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Implanting Isolated Ru Atoms into Edge-rich Carbon Matrix for Efficient Electrocatalytic Hydrogen Evolution

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Abstract

Although the maximized dispersion of metal atoms has been realized in the single-atom catalysts, further improving the intrinsic activity of the catalysts is of vital importance. Here, we report the decoration of isolated Ru atoms into an edge-rich carbon matrix for electrocatalytic hydrogen evolution reaction. The developed catalyst displays high catalytic performance with low overpotentials of 63 and 102 mV for achieving the current densities of 10 and 50 mA cm⁻², respectively. Its mass activity is about 9.6 times higher than that of the commercial Pt/C-20% catalyst at the overpotential of 100 mV. Experimental results and density functional theory calculations suggest that the edges in the carbon matrix enhance the local electric field at the Ru site and accelerate the reaction kinetics for hydrogen evolution. The present work may provide insights into electrocatalytic behavior and guide the design of advanced electrocatalysts.

Keywords: edge-rich carbon matrix, hydrogen evolution reaction, Ru, electrocatalysts

Hydrogen has been referred as the most promising sustainable and clean energy source for its high combustion enthalpy and no carbon emission.^[1-3] Electrocatalytic water splitting is regarded as an attractive approach for producing hydrogen fuel.^[4] Currently, Pt-based materials display unrivaled electrocatalytic performance for hydrogen evolution.^[5] However, the practical application of Pt-based electrocatalysts is greatly limited by the high cost and scarcity. Developing cost-efficient and highly active alternatives is considered as one important component for the hydrogen economy.^[6] As a cheaper alternative to Pt, Ru possesses a similar bond strength with hydrogen (~ 65 kcal mol⁻¹) but has been less studied as a viable electrocatalyst for hydrogen evolution reaction (HER).^[7] This initiates our desire to investigate the Ru active sites in the atomic level for improving the HER performance. Decorating the Ru centers into the desired architecture with precise configuration is of great importance for optimizing the catalytic performances but remains a considerable challenge.

As an ideal model bridging homogeneous and heterogeneous catalysis, single-atom catalysts represent the maximized atom utilization efficiency and often exhibit superior activity towards catalytic reactions.^[8-10] The performance of isolated active sites is highly relevant to their structures, such as configuration, dispersion state as well as the morphology of the supports.^[11, 12] Thus, the intrinsic activity of the single-atom catalyst is not the limitation and there is still much room for further improvement.^[13] A carbon matrix with good stability, high conductivity and confined microenvironment is believed as the excellent support for stabilizing isolated Ru centers for electrocatalysis.^[14-16] Moreover, the electronic density of states has been demonstrated to be strongly enhanced at the edges compared with the plane of graphene, it is thus anticipated that the intrinsic activity of single-atom catalysts can be further improved if the single-atom catalysts are

decorated over the edges of the carbon matrix, but this is rarely explored.^[17-19]

Here, we develop a feasible strategy to decorate isolated Ru sites with precise configuration into the edge-rich carbon matrix (ECM@Ru). Polydopamine particles with multi-edged morphology, integrating with the Ru species, are applied as the precursor for making the efficient catalyst. X-ray absorption fine structure spectroscopy verifies that isolated Ru atoms are surrounded by N atoms in unsaturated geometry. Based on the experimental and density functional theory (DFT) calculation results, it is thought that the edges lead to the accumulation of electrons around the Ru species, resulting in a local electric field enhancement and highly accelerated catalytic kinetics.

The synthetic procedure of ECM@Ru is shown in **Figure 1a**. First, the dual-soft-template strategy is used to fabricate porous polydopamine (PDA) nanoparticles with multi-edges.^[20] Field-emission scanning electron microscopy (FESEM) image confirms that the as-synthesized nanoparticles are uniform with a diameter of around 190 nm (Figure S1, Supporting Information). Closer observations of the particles reveal that each nanosphere is constructed from continuously bent PDA edges. Subsequently, the as-synthesized edge-rich particles are mixed with an ethanol solution of RuCl₃ at room temperature for loading the Ru species. As the PDA particles possess the opposite interfacial charges to that of Ru species, they are integrated spontaneously with weak coordination. X-ray photoelectron spectroscopy (XPS) investigation not only confirms the existence of Ru species, but also verifies the Ru-N interaction in the newly generated hybrid (Figure S2, Supporting Information). The Ru-loaded polydopamine particles further undergo pyrolysis under high temperature in Ar atmosphere. The carbonization process and related structural transition are recorded by thermogravimetric (TG) analysis. A quick weight loss process starts at about 200°C and ends at about 400°C, which corresponds to the transformation of PDA into the carbon matrix and

the fusion of the Ru species into the edges of the carbon matrix (Figure S3, Supporting Information).

FESEM images show that the ECM@Ru particles preserve the original morphology with multi-edges (Figure 1b and c). As confirmed by the transmission electron microscope (TEM) images, the ECM@Ru particles retain their accessible edges and pore structure with a slight shrinkage after the thermal treatment (Figure 1d-g). High-resolution TEM (HRTEM) investigation confirms that no obvious nanoparticles or clusters are observed in ECM@Ru. The result also indicates that most of the Ru species should be presented in the form of isolated atoms (Figure 1h). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping images verify that the isolated Ru atoms are homogeneously distributed over the whole architecture (Figure 1i-k). Inductively coupled plasma mass spectrometry (ICP-MS) confirms that the loading amount of Ru species is about 0.68 wt% in ECM@Ru. X-ray diffraction (XRD) patterns of the as-synthesized samples show that only typical diffraction peaks of graphitic carbon have been detected, confirming the graphitic nature of ECM and the well-dispersion of these Ru sites (Figure S4, Supporting Information). For comparison, Ru-decorated carbon matrix (CM@Ru) particles without edges have also been synthesized as the reference sample (Figure S5 and S6, Supporting Information).

XPS analysis is further explored for elaborating the chemical structure of the hybrids. The N 1s spectrum (Figure S7a, Supporting Information) of ECM@Ru confirms the existence of graphitic, pyridinic, and pyrrolic nitrogen species with the binding energies of 401.1, 400.2, and 398.8 eV, respectively.^[21, 22] These nitrogen species can function as anchor sites and coordinate with the isolated Ru sites, which is evidenced by the N 1s spectrum with the binding energy of 398.2 eV.^[23]

Besides, two peaks with binding energies of 484.3 and 462.6 eV in the Ru 3p spectrum of ECM@Ru should be attributed to the Ru 3p_{1/2} and Ru 3p_{3/2}, respectively (Figure S7b, Supporting Information). According to the reported 3p_{3/2} peaks at 461.2 eV for Ru foil and 463.2 eV for RuO₂, the oxidation state of Ru species in the ECM@Ru catalyst should be lower than that of RuO₂, but higher than that of Ru foil.^[24, 25] Raman spectroscopy has been used to detect the defect level of the synthesized hybrids (Figure S8, Supporting Information). The intensity ratios of D band to G band (I_D/I_G) for the ECM@Ru and CM@Ru are confirmed as 1.06 and 0.97, respectively. The obtained results demonstrate the edges in the carbon matrix induce the generation of more defects.^[26] We have also investigated the formation of the hybrids by theoretical calculations. The calculation results clearly show that the fusion of the isolated atoms into the carbon matrix is an endothermic process. The generated defects are favorable for the stabilization of the isolated atoms and thus the formation energies are greatly reduced from 0.95 eV of CM@Ru to 0.36 eV of ECM@Ru (Figure 11). These results may also indicate that the isolated atoms are preferably stabilized over the edges of the carbon matrix.^[27]

To further reveal the coordination environment of the Ru species, we have conducted extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) analyses. As shown in **Figure 2a**, ECM@Ru exhibits similar Ru K-edge EXAFS magnitude to that of CM@Ru and displays the main peak at about 1.47 Å, which should be ascribed to the Ru-N interaction.^[28] Besides, no Ru-Ru bonding at the distance of 2.32 Å is detected in ECM@Ru and CM@Ru. These results directly evidence that Ru atoms should exist in the form of isolated atoms in the hybrids. Quantitative EXAFS curve-fitting analyses for ECM@Ru and CM@Ru verify that the coordination numbers of the Ru-N bonding in the first coordination sphere are 4.3 and 4.1 at the

distance of 1.98 Å and 1.99 Å, respectively (Figure 2b, d, Figure S9 and Table S1, Supporting Information). These results not only confirm the isolated Ru centers adopt the square-planar configuration but also demonstrate the existence of unsaturated active sites for the catalytic reaction.^[29] Wavelet transform (WT) analysis can provide the resolution in the K space and a radial distance resolution. The WT intensity maxima near 5.4 Å⁻¹ and 5.2 Å⁻¹ associated with the light atom coordination are well resolved at 1.0 to 3.0 Å for ECM@Ru and CM@Ru, respectively, whereas an intensity maximum at about 9.1 Å⁻¹ arising from the Ru-Ru coordination is not detected (Figure 2c). The apparent distinction of XANES profiles between ECM@Ru and Ru foil also rules out the Ru-Ru coordination in ECM@Ru (Figure 2e).^[30] The XANES profile of ECM@Ru is nearly identical to that of CM@Ru, confirming that they possess a similar configuration and chemical state.

The electrocatalytic hydrogen evolution performances of the electrocatalysts are examined by a typical three-electrode setup. **Figure 3a** shows the *iR*-compensated polarization curves recorded by linear sweep voltammetry (LSV) in 0.5 M H₂SO₄. As observed, the pure ECM without Ru decoration exhibits rather poor activity. Great enhancement has been observed for ECM@Ru, in which the onset potential is nearly 0 V versus the reversible hydrogen electrode (RHE). To achieve the current densities of 10 mA cm⁻² and 50 mA cm⁻², the ECM@Ru requires the overpotentials of 63 and 102 mV, respectively (Figure 3b). These values are slightly higher than required overpotentials (47 mV for 10 mA cm⁻² and 82 mV for 50 mA cm⁻²) of commercial Pt/C-20% but much lower than the values (109 mV for 10 mA cm⁻² and 239 mV for 50 mA cm⁻²) of CM@Ru. The kinetics of HER processes has also been investigated for further analyses of the HER performance with the Tafel plots (Figure 3c). ECM@Ru shows a Tafel slope of 47 mV dec⁻¹,

whereas Pt/C-20% and CM@Ru exhibit Tafel slopes of 29 and 76 mV dec⁻¹, respectively. All these results compare favorably with the values reported for most HER catalysts under similar conditions (Table S2, Supporting Information). The value of the Tafel slope can reflect the rate-determining step (RDS) of a catalytic process. This illustrates that the Volmer-Tafel mechanism dominates in the HER process, where the recombination of adsorbed H* is the RDS for ECM@Ru.^[31-34] This result also suggests that the carbon edges interacting with the isolated atoms can cast influence on the RDS in the catalytic process. The mass activity is also an important quantitative parameter applied for defining the activity of a catalyst. The value can be obtained by dividing the mass of loaded catalyst by the current density at a given overpotential. As shown in Figure 3d, the mass activities of ECM@Ru, at the overpotentials of 50 and 100 mV, are about 6.4 and 9.6 times higher than that of Pt/C-20%, and about 2.7 and 4.1 times higher than that of CM@Ru, respectively.

We have also investigated the electrocatalytic performances of the catalysts in an Ar-saturated alkaline medium (1.0 M KOH). ECM@Ru displays good electrocatalytic performance for HER in this alkaline electrolyte, with a small overpotential of 83 mV at the current density of 10 mA cm⁻². The required overpotential is relatively larger than that of Pt/C-20% (52 mV) but much lower than that of CM@Ru (142 mV) (Figure S10a, Supporting Information). The Tafel slope of ECM@Ru is confirmed as 59 mV dec⁻¹ in the alkaline solution, much lower than that of CM@Ru (106 mV) (Figure S10b, Supporting Information). The current density of the ECM@Ru rises much faster than that of the CM@Ru. Specifically, ECM@Ru could display a current density of 50 mA cm⁻² at the overpotential of 143 mV, which is 82 mV lower than that of the CM@Ru for reaching the same current density (Figure S11a, Supporting Information). The mass activities of the catalysts have also been calculated and compared. As observed, the mass activities of ECM@Ru are about 5.3 times

and 6.8 times higher than that of Pt/C-20% at the overpotentials of 50 mV and 100 mV, respectively. In contrast, the mass activities of CM@Ru are slightly less than that of Pt/C-20% (Figure S11b, Supporting Information). Besides, we have also investigated the stability of the catalysts for its crucial role in real applications. To evaluate the stability of the catalysts, chronopotentiometry (CP) is tested. For ECM@Ru, the required potentials could be well maintained and with no obvious increase at the current density of 10 mA cm⁻² for 20 h in both acidic and alkaline media (Figure S12 and S13, Supporting Information).

We have further investigated the electrochemically active surface area (ECSA) for accounting the greatly boosted catalytic performance of ECM@Ru. The ECSA is estimated from the cyclic voltammetry (CV) measurements, which is generally proportional to the double-layer capacitance (C_{dl}) of the electrocatalyst.^[35] The results show that the C_{dl} of ECM@Ru is 1.08 mF cm⁻², which is substantially larger than that of CM@Ru (0.27 mF cm⁻²) (Figure 3e and Figure S14, Supporting Information). These results provide direct evidence that the enlarged ECSA should be related to generated defects over the ECM, which may provide more active sites for enhanced HER activity. The electrochemical impedance spectroscopy (EIS) has been employed for accounting the charge transfer kinetics. The fitted results confirm that ECM@Ru displays much smaller charge-transfer resistance than CM@Ru, suggesting that the edges over the carbon matrix facilitate the electron transfer in the catalytic process (Figure 3f; Figure S15 and Table S3, Supporting Information).^[36, 37]

For interpreting the experimental results discussed above, first-principles calculations are performed to provide deeper electronic structure insight into the catalytic activity contributions from edges and isolated Ru atoms. The density of states (DOS) at the conduction band minimum and the valence band maximum are highly relevant to the electron donating and accepting mechanisms,

which are always applied for selecting the potential active sites for HER (**Figure 4a** and Figure S16, Supporting Information).^[38,39] As indicated by the partial density of states (PDOS) projected on the C-2p orbital, the band center of ECM is much closer to the Fermi level when compared with that of CM (Figure S17, Supporting Information). Correspondingly, the former site exhibits a stronger interaction with adsorbed H* compared with the latter one. Besides, some new hybridized electronic states are generated after the decoration of Ru species.^[40] The emerged new electronic states should relate to the hybridization between Ru-4d orbitals and the coordinated nonmetal.^[41] The interaction between Ru and coordinated atoms involves the effective charge transfer, which should be responsible for stronger adsorption of H* and higher electronic conductivity. This conclusion has also been verified by the related distribution of charge density. The defects originated from the edges of the carbon matrix cause a localized electric field and high reactant concentration around the active sites, which contribute favorably to charge density distribution and the catalytic activity (Figure 4b and Figure S18, Supporting Information).^[42] We further calculate the Gibbs free energy of H* adsorption (ΔG_{H^*}). A moderate ΔG_{H^*} (close to zero) is necessary for a good electrocatalyst to overcome the adsorption and desorption barriers.^[43] As is shown in Figure 4c, from a theoretical perspective the most active model is ECM@Ru represented by a low ΔG_{H^*} value of -0.09 eV, which is much closer to zero when compared with that of CM@Ru (-0.29 eV) and ECM (1.41 eV).

In conclusion, isolated Ru atoms have been decorated on an edge-rich carbon matrix as an efficient electrocatalyst for hydrogen evolution. This system also serves as an elegant platform for understanding the electrocatalytic hydrogen evolution in atomic level. Our current research highlights the importance of the edges on the carbon matrix in providing specific electronic field for

the isolated Ru atoms. The newly developed electrocatalyst not only maximizes the atom utilization efficiency but also displays further structure-enhanced activity, thus achieving a comparable HER activity to that of the commercial Pt/C-20% electrocatalyst. Experimental results and DFT calculations confirm that the intrinsic electronic structure of isolated Ru atoms is greatly modified with the existence of edges in carbon matrix, enabling the integration of efficient charge delivery and a strong local electric field effect. These results also suggest that tuning intrinsic surface structure of support for stabilizing isolated atoms represents a general and powerful strategy for boosting specific activity and mass activity of electrocatalysts. Moreover, the present synthetic strategy can be extended for fabricating other non-precious metal based single-atom catalysts for a broad range of catalytic applications.

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Figures and Captions

Figure 1. (a) Schematic illustration of the synthetic procedure of ECM@Ru: (I) loading of the Ru species onto the surface of PDA with multi-edges, (II) pyrolysis of the Ru-loaded PDA for obtaining the ECM@Ru catalyst. (b, c) FESEM images, and (d-g) TEM images of the ECM@Ru. (h) HRTEM image of the ECM@Ru. (i, j) HAADF-STEM image of HCM@Ru, and related EDX elemental mapping images. (k) Linear EDX scanning of ECM@Ru. (l) Calculated free energy of formation for ECM@Ru and CM@Ru.

Figure 2. (a) Fourier-transformed magnitudes of the experimental Ru K-edge EXAFS spectra. (b, d) Fourier-transformed magnitudes of Ru K-edge EXAFS spectra in R space (b) and K space (d) for ECM@Ru. (c) WT for the k^3 -weighted EXAFS signal. (e) Ru K-edge XANES experimental spectra.

Figure 3. (a) LSV curves and (b) the related Tafel plots of the electrocatalysts in 0.5 M H₂SO₄. (c) Overpotentials required for $J = 10$ and 50 mA cm^{-2} in 0.5 M H₂SO₄. (d) Comparison of mass activities among catalysts at different overpotentials in 0.5 M H₂SO₄. (e) Capacitive $\Delta J/2$ as a function of the scan rate for ECM@Ru and CM@Ru. (f) Nyquist plots of ECM@Ru and CM@Ru.

Figure 4. (a) Calculated TDOS of ECM@Ru, CM@Ru and ECM. (b) Calculated distribution of charge density for ECM@Ru. (c) Calculated ΔG_{H^*} on ECM@Ru, CM@Ru and ECM.

For Table of Content Entry

Isolated Ru atoms have been decorated on an edge-rich carbon matrix and applied as an efficient electrocatalyst for the hydrogen evolution reaction. This work unveils that the edges in carbon matrix enables the integration of efficient charge delivery and a strong local electric field effect, which may shed light on the future design of efficient electrocatalysts.