ABSTRACT: Atomically dispersed precious metal catalysts have emerged as a frontier in catalysis. However, a robust, generic synthetic strategy toward atomically dispersed catalysts is still lacking, which has limited systematic studies revealing their general catalytic trends distinct from those of conventional nanoparticle (NP)-based catalysts. Herein, we report a general synthetic strategy toward atomically dispersed precious metal catalysts, which consists of “trapping” precious metal precursors on a heteroatom-doped carbonaceous layer coated on a carbon support and “immobilizing” them with a SiO₂ layer during thermal activation. Through the “trapping-and-immobilizing” method, five atomically dispersed precious metal catalysts (Os, Ru, Rh, Ir, and Pt) could be obtained and served as model catalysts for unravelling catalytic trends for the oxygen reduction reaction (ORR). Owing to their isolated geometry, the atomically dispersed precious metal catalysts generally showed higher selectivity for H₂O₂ production than their NP counterparts for the ORR. Among the atomically dispersed catalysts, the H₂O₂ selectivity was changed by the types of metals, with atomically dispersed Pt catalyst showing the highest selectivity. A combination of experimental results and density functional theory calculations revealed that the selectivity trend of atomically dispersed catalysts could be correlated to the binding energy difference between *OOH and *O species. In terms of 2 e⁻ ORR activity, the atomically dispersed Rh catalyst showed the best activity. Our general approach to atomically dispersed precious metal catalysts may help in understanding their unique catalytic behaviors for the ORR.

KEYWORDS: atomically dispersed catalysts, H₂O₂ production, preparation mechanism, oxygen reduction reaction, selectivity

Precious-metal-based heterogeneous catalysts have been mainstays in modern chemical industries,¹⁻³ including energy conversion, fine chemical production, and automotive exhaust gas abatement. However, precious metals such as Pt, Ir, and Rh are prohibitively expensive and scarce. Furthermore, widely used nanoparticle (NP)-based heterogeneous catalysts can exploit only a small fraction of the total metal atoms. The inherent limitations of NP-based catalysts have triggered a recent drive toward atomically dispersed catalysts or single-atom catalysts,⁴⁻³⁸ which can maximize atom efficiency and provide unusual catalytic activity,¹³,¹⁵⁻²⁵ and selectivity,¹⁶⁻³² for a diverse set of thermo-, photo-, and electrocatalytic reactions. Owing to their extraordinary catalytic properties, atomically dispersed catalysts have received tremendous attention recently as a research frontier in the field of catalysis.

The most straightforward and widely used method for synthesizing atomically dispersed precious metal catalysts is an impregnation–thermal activation method. However, this method is effective only with very low metal loadings;³⁹,⁴⁰ high metal loadings often lead to agglomeration into NPs owing to the high surface energy of the atomically dispersed...
Hence, considerable efforts have been made toward developing new synthetic strategies for atomically dispersed precious metal catalysts, including thermal conversion of metal–organic frameworks, defect engineering strategies, nanopore confinement, photochemical reduction, atomic layer deposition, galvanic replacement, and high-temperature redispersion of NPs. Nevertheless, there is still a lack of generic, robust preparation methods that can afford atomically dispersed catalysts of a wide range of precious metals. More importantly, the mechanisms underlying the formation of atomically dispersed precious metal catalysts have mostly remained elusive, hindering their rational design.

Such synthetic difficulties have hampered systematic investigations of general catalytic trends of atomically dispersed catalysts distinguished from those of conventional NP-based catalysts. The dearth of systematic studies may result in controversy over the catalytic properties manifested by atomically dispersed precious metal catalysts. For the oxygen reduction reaction (ORR), which is a performance-limiting key reaction in fuel cell technologies, there exists an ongoing controversy over selectivity of the ORR on atomically dispersed Pt catalysts. Some groups revealed that the ORR over atomically dispersed Pt catalysts proceeds via a 2-electron ($2e^-$) pathway that predominantly generates $H_2O_2$, whereas other groups reported that oxygen reduction via a 4 $e^-$ pathway is favored for single-site Pt catalysts.

In this work, we propose a generalized preparation method for carbon-supported atomically dispersed precious metal catalysts. The synthetic strategy consists of “trapping” precious metal precursor molecules on a heteroatom-doped carbonaceous layer coated on a carbon support and then “immobilizing” them during thermal activation via coating with a SiO$_2$ protective layer. By combining X-ray absorption...
spectroscopy (XAS) and mass spectrometry (MS) during thermal activation processes, we found that the strong interaction between the metal precursors and the support provides stable, isolated anchoring of metal precursors during the impregnation step and retards precursor decompositions during the activation step, which assists the conversion of the precursor into an isolated single-atom site. The SiO2 protective layer could mitigate agglomeration of the isolated metal sites during the thermal activation step, thus maximizing the density of atomically dispersed sites. Through this "trapping-and-immobilizing" strategy, a series of atomically dispersed precious metals (Os, Ru, Rh, Ir, and Pt) were prepared. We exploited the prepared atomically dispersed precious metal catalysts and their NP counterparts as model catalysts for investigating the catalytic reactivity trends in the ORR. We found that NP catalysts favored complete 4 $e^-$ reduction with near 0% of H$_2$O$_2$ yield regardless of types of metals, whereas atomically dispersed catalysts showed higher H$_2$O$_2$ yields compared to their counterpart NPs owing to the isolated geometry of their active sites. The H$_2$O$_2$ yields of atomically dispersed catalysts were varied depending on the types of metals, with Pt-based catalyst showing the best selectivity. A combination of experimental results and density functional theory (DFT) calculations revealed that binding energy difference between *OOH and *O species is a key parameter for dictating the ORR selectivity of atomically dispersed catalysts. Comparing ORR activity for 2 $e^-$ ORR, atomically dispersed Rh catalyst showed the best activity.

RESULTS AND DISCUSSION

Trapping-and-Immobilizing Strategy to Atomically Dispersed Precious Metal Catalysts. During the preparation of supported metal catalysts by the impregnation—activation method, metallic species can agglomerate during the impregnation step, the thermal activation step, or both. To mitigate agglomeration into NPs during each step, we designed a synthetic approach for atomically dispersed precious metal
catalysts, as illustrated in Figure 1a. First, an ionic liquid (IL) containing various heteroatoms was coated on a carbon nanotube (CNT) support, which was then annealed at 450 °C. The heteroatoms, including N and O, contained in the resulting heteroatom-doped carbonaceous layer could act as favorable anchoring sites for trapping metal precursor molecules, thus inducing an isolated geometry of adsorbed precursors. After impregnation of a metal precursor, a SiO2 protective layer was coated on the surface to immobilizing the isolated metal precursors during the thermal activation step.56,57

The effectiveness of our strategy was visualized using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of a series of Pt catalysts (3 wt % Pt loading, denoted as 3Pt) prepared by three different protocols (Figure 1b–d). When the Pt precursor (H2PtCl6·6H2O) was impregnated onto the CNT and activated without the IL and SiO2 coating steps (3Pt/CNT_IL), Pt NPs of ca. 1 nm were generated (Figure 1b). The addition of the IL coating step before the impregnation of H2PtCl6·6H2O (3Pt/CNT_IL) resulted in the generation of atomically dispersed Pt sites as well as Pt NPs (Figure 1c). Interestingly, when both the IL and SiO2 coating steps were exploited (3Pt/CNT_IL_SiO2), only atomically dispersed Pt sites were generated (Figure 1d). The Pt L3-edge k3-weighted extended X-ray absorption fine structure (EXAFS) analysis of the three catalysts (Figure 1e–g and Table S1) corroborated this trend. In the EXAFS spectra of the catalysts, 3Pt/CNT showed scattering peaks corresponding to Pt–Pt and Pt–C, indicating the formation of supported Pt NPs (Figure 1e), whereas 3Pt/CNT_IL_SiO2 only exhibited scattering peaks for light elements (Pt–N and Pt–Cl) that could stabilize atomically dispersed Pt (Figure 1g).59 3Pt/CNT_IL showed EXAFS peaks for both NPs and atomically dispersed sites (Figure 1f).

The HAADF-STEM and EXAFS analyses clearly verify our rationale for preparing atomically dispersed precious metal catalysts.

We extended our approach to the preparation of Pt catalysts with a broad range of Pt loadings (1, 3, 5, and 10 wt %). The HAADF-STEM images and corresponding size distribution histograms of Pt/CNTs (Figures 2a–d and S1a–d) clearly revealed that Pt NPs were formed on the bare CNT, regardless of the Pt loading. In the case of the Pt/CNT_IL catalysts, atomically dispersed Pt sites were generated at 1 wt % loading (Figures 2e and S1e). However, an increase in Pt loading resulted in a gradual increase in the density of Pt NPs at the expense of atomically dispersed Pt sites (Figures 2f–h and S1f–h). For the Pt/CNT_IL_SiO2 catalysts, the formation of Pt NPs was further impeded. Atomically dispersed Pt sites were exclusively formed at 1 and 3 wt % loading (Figures 2i,j and S1i,j), whereas some Pt NPs were evolved at 5 wt % loading and the proportion of NPs was increased at 10 wt % loading (Figures 2k,l and S1k,l). The X-ray diffraction (XRD) patterns of the series of catalysts (Figure S2) confirmed the HAADF-STEM results. At Pt loadings of 3, 5, and 10 wt %, the XRD peak around 39.8° corresponding to the (111) facet of face-centered-cubic (fcc) Pt intensified gradually in the order of Pt/CNT_IL_SiO2, Pt/CNT_IL, and Pt/CNT (Figure S2), which is consistent with the increasing formation of Pt NPs, as observed by HAADF-STEM. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Table S2) indicated that the actual Pt loadings were similar to the nominal loadings for all the series of catalysts. The HAADF-STEM, XRD, and ICP-OES results demonstrated that our trapping-and-immobilizing strategy is generally effective for generating very small NPs down to single atoms.

**Role of IL and SiO2 Coatings.** To clarify the role of the IL and SiO2 coatings in generating atomically dispersed precious metal catalysts, the separate synthesis steps were investigated in detail. After IL adsorption and low-temperature annealing at 450 °C, an amorphous carbonaceous layer was uniformly generated on the CNT, as revealed by high-resolution transmission electron microscopy (HRTEM) images of CNT and CNT_IL (Figure S3). The XRD patterns (Figure S4) and X-ray photoelectron spectroscopy (XPS) spectra (Figure S5) of these samples further confirmed the formation of an amorphous layer (see the Supporting Information). The elemental analysis results for CNT and CNT_IL (Table S3) indicated that the heteroatom contents increased significantly in CNT_IL (13.6 wt % nitrogen and 10.8 wt % oxygen) compared with those in CNT (0 wt % nitrogen and 2.5 wt % oxygen).

The XAS analysis (Figure S6 and S7) provided important evidence for enhanced interactions between the Pt precursor and the support after the formation of the heteroatom-enriched carbon layer. The Pt L3-edge X-ray absorption near edge structure (XANES) spectra of H2PtCl6·6H2O and H2PtCl6·6H2O-impregnated CNT (3Pt/CNT_Imp) and CNT_IL (3Pt/CNT_IL_Imp) revealed clear differences between the precursor and impregnated states in the edge and postedge regions (Figure S6 and see the Supporting Information). While the XANES spectra of 3Pt/CNT_Imp and 3Pt/CNT_IL_Imp showed similar changes compared with that of H2PtCl6·6H2O, the two samples showed a clear difference in the intensity of peak B, which is ascribed to the hybridization of Pt 5d and Cl 3d states.58,59 The intensity of peak B decreased only slightly for 3Pt/CNT_Imp relative to that of H2PtCl6·6H2O, whereas a marked decrease was observed for 3Pt/CNT_IL_Imp, likely indicating the occurrence of additional Pt–Cl bond breaking. The EXAFS analysis of this series of samples (Figure S7 and Table S4) indicated that the peak for Pt–N scattering was newly evolved in 3Pt/CNT_IL_Imp along with Pt–Cl scattering, whereas 3Pt/CNT_Imp had only Pt–Cl scattering. We suppose that H2PtCl6·6H2O could be further stabilized by ligand exchange from Cl to N in CNT_IL during the impregnation process, which would provide strong adsorption sites for Pt precursors.

The strong interaction between H2PtCl6·6H2O and 3Pt/CNT_IL_Imp could influence the activation process of impregnated Pt precursors, thus affecting the dispersion state of the final Pt species. We analyzed the thermal activation processes of the impregnated catalysts by monitoring the consumed and desorbed gases in a quartz flow reactor coupled to a mass spectrometer while raising the temperature from room temperature (RT) to 500 °C under 2% H2/Ar gas flow (Figure 3). When activating 3Pt/CNT_Imp, a sharp peak for H2 consumption was observed near 150 °C (Figure 3a) accompanied by a peak for HCl generation (Figure 3b), implying that H2PtCl6·6H2O decomposed into HCl. Further decomposition into Cl2 was observed near 200 °C (Figure 3c) without H2 consumption. These MS results suggest that the H2PtCl6·6H2O molecules decomposed by H2 became mobile enough to agglomerate into Pt NPs via the reaction Pt–Cl + Cl–Pt → Cl2 + Pt–Pt, thus generating Cl2 gas. Contrary to the rapid activation observed on 3Pt/CNT_Imp, this process was slowed down for 3Pt/CNT_IL_Imp, as revealed by the broad
peaks for H\textsubscript{2} consumption (Figure 3a) and HCl production (Figure 3b). In addition, for 3Pt/CNT\_IL\_Imp, Cl\textsubscript{2} was evolved at higher temperatures and the peak area for Cl\textsubscript{2} decreased drastically compared with that for 3Pt/CNT\_Imp (Figure 3c). It appears that strong anchoring of H\textsubscript{2}PtCl\textsubscript{6}\cdot 6H\textsubscript{2}O on 3Pt/CNT\_IL\_Imp retards its decomposition, allowing the generated atomically dispersed sites to be stably isolated while suppressing agglomeration into NPs.

Next, we investigated the role of the SiO\textsubscript{2} coating. The SiO\textsubscript{2} coated sample was prepared by mixing the H\textsubscript{2}PtCl\textsubscript{6}\cdot 6H\textsubscript{2}O-impregnated powders with tetraethyl orthosilicate (TEOS), and the resulting sample was denoted as 3Pt/CNT\_IL\_Imp\_SiO\textsubscript{2}. We note that the polymerization of TEOS was catalyzed by impregnated H\textsubscript{2}PtCl\textsubscript{6}\cdot 6H\textsubscript{2}O without the use of any acid or base catalyst, inducing the formation of a SiO\textsubscript{2} layer exclusively on the surface of Pt/CNT\_IL. The HAADF-STEM images of 3Pt/CNT\_IL\_SiO\textsubscript{2} before HF etching showed that the SiO\textsubscript{2} protective layer coated the atomically dispersed Pt supported on CNT\_IL (Figure S8a–c). The HAADF-STEM and energy-dispersive X-ray spectroscopy (EDS) mapping images of 3Pt/CNT\_IL\_SiO\textsubscript{2} indicated the presence of Si and O, along with Pt, C, and N (Figure S8d–i). XANES and XPS analyses indicated no significant chemical interaction between Pt and the SiO\textsubscript{2} layer (Figure S9 and see the Supporting Information). However, the SiO\textsubscript{2} layer could influence the thermal activation behavior of impregnated H\textsubscript{2}PtCl\textsubscript{6}\cdot 6H\textsubscript{2}O. The MS spectrum of 3Pt/CNT\_IL\_Imp\_SiO\textsubscript{2} recorded under H\textsubscript{2}/Ar gas flow showed a broad peak for HCl with concomitant consumption of H\textsubscript{2}, similar to that of 3Pt/CNT\_IL\_Imp (Figure 3a,b). Interestingly, the Cl\textsubscript{2} evolution peak of 3Pt/CNT\_IL\_Imp\_SiO\textsubscript{2} was shifted to higher temperatures compared with that of 3Pt/CNT\_IL\_Imp (Figure 3c,d), suggesting that the SiO\textsubscript{2} coating could further mitigate the agglomeration of Pt species.

**General Applicability of the Developed Strategy.** We applied the trapping-and-immobilizing strategy to other precious metals, namely, Os, Ru, Rh, and Ir. For fair comparison of reactivity of these catalysts, the amount of loaded metals on CNT was adjusted to contain similar atomic percent. Hence, metal loadings were 3 wt % for Os and Ir and 1.5 wt % for Ru and Rh. Consistent with the series of Pt catalysts, the HAADF-STEM images (Figures 4 and S10) and the corresponding size distribution histograms (Figure S11) clearly revealed that the IL and SiO\textsubscript{2} coating steps gave rise to atomically dispersed precious metal species (M/CNT\_IL\_SiO\textsubscript{2}; M = Os, Ru, Rh, and Ir), whereas metal NPs were generated on bare CNT (M/CNT). The HAADF-STEM images (Figures 4 and S10) and the corresponding size distribution histograms (Figure S11) clearly revealed that the IL and SiO\textsubscript{2} coating steps gave rise to atomically dispersed precious metal species (M/CNT\_IL\_SiO\textsubscript{2}; M = Os, Ru, Rh, and Ir), whereas metal NPs were generated on bare CNT (M/CNT).
results were further corroborated by Os L3-, Ru K-, Rh K-, and Ir L3-edge EXAFS analyses (Figure S12 and Table S5). The EXAFS spectra of the M/CNT_IL_SiO2 samples, with the exception of Ru/CNT_IL_SiO2, showed peaks only for scattering with light elements (M−N and M−Cl), whereas those of the M/CNT samples exhibited scattering peaks for M−M along with M−C. In Ru/CNT_IL_SiO2, some small clusters were generated, but the majority of Ru was found in atomically dispersed sites (Figure S11d).

**ORR Activity and Selectivity Trends.** A series of atomically dispersed precious metal catalysts covering a wide range of compositions can serve as a platform for investigating catalytic trends. By exploiting five sets of M/CNT_IL_SiO2 and M/CNT catalysts as respective model systems for atomically dispersed and NP catalysts, we investigated their catalytic activity and selectivity trends for the ORR. The electrocatalytic properties of the catalysts were evaluated using the rotating ring-disk electrode (RRDE) technique in an acidic electrolyte (0.1 M HClO4). The ORR polarization curves and H2O2 yields of Os (a), 1.5Ru (b), 1.5Rh (c), 3Ir (d), and 3Pt (e) supported on CNT and CNT_IL_SiO2. (f) H2O2 yields of the 10 catalysts at −0.5 mA cm−2 (M/CNT and M/CNT_IL_SiO2 are denoted as MNP and M1, respectively).

**Figure 5.** ORR activities and selectivities of atomically dispersed metal catalysts and their NP counterparts. (a–e) ORR polarization curves and H2O2 yields of 3Os (a), 1.5Ru (b), 1.5Rh (c), 3Ir (d), and 3Pt (e) supported on CNT and CNT_IL_SiO2. (f) H2O2 yields of the 10 catalysts at −0.5 mA cm−2 (M/CNT and M/CNT_IL_SiO2 are denoted as MNP and M1, respectively).
the reactivity trends of these catalysts could be dictated by atomically dispersed metal species.

The atomically dispersed 3Pt/CNT_IL_SiO₂ catalyst showed excellent durability; its activity and selectivity were preserved after an accelerated degradation test (ADT), which was performed by cycling the potential between 0.6 and 1.0 V under N₂-saturated conditions at a scan rate of 50 mV s⁻¹ for 5000 cycles (Figure S15a). The HAADF-STEM image after the ADT (Figure S15b) showed that the atomically dispersed Pt sites were well-preserved without agglomeration.

To unravel the origins of the catalytic properties manifested by the atomically dispersed M/CNT_IL_SiO₂ catalysts, we focused on the selectivity trends for these catalysts. Considering the associative mechanism, O₂ is adsorbed on the catalyst surface in the form of *OOH and sequentially reduced with O−O bond cleavage to generate H₂O (reactions 1−3).

\[ *O_2 + (H^+ + e^-) \rightarrow *OOH \quad (1) \]

\[ *OOH + (H^+ + e^-) \rightarrow *O + H_2O \quad (2) \]

\[ *O + (2H^+ + 2e^-) \rightarrow H_2O \quad (3) \]

In this mechanism, if cleavage of the O−O bond in *OOH is not favored during reduction, H₂O₂ is produced (reactions 1 and 4).

\[ *OOH + (H^+ + e^-) \rightarrow H_2O_2 \quad (4) \]

These mechanistic considerations suggest that the selectivity of the ORR is determined by the propensity for O−O bond cleavage. Hence, the higher H₂O₂ selectivity of M/CNT_IL_SiO₂ relative to that of M/CNT can be accounted for primarily by a geometric effect, where dissociative adsorption of O₂ cannot occur owing to the absence of ensemble or hollow sites. However, the variation in the H₂O₂ yields among the five M/CNT_IL_SiO₂ catalysts cannot be fully explained by the geometric effect alone. To clarify the variation in selectivity observed for the atomically dispersed.
catalysts, we further investigated the determining factors for selectivity in the associative mechanism of the ORR.

In the associative mechanism, the propensity for O–O bond cleavage is determined by two competing reactions (reactions 2 and 4). Consequently, the relative stabilities of °OOH and °O provide the thermodynamic driving force for O–O bond cleavage (Figure 6a). We calculated the DFT energetics for the oxygen binding energies of 10 model catalysts. For calculations of the atomically dispersed catalyst models, M–N₄ systems, the most general form of atomically dispersed metals that can be stably placed on N-doped carbon supports65,64 were used. As NP catalyst models, hexagonal-close-packed (hcp) (0001) surfaces of Os and Ru and fcc (111) surfaces of Rh, Ir, and Pt were used. For these models, the binding energies of O, °OOH, and °O₂ species were calculated (Figures S16–S18 and Table S6). The atomically dispersed catalysts and NP-based catalysts are denoted as M₁ and MNP (M = Os, Ru, Rh, Ir, and Pt), respectively.

The calculation results revealed that the difference between the O and °OOH binding energies, ΔGₒ – ΔG°OOH which describes the thermodynamic propensity for O–O bond preservation, had a linear relationship with the experimental H₂O₂ yields of the atomically dispersed catalysts (Figure 6b). We note that there is a scaling relationship between ΔGₒ – ΔG°OOH and ΔGₒ (Figure S19). Hence, as the O binding energy is weakened, the H₂O₂ selectivity increased proportionally (Figure 6c). Similar trends were observed with the other oxygen species (OOH and °O₂) for the atomically dispersed catalysts owing to the scaling relationships among ΔGₒ, ΔG°OOH, and ΔGₒ (Figures S20 and S21).

Inspired by these relationships, we performed O₂ temperature-programmed desorption (TPD) experiments to obtain the binding strengths of chemisorbed O₂ on the atomically dispersed catalysts (Figure S22a–c). Interestingly, the peak temperatures for O₂ desorption from the catalysts, which represent the oxygen binding strength, had an inverse linear relation with their H₂O₂ yields (Figure S22d,e), confirming the relationship derived from the DFT calculations. We also tried to obtain a general selectivity trend encompassing both the NP-based and atomically dispersed catalysts (Figures S23–S25). It was found that a linear relation was obtained only with the ΔGₒ – ΔG°OOH descriptor (Figure S26).

Next, we discuss the activity trends of the atomically dispersed catalysts for the ORR. Panels d and e of Figure 6 display the onset potentials of the atomically dispersed and NP-based catalysts as a function of the °O binding energies for the 4 e⁻ and 2 e⁻ ORR pathways, respectively. For the 4 e⁻ ORR pathway (Figure 6d), the NP-based catalysts showed higher onset potentials, whereas for the 2 e⁻ ORR pathway (Figure 6e), the atomically dispersed catalysts exhibited onset potentials that were higher than or similar to those of the NP-based catalysts. Given that a proper oxygen binding energy of the 2 e⁻ ORR pathway is placed on the weaker oxygen binding energy side than that of the 4 e⁻ ORR pathway, the atomically dispersed catalysts that have weak oxygen binding energies are more likely to show better activity for the 2 e⁻ ORR pathway. Conversely, the NP-based catalysts with relatively strong oxygen binding energies are appropriate for the 4 e⁻ ORR pathway. Accordingly, PtNP appeared on the top of the volcano for the 4 e⁻ ORR pathway as expected, whereas for the 2 e⁻ ORR pathway, Rh₁ was located on the top of the volcano with an onset potential of 0.68 V. We note that although Rh₁ showed the highest activity for the 2 e⁻ ORR pathway, its selectivity was lower than that of Pt₁.

Overall, the oxygen binding energy can serve as a descriptor for both the selectivity and activity of the 2 e⁻ ORR pathway. For selectivity, a catalyst with weaker oxygen binding yields higher selectivity for H₂O₂. In the case of activity, the optimal binding energy is needed to achieve superior activity. Therefore, there might be a trade-off between activity and selectivity in the 2 e⁻ ORR pathway, which should be considered when designing atomically dispersed catalysts for the ORR. Our results suggest that the unique ORR selectivity and activity trends of the atomically dispersed precious metal catalysts originate from their abnormally weak oxygen binding energies in conjunction with their geometric configurations.

CONCLUSIONS

In summary, we have proposed a new general preparation route to atomically dispersed precious metal catalysts. Our method consists of trapping metal precursors with a heteroatom-enriched layer during impregnation and immobilizing the precursors with a SiO₂ layer during thermal activation, which could preferentially produce atomically dispersed sites. This method enabled the preparation of various atomically dispersed precious metals catalysts (Os, Ru, Rh, Ir, and Pt), which served as model catalysts for investigating the activity and selectivity trends of the ORR. The atomically dispersed catalysts exhibited higher H₂O₂ selectivities and lower ORR activities compared with their NP counterparts, as attributed to their weak oxygen binding energies in combination with their unique geometric arrangements. Among the atomically dispersed catalysts, the relative binding energies of °OOH and °O species were identified as key parameters for determining the selectivity for H₂O₂ production, with atomically dispersed Rh showing the highest onset potential. We envisage that this work will provide insights into the preparation of atomically dispersed catalysts and a better understanding of their catalytic properties not only for the ORR but also for other electrochemical energy conversion reactions.

MATERIALS AND METHODS

Ionic Liquid Coating on CNT. Prior to use, the CNT (MR 99, Carbon Nanomaterial Technology Co.) was purified by thermal annealing and acid treatments to remove metallic impurities according to reported procedures66,67. Then, 0.1 g of the acid-treated CNT was mixed with 1.44 g of IL (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, Aldrich, 98%) in an agate mortar for 15 min. The sticky mixture was transferred to a crucible, heated to 450 °C at a ramping rate of 5.3 °C min⁻¹, and maintained at 450 °C for 1 h under N₂. The heat-treated powder was ground using a mortar, washed with a sufficient amount of acetone (Samchun Chemicals, 99.5%) by vacuum filtration to remove physisorbed IL from the CNT, and dried in a 60 °C oven.

Preparation of Catalysts. The catalysts were prepared by a wet impregnation and thermal reduction method. To prepare the M/CNT and M/CNT IL catalysts, the desired amounts of support (CNT or CNT_IL) and metal precursor were mixed in acetone and dried at RT with stirring. For Os, Ru, Rh, Ir, and Pt, H₂OsCl₆·xH₂O (Alfa Aesar), RuCl₃·xH₂O (Aldrich), RhCl₃·xH₂O (Alfa Aesar), H₂IrCl₆·xH₂O (Alfa Aesar), and H₂PtCl₆·xH₂O (Unicom) were used as the metal precursors, respectively. For Pt catalysts, the metal loading was varied from 1 to 10 wt %. The metal-precursor-impregnated support was activated by heating from RT to 200 °C at a ramping rate of 0.58 °C min⁻¹ and maintaining at 200 °C for 2 h in an H₂ flow. Hydrogen adsorbed on the metals was removed by heating...
from 200 to 350 °C (ramping rate: 2.5 °C min⁻¹) and maintaining at 350 °C for 3 h in a N₂ flow. To prepare the M/CNT IL-SiO₂ catalysts, 0.1 g of the metal-precursor-impregnated CNT_IL was mixed with 2.5 mL of TEOS (Acros Organics, 98.5%) in an agate mortar for 5 min and dried overnight at RT. After the activation process, the composite was dissolved in 10 wt % HF (J.T. Baker) and rinsed with copious amounts of ethanol (Samchun Chemicals, 94.5%) to etch the SiO₂ layer.

**Physicochemical Characterization.** HRTEM and HAADF-STEM images were acquired using a JEOL JEM-2100F and a FEI Titan 3 G2 60-300 TEM equipped with a double-sided spherical aberration (Cs) corrector operating at an accelerating voltage of 200 kV. XRD patterns of the catalysts were obtained using a high-power X-ray diffractometer (Rigaku, D/MAX2500 V/PC) equipped with a Cu Kα radiation source operating at 40 kV and 200 mA. The Pt content in the catalysts was determined by ICP-OES (Varian, 700-ES). The elemental analyses for C, H, N, O, and S were carried out using a thermal analyzer (Thermo Scientific, Flash 2000). XPS spectra were recorded using an instrument equipped with a monochromatic Al Kα radiation source (Thermo Fisher Scientific, ESCALAB 250XI). The XPS spectra were deconvoluted using the XPSSpeak41 software with the mixed (Gaussian 70, Lorentzian 30) function after Shirley-type background correction.

**X-ray Absorption Spectroscopy.** XAS was performed at Beamlines 6D, 8C, and 10C of the Pohang Accelerator Laboratory. The storage ring was operated at an energy of 3 GeV and a beam current of 400 mA. A Si(111) double-crystal monochromator was used to filter the incident photon energy, which was detuned by 30% for Os L₃-, Ir L₃-, and Pt L₃-edges to remove high-order harmonics. The storage ring was operated at an energy of 3 GeV and a beam current of 400 mA. A Si(111) double-crystal monochromator was used to filter the incident photon energy, which was detuned by 30% for Os L₃-, Ir L₃-, and Pt L₃-edges to remove high-order harmonics. The X-ray Absorption Spectroscopy. XAS was performed at Beamlines 6D, 8C, and 10C of the Pohang Accelerator Laboratory. The storage ring was operated at an energy of 3 GeV and a beam current of 400 mA. A Si(111) double-crystal monochromator was used to filter the incident photon energy, which was detuned by 30% for Os L₃-, Ir L₃-, and Pt L₃-edges to remove high-order harmonics. The X-ray Absorption Spectroscopy. XAS was performed at Beamlines 6D, 8C, and 10C of the Pohang Accelerator Laboratory. The storage ring was operated at an energy of 3 GeV and a beam current of 400 mA. A Si(111) double-crystal monochromator was used to filter the incident photon energy, which was detuned by 30% for Os L₃-, Ir L₃-, and Pt L₃-edges to remove high-order harmonics. The X-ray Absorption Spectroscopy. XAS was performed at Beamlines 6D, 8C, and 10C of the Pohang Accelerator Laboratory. The storage ring was operated at an energy of 3 GeV and a beam current of 400 mA. A Si(111) double-crystal monochromator was used to filter the incident photon energy, which was detuned by 30% for Os L₃-, Ir L₃-, and Pt L₃-edges to remove high-order harmonics.

**Electrochemical Characterization.** Electrochemical characterization of the catalysts was performed using a three-electrode electrochemical cell with an RRDE (Pine Research Instrumentation, CHI Instruments, CHI760E) in a three-electrode electrochemical cell with an RRDE (Pine Research Instrumentation, CHI Instruments, CHI760E). First, 30 mg of sample was degassed at 350 °C for 1 h (ramping rate: 10 °C min⁻¹) under a He flow to remove preadsorbed O₂ or H₂O molecules. After degassing, the sample was cooled to −50 °C and O₂ adsorption was carried out for 1 h under 10% O₂/He gas conditions, followed by He purging for 2 h at −50 °C to remove weakly adsorbed O₂. Then, the TPD experiment was performed by heating the sample to 500 °C (ramping rate: 10 °C min⁻¹) under a He flow.

**Density Functional Theory Calculations.** To understand the selectivity and activity trends of the atomically dispersed catalysts, DFT calculations were performed using the Vienna ab initio software package (VASP) with the Perdew-Burke-Ernzerhof (PBE) exchange–correlation functional. The projector-augmented-wave (PAW) scheme was employed to model the electron–ion interactions, and an additional vacuum of 20 Å and a dipole correction along the surface normal direction (chosen as the z-direction) were considered to prevent interaction, which occurs because of the periodic boundary condition in the z-direction. The active center of atomically dispersed catalysts was modeled using a metal atom (M) coordinated to four nitrogen atoms embedded in a graphene layer (M–N₄), using a (5 × 5) graphene unit cell (Figure S27). For the M–N₄ active sites, the energy cutoff was set at 500 eV, and a Γ centered (3 × 3 × 1) mesh was used to sample the reciprocal space. By contrast, the active centers of NP catalysts were modeled using a surface slab of the close-packed surface. First, the bulk structures of Os, Ru, Rh, Ir, and Pt were optimized using an energy cutoff of 650 eV and a Γ centered (14 × 14 × 10) k-point mesh. Then, 4 layers of (2 × 2) surface slabs of (0001) surfaces for hcp metals (Os and Ru) and (111) surfaces for fcc metals (Rh, Ir, and Pt) were constructed and optimized. An energy cutoff of 500 eV and a Γ centered (8 × 8 × 1) k-point mesh were employed for the slab model calculations, where the bottom two layers were fixed at their lattice sites during DFT optimization. We investigated all possible highly symmetric binding sites on the closed packed metal surfaces, i.e., on-top, bridge, fcc, and hcp sites (Figure S28), among which the most stable sites were used for the binding energy calculations. For the M–N₄ system, an embedded metal atom was considered as the binding site. The binding energies of *O*ₙₒ, *OH*, and *O* were defined using the gas-phase reference states of H₂O and H₂O⁻:

\[
\Delta G_{O_2} = G(*O) - G(*) - (2G_{H_2O} - 2G_{H}) \quad (5)
\]

\[
\Delta G_{OOH} = G(*OOH) - G(*) - (2G_{H_2O} - 3/2G_{H}) \quad (6)
\]

\[
\Delta G_O = G(*) - G(*) - (2G_{H_2O} - G_{H}) \quad (7)
\]

Here, G(*), G(*OOH), and G(*OH) represent the free energies of the initial, intermediate, and final states. The Gibb’s free energies were calculated as \( G = E_{SCF} + ZPE + \Delta G_{ vib} \), where \( E_{SCF} \) is the electronic self-consistent field energy from DFT, ZPE the zero-point energy, and \( \Delta G_{ vib} \) the vibrational free energy. The last two terms were calculated by performing partial Hessian diagonalization for the adsorbate species. For the gas molecules, rotational and translational entropies were included in addition to the aforementioned terms.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nano.9b08494.

EXAFS, particle size distribution histograms, XRD, and ICP-OES data of Pt catalysts; HRTEM, XRD, XPS, and elemental analysis data of supports; XANES, EXAFS, HAADF-STEM and EDS elemental mapping, and XPS data of intermediate samples; particle size distribution histograms and EXAFS data of Os, Ru, Rh, and Ir catalysts; electrocatalytic properties of Pt-loading-controlled catalysts and supports; ORR durability of 3Pt/CNT_IL_SiO\(_2\); binding energies of oxygen intermediates and H\(_2\)O\(_2\); yields; O\(_2\) TPD results; model systems for DFT calculations (PDF)

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Notes
The authors declare no competing financial interest.

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