles for the majority of the ORR activity. In addition, the lower loading of Ru atoms here might be improved by introducing more N-binding sites on the substrate in future work.

**X-ray Absorption Fine Structure Analysis.** The structure of the active sites in Ru-N/G catalysts was further investigated by extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopies. The EXAFS Fourier transforms and wavelet transforms are shown in Figures S1a,b and S15, respectively, and the assignment of the signals from 1.0 to 5.0 Å to either Ru–N(O) or Ru–Ru interaction is based on a EXAFS wavelet transform analysis of the references. The detection of WT intensity maxima near 9.2 Å⁻¹, corresponding to the Ru–Ru bond in 2Ru-N/G-750, Ru-N/G-800, and Ru-G-750, reveals the presence of Ru nanocrystallites having the size relation of Ru-N/G-750 > Ru-N/G-800, while only one wavelet transform (WT) intensity maximum at 5.4 Å⁻¹ is well resolved at 0.8–3.0 Å in Ru-N/G-750 and can be associated with the Ru-N(O) contribution. Hence, more Ru content loading and higher annealing temperatures would lead to the formation of metallic Ru, whereas almost all Ru exists as mononuclear Ru centers in the Ru-N/G-750 sample. The bonding environment for the Ru atoms in Ru-N/G-750 is then investigated by least-squares EXAFS curve fitting analysis (Figure S16 and Table S1). The coordination numbers of the Ru-N/O bonding in the first coordination sphere are estimated to be 4.1 and 0.7 at distances of 2.07 and 1.99 Å, respectively, suggesting that the Ru-N/O bonding may adopt a square-pyramidal or a distorted octahedral configuration, similar to the Fe-N/O bonding coordination reported in Fe-N-C catalysts. However, the number of light atoms in the second coordination sphere of Ru, 3.8 at a distance of 2.73 Å, is much smaller than that of the FeN₅C₅ moieties based on the porphyrinic architecture (which are expected to be larger than 10). It is noted that a rather similar coordination was proposed in pyridinic-N-based CoN₅C₅ moieties in Co-N-C catalysts.

Due to the higher sensitivity to the arrangement of atoms around the photoabsorber, XANES was applied to better identify the active site structure. From Figure S5c, it can be observed that the entire XANES spectra of 2Ru-N/G-750 and Ru-G-750 are much closer to the reference of metallic Ru, which confirms the formation of large fractions of Ru nanocrystallites, while the overall profiles for Ru-N/G-800 and Ru-N/G-750 are drastically different from those of RuO₂ and metallic Ru, which suggests the existence of the Ru-N species. Moreover, the derivative XANES of Ru-N/G-750 and Ru-N/G-800 are similar to that of RuO₂, implying that their stable valence states are +3 to +4, compatible with the XPS results. The pre-edge peak, which is due to a 1s–4pₓ shakedown transition characteristic for a square-planar configuration, shows weak intensity for Ru-N/G-750, thereby calling for axial ligands. Similar results were observed in Fe-N-C and Co-N-C catalysts, however, the XANES profile for Ru-NG-750 (Figure S5c) shows a dramatic difference from the result of Fe-N-C and Co-N-C catalysts, suggesting the probability of a distinct coordination architecture for RuNₓCₜ moieties. We then resorted to XANES simulation of various DFT-optimized architectural models. The calculation was first validated by the excellent agreement between the experimental spectra and the calculated results for Ru foil and RuO₂ (Figure S17). Just as expected, the agreement between the experimental and the simulated spectra for the RuNₓ moieties represented by a porphyrinic or pyridinic geometry is unsatisfactory, particularly for the postedge features (e.g., the shoulder d), even with various axial oxygen or nitrogen ligands considered (Figures S18 and S19). However, surprisingly, we found that all the postedge features d–f are well reproduced by the structure of Ru-Nₓ moieties embedded in a graphene sheet (Figure S20). The discrepancies, presented for the near-edge features a–c (Figure S20), can be due to the non-muffin-tin effect. Since the pre-edge peak intensities are well established to be directly proportional to the coordination deviation of the photoabsorbers from centrosymmetry, significant improvements are achieved by the full-potential finite difference method (FDM) calculation that fairly reproduces this tendency (Figure Sd–f). By contrast, we found that the enclosed Ru-Nₓ moieties having one oxygen molecule ligand along the five-member rings

**Figure 6.** (a) Free-energy diagram of the ORR on selected nitrogen-coordinated metal moieties embedded on graphene sheets. The proposed associative mechanism involves the following steps: (1) O₂→O₂; (2) O₂ + H⁺ + e→OOH⁻; (3) OO⁻ + H⁺ + e→O₂ + H₂O; (4) O²⁻ + H² + e→OH⁻; (5) OH⁻ + H² + e→H₂O where * denotes the adsorption site on the catalyst surface. (b) Proposed reaction scheme of the associative mechanism for the ORR on Ru-oxo-N₂ moiety in acidic medium.
direction in the axial position of graphene sheet plane could best reproduce all the features of the experimental spectrum, particularly for the weak pre-edge peak a and the relative intensities between peaks b and c (Figure 5e). Moreover, this structure is in accord with the EXAFS results, as it has four nitrogen atoms and one adsorbed oxygen atom in the first coordination sphere and five light atoms in the second coordination sphere. The slightly smaller coordination number for the light atoms in the second coordination sphere of Ru (i.e., 3.8) obtained by EXAFS indicated that the RuN(C) moiety may form in defective graphene sheets with considerable vacancies at more distant coordination shells. Except for the absorbed molecular dioxygen, this RuN(C) architecture is characterized by four N atoms, four C atoms, and six C atoms in the first three coordination spheres, respectively. It is in marked contrast to the porphyrinic-N-based moiety where the number of C atoms in the second coordination sphere is expected to be larger than 10 and the pyridinic-N-based moiety that has four C atoms in both the second and third coordination spheres. Therefore, the combination of EXAFS and XANES analyses on Ru-N/G-750 catalysts free of Ru crystalline structures has revealed the existence of RuN(C) moieties enclosed in a graphene sheet.

Free-Energy Calculations of ORR Pathway. In order to understand the mechanism and the active site of the oxygen reduction reaction on the Ru/N-doped graphene, we performed spin-polarized density functional theory (DFT) calculations using the Vienna ab Initio Simulation Package (VASP). It is well established that the associative mechanism is a more favorable pathway compared to the dissociative mechanism for O2 reduction on a mononuclear metal catalytic site on a graphene surface. Thus, four intermediates, which can be generated in succession by the associative mechanism: O2*, OO*, O*, and OH* (with the asterisk denoting the adsorption site), with stepwise addition of H+ and electrons to form two molecules of H2O, were considered in our reaction models. The calculated free-energy diagrams of the ORR intermediates bound on the active site at 1.23 V with optimized geometries are presented in Figure 6a. Following the result of X-ray absorption characterization, we first calculated the reaction pathway on the Ru-N4 moieties enclosed in the graphene sheet, a structure with axial oxygen molecule that has the best fitting agreement with experimental XANES results, as the potential ORR catalytic site of Ru-N/G-750 (black line in Figure 6a). Meanwhile, the ORR pathway on active sites with Fe-N4 moieties embedded on graphene has been calculated for comparison (red line in Figure 6a). In contrast with the electrochemical result, DFT calculations unveil that the Gibbs free energy of intermediates on the Ru-N4 moiety is largely more negative than that of the Fe-N4 moiety, indicating that the chemical adsorption of oxygen species on Ru-N4 is so strong that the activation energy barrier and ORR overpotential will both be significantly increased as ~1.26 eV and 1.26 V at 1.23 V. In addition, high-valent Ru-oxo (Ru==O) species have been extensively reported for participating in various catalytic oxidation reactions. Thus, the Ru-oxo-N4 moiety was postulated as a possible explanation for ORR activity here. As the blue line shows in Figure 6a, in the case of the Ru-oxo-N4 moiety, due to the higher oxidation state of Ru center, the reaction intermediates’ free energies are positively shifted from the Ru-N4 moiety and are more suitable for ORR catalysis. The first reduction step of chemisorbed O2 to form OOH, with a reaction barrier of ~0.76 eV at 1.23 V, appears to be the overall rate-limiting step in the oxygen reduction pathway (Figures S21a and 22 and Table S2). The reaction barrier on Ru-oxo-N4 site is comparable to that for the Fe-N4 moiety (0.94 eV), which is widely considered as an efficient nonplatinum ORR catalytic site in acidic medium. Figure 6b summarizes our proposed mechanism of ORR on the Ru-N/G-750 catalyst. The Ru-N4 moiety embedded in graphene layer with axial oxygen molecule from best-fit XANES analysis (Figure 5e) was selected as the initial active site in ORR pathway. The dissociation of axial adsorbed oxygen on embedded Ru-N4 moiety first leads to the formation of the Ru-oxo-N4 center, on which the O2 molecule is chemically adsorbed, instead of converting to an unfavorable Ru-N4 moiety (Figure S21a). Subsequently, the activated O2 molecule captures a proton from acidic electrolyte with simultaneous electron transfer through graphene, forming the OOH species (as the rate-limiting step). Once the peroxide species is generated, it will undergo direct reduction to form H2O and adsorbed O*, according to the experimentally observed four-electron pathway. Next, the adsorbed O atom is further reduced via proton-coupled electron transfers, giving rise to OH* and the second H2O molecule. The DFT calculation result is also consistent with the observed low overpotential of Ru-N/G-750 in the electrochemical test and positively shifted Ru 3p1/2 peaks in XPS spectra after testing (Figure S23), suggesting that the high-valent Ru-oxo-N4 moieties are likely the origin of ORR catalytic performance, particularly under oxidative acidic conditions.

CONCLUSION

A Ru-N/G catalyst on which the Ru was atomically dispersed was successfully synthesized and demonstrated as an efficient ORR electrocatalyst in acidic medium. The Ru-N/G catalyst was readily prepared by annealing GO and Ru salts under an NH3 atmosphere. This catalyst showed excellent catalytic performance with superior onset potential, electron-transfer number, durability, tolerance against methanol crossover, and carbon monoxide poisoning in acidic medium. It was found that the ORR activity of this graphene-based material is strongly determined by the incorporation of a small amount of Ru. HAADF-STEM characterization supported the conclusion that homogeneously dispersed Ru atoms were present on the nitrogen-doped graphene. The formation of nanoparticles or the absence of nitrogen doping both weakened the ORR activity in the control samples. Based on these results, the isolated Ru atoms with nitrogen coordination are suggested to be the dominant active sites in the catalyst. The quantitative analysis of the EXAFS and XANES has revealed the existence of Ru-N4 moieties embedded in graphene sheets with axial oxygen adsorption. DFT calculations further indicated that ORR catalytic activity of Ru-N/G-750 preferably originated from the Ru-oxo-N4 moieties instead of Ru-N4 during the oxidative electrocatalytic condition. These findings shed light on future designs for high-performance electrocatalysts for ORR in acid medium.

EXPERIMENTAL METHODS

Material Synthesis. All chemicals were purchased from Sigma-Aldrich unless otherwise specified. GO was synthesized from graphite flakes (~150 μm flakes) using the improved Hummers’ method. General Preparation of Metal/Nitrogen-Doped Graphene. An aqueous suspension of GO (2 mg mL−1) was first prepared by adding 100 mg of GO into 50 mL of deionized water and sonicating
for 24 h (Fisher scientific, model FS110H). A 0.0125 M solution of metal salt was prepared using Ru(NH₃)₆Cl₃ (for the Ru catalyst) or FeCl₃ (for the Fe catalyst), respectively. 0.5 mL of the metal salt solution was added into the GO solution, and the mixture was sonicated for 3 h. This precursor solution was freeze-dried for at least 24 h to produce a precursor foam. The dried GO foam was then placed in the center of an 1 in. quartz tube furnace (calibrated using a k-type thermocouple probe). After pumping and purging the system with Ar 3 x, the temperature was ramped at 20 °C min⁻¹ up to 750 °C while feeding Ar (100 sccm) and NH₃ (50 sccm) at room pressure. The reaction was carried out for 1 h, then the furnace was cooled to room temperature under Ar protection. The final product of metal/nitrogen-doped graphene was then obtained. The temperature-controlled Ru-N/G samples were prepared by varying the annealing temperature (550, 650, 750, and 800 °C), with the rest of the procedure kept the same. The Ru-G-750 sample was prepared using the no NH₃ present during the annealing process, and the 2Ru-N/G-750 sample was prepared by doubling the amount of Ru(NH₃)₆Cl₃ added into the precursor solution, with the annealing temperature kept the same. The pure nitrogen-doped graphene (N/G-750) was synthesized without the addition of Ru(NH₃)₆Cl₃ in the precursor solution.

Characterizations. TEM images were obtained on a JEOL-2100F field emission gun TEM equipped with an EDS detector at an acceleration voltage of 200 kV. SEM images were acquired on a JEOL-6500F SEM. Abrasion-corrected TEM and HAADF-STEM measurements were carried out at 80 kV using a FEI Titan Themis Σ/TEM equipped with image and probe spherical aberration correctors. Chemical compositions and elemental oxidation states of the samples were investigated by XPS spectroscopy with a base pressure of 5 × 10⁻¹⁰ Torr. The survey spectra were recorded in a 0.5 eV step size with a pass energy of 140 eV. Detailed scans were recorded in 0.1 eV step sizes with a pass energy of 26 eV. The elemental spectra were all shifted with respect to C 1s peaks at 284.5 eV as reference. XRD analysis was performed by a Rigaku D/Max Ultima II (Rigaku Corporation) equipped with a Cu Kα radiation, graphite monochromator, and scintillation counter. Quantitative analysis of Ru loading was carried using a PerkinElmer Optima 4300 DV ICP-OES. A Renishaw Raman microscope using 514 nm laser excitation at room temperature in air with a laser power of 5 mW was employed to obtain OES. A Renishaw Raman microscope using 514 nm laser excitation at room temperature with a laser power of 5 mW was employed to obtain OES. A Renishaw Raman microscope using 514 nm laser excitation at room temperature with a laser power of 5 mW was employed to obtain OES. A Renishaw Raman microscope using 514 nm laser excitation at room temperature with a laser power of 5 mW was employed to obtain OES.

Device Fabrication and Electrochemical Measurement. RDE and RRDE experiments were conducted in an electrochemical cell (AUTOLAB PGSTAT302) using a Pine Instrumentator (model: AFM3RCE) that was connected to a CH Instruments electrochemical analyzer (model 608D) with an Hg/HgSO₄ reference electrode (Figure S24 and Supporting Note S2) and a Pt wire counter electrode. A catalyst ink was prepared by dispersing 4 mg of catalyst and 80 μL of the catalyst ink was loaded onto a glassy carbon electrode (5 mm in diameter). A flow of O₂ (~100 sccm), generated from a constant stream bubbling in the cell solution, was maintained over the electrolyte during the measurement to ensure continuous O₂ saturation. CV was carried out with potential ranging from 0.1 to 1.1 V (vs RHE) at a scan rate of 20 mV s⁻¹ (the electrolyte was sparged with Ar gas for Ar saturation). ORR activity was recorded in an O₂-saturated 0.1 M HClO₄ electrolyte with linear sweep voltammetry (LSV) performed with a potential ranging from 1.2 to 0.1 V (vs RHE) at a scan rate of 5 mV s⁻¹ rotation speed of 1600 rpm. The half-wave potential of Ru-N/G-750 catalyst was estimated by determining the maxima of the derivatives of ORR reduction current (vs RHE). Measurements were all carried out in 0.1 M HClO₄ (pH 1). For RRDE experiments, the electrode rotation speed was set at 1600 rpm (scan rate, 0.05 V/s; platinum data collected from anodic sweeps), while the Pt ring electrode potential was held at 1.2 V vs RHE (see more details in Supporting Note S3).

X-ray Absorption Spectra Data Collection, Analysis, and Modeling. Ru K-edge X-ray absorption spectra were acquired at room temperature in fluorescence mode at beamline BL14W1 of Shanghai Synchrotron Radiation Facility (SSRF) using a Si(111) double-crystal monochromator. The storage ring of SSRF was operated at 3.5 GeV with a current between 150 and 210 mA. The energy was calibrated using Ru foil, while the incident and fluorescence X-ray intensities were monitored by using standard Au- and Fe-filled ion chamber and 7-element high-purity Germanium detectors, respectively. The XAFS raw data were background-subtracted, normalized, and Fourier transformed by the standard procedures with the ATHENA program. Least-squares curve fitting analysis of the EXAFS χ(k) data was carried out using the ARTEMIS program with the theoretical scattering amplitudes, phase shifts, and the photoelectron mean free path for all paths calculated by ab initio code FEFF9.05. The details of curve fitting are discussed in the Supporting Note S4.

The Ru K-edge theoretical XANES calculations were carried out with the FDMNES code in the framework of real-space full multiple-scattering (FMS) scheme using the muffin-tin (MT) approximation for the potential.70–72 The energy-dependent exchange–correlation potential was calculated in the real Hedin–Lundqvist scheme, and then the spectra are convoluted using a Lorentzian function with an energy-dependent width to account for the broadening due both to the core-hole width and to the final state width. A cluster of 5.0 Å radius having ~30 atoms surrounding the absorber was used for the self-consistency, and a cluster of 11.0 Å radius having ~140 atoms was used for FMS, with satisfactory convergence being achieved. Due to the important non-MT effects in asymmetrical or sparse systems, the full potential approach on the basis of FDM was also applied to some archetypical structural models using a relatively smaller cluster of 8.0 Å radius having ~80 atoms. Generally, the RuNₓCₓ moieties were built based on three architectures, namely the porphyrinic and pyridinic ones and those enclosed in a graphene sheet; the probability of various axial oxygen or nitrogen ligands was considered in the calculation.

DFT Modeling. The structural relaxation and electronic energy calculations are computed by DFT implemented in Vienna ab Initio Simulation Package (VASP)73–74 with Perdew, Burke, and Ernzerhof functionals.75–76 The graphene supercell is 5 × 6 with 12 Å spacing in periodic direction to eliminate the interaction of periodic images of the systems. The K-point mesh is 3 × 3 × 1. The force for relaxation is converged to <0.01 eV/Å. The cutoff energy for plane wave basis is 400 eV. The Gibbs free energy G is calculated as G = E_diss + E_FEE – T&S(abs), where the zero point energy estimated for the adsorbed species under harmonic approximation, and S(abs) is the vibrational entropy estimated as in eq 1:

\[
S_{abs} = \sum_i \left[ \frac{\beta \varepsilon_i}{\exp(\beta \varepsilon_i)} - 1 \right] \left[ 1 - \exp(-\beta \varepsilon_i) \right]
\]

where \( \varepsilon_i \) is the vibrational energy of adsorbed molecules as calculated within DFT. The configurational entropy is neglected. Based on computational hydrogen electrode model, the chemical potential of H⁺ + e⁻ can be calculated as in eq 2:

\[
\mu(H^+) + \mu(e^-) = 1/2\mu(H_2(g)) - eU
\]

The chemical potential of H₂ is used in 1 atm, while H₂O is under 0.034 atm, corresponding to the vapor pressure of liquid water at 300 K.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b02148.

SEM, HAADF-STEM, and EDS images; Raman, XRD, XPS, and XAFS spectra; DFT calculation and additional experimental details (PDF)
This work was supported by the Air Force Office of Scientific Research (FA9550-14-1-0111). J.S. thanks the China Scholarship Council for partial funding. S.Y. and E.R. acknowledge support from the Jianlin Xie Foundation of Institute of High Energy Physics, China, and the Welch Foundation (C-1590). J.D. and D.C. acknowledge support from the Office of Energy BES grant DE-SC0012547 and by the Robert Welch Foundation for partial funding. S.Y. and E.R. acknowledge financial support from the National Natural Science Foundation of China (grant nos. 11475212 and 11605225). J.D. acknowledges support from the Jianlin Xie Foundation of Institute of High Energy Physics, Chinese Academy of Science.

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