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Holey Ruthenium Nanosheets with Moderate Aluminum Modulation toward Hydrogen Evolution

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S Supporting Information

ABSTRACT: Theoretical calculations reveal that aluminum (Al) doping can effectively modulate the electronic structures of 2D ruthenium (Ru) catalysts. Moderate Al incorporation can endow Ru nanosheets with more delocalized electrons and optimal hydrogen adsorption Gibbs free energy, providing opportunities to achieve improved hydrogen evolution performance. Thus, Aldoped Ru nanosheets have been synthesized by a solvothermal strategy, in which they exhibit holey nanosheet structures and have more active sites exposed on the basal plane. The characterizations unraveling the Ru structure can be well maintained, and electrochemical measurements confirm the appropriate amount of Al modulation that can extremely enhance its hydrogen evolution activity.

The rapid depletion of traditional fossil fuels and their pollution of the environment have driven us to explore appropriate alternatives.¹ Molecular hydrogen is a central energy carrier owing to its high energy density (120 MJ kg⁻¹) and carbon-free feature.^{2,3} Electrocatalytic water splitting is efficient to produce hydrogen $(H_2O \rightarrow H_2 + O_2)$, and exploring efficient and inexpensive catalysts for hydrogen evolution reaction (HER; $2H^+ + 2e^- \rightarrow H_2$) is highly desired.^{4,5} Although platinum (Pt)-based materials can exhibit excellent performance for HER, their high cost and limited reserve prevent their large-scale applications.⁶

Compared with Pt, ruthenium (Ru) is much cheaper and has comparable activity toward hydrogen generation.^{7,8} Structure engineering to obtain a particular morphology, such as 2D nanosheets, can expose more active sites and reduce the amount of Ru usage.⁹ Moreover, introducing lowcost metals as dopants to partially replace Ru can further decrease the catalyst cost. Meanwhile, the selection of appropriate dopants can modify its surface electronic structure, facilitating hydrogen adsorption and thus accelerating hydrogen generation. For instance, Kim and co-workers have designed hybrid nickel (Ni)- and Ru-based architectures. The synergetic and antagonistic effects of the hybrid material make it a superior bifunctional electrocatalyst for water splitting.¹⁰ Chen and co-workers reported a cobalt (Co) modulation effect for Ru-Co nanoalloys and revealed their advances for hydrogen production.¹¹ Yet, exploring Ru-based catalysts with improved HER behavior is still challenging.

In general, the intrinsic activity of a single active site, the amount of accessible active sites on the surface, and the conductivity are three indicators determining the activity of electrocatalysts. Given that metallic Ru normally has good conductivity, enhancing the catalytic capability and exposing more active sites at the same time should be a good choice for the design of new and effective Ru-based catalysts. As is known, aluminum (Al) modulation has rarely been reported as an efficient strategy on electrocatalysts, especially for HER. In this study, we find that the introduction of Al can efficiently modify the surface electronic states of Ru nanosheets, affording them with more delocalized electrons and optimal hydrogen adsorption. Meanwhile, the 2D nanosheet morphology can be well maintained by moderate Al doping. Moreover, holey structures are generated on the nanosheets, which benefit the exposure of active sites and facilitate the diffusion of reactants and products. Therefore, the as-prepared Ru-Al alloys can exhibit extremely improved electrocatalytic kinetics toward HER.

Density functional theory (DFT) calculations are performed on pristine and Al-doped Ru nanosheets to directly visualize and understand the effect of Al incorporation on electronic structures and the HER performance. Hexagonal Ru(001) is constructed with the optimized structure shown in Figure 1a, and a series of Ru-Al alloy models with different amounts of



Figure 1. DFT calculations for pristine and Al-doped Ru nanosheets: (a) optimized 2D Ru structure; (b) charge-density distribution on the surface, with hydrogen adsorption sites marked; (c and d) DOSs (inset: enlarged images for states around the Fermi level); (e) HER free-energy diagrams.

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Al incorporation are considered. Figure 1b depicts the surface static electron distributions, where Ru_{0.94}Al_{0.06} exhibits more delocalized electron distribution than pristine Ru, which is beneficial to activating and enriching the electrically active sites and further accelerating the HER process.¹² Densities of states (DOSs) are also calculated in Figure 1c,d. Compared with pristine Ru, Ru_{0.94}Al_{0.06} possesses more states at edges in the valence band, which benefits electron transfer from the catalyst surface to the adsorbed H⁺, expediting its reduction. Meanwhile, compared with Ru_{0.97}Al_{0.03} (light-doping structure) and Ru_{0.92}Al_{0.08} (heavy-doping structure), Ru_{0.94}Al_{0.06} shows many more states around the Fermi level, indicating that it has the highest concentration of charge carriers and superior electronic conductivity. After that, three sites, as marked in Figure 1b, are considered for hydrogen adsorption, and the hollow site (H) exhibits the most stable configuration. Figure 1e illustrates the calculated free-energy diagrams. Remarkably, Al incorporation can effectively modify its $|\Delta G_{H^*}|$. The $|\Delta G_{H^*}|$ value of Ru_{0.94}Al_{0.06} is 0.2 eV, significantly smaller than that of pristine Ru (0.43 eV) and both heavy and light Al-doped Ru models. $|\Delta G_{H^*}|$ is a catalytic descriptor for the HER, and the optimal value should be close to 0.13 Henceforth, it is anticipated that moderate Al doping can provide higher HER activity on Ru nanosheets.

On the basis of these theoretical predictions, we have tried to prepare Ru nanosheets with optimized Al incorporation via a facile solvothermal reaction. The detailed preparation can be found in the Supporting Information. Figure S1 shows the Xray diffraction (XRD) patterns measured on these samples. Four peaks appearing at 38.4, 42.2, 44.1, and 69.4° are indexed to the (100), (002), (101), and (110) planes of the hexagonalclose-packed Ru metal (PDF 06-0663), suggesting that they are in the metallic Ru phase (Figure S1a). Clearly, there is no big difference between Ru₃Al and pristine Ru, implying that Al is appropriately incorporated for Ru₃Al, without a significant crystal structure change occurring in the Ru matrix. We speculate that the formation of Ru₃Al experiences the same attachment-growing process as that for pristine Ru nanosheets.⁹ However, when more Al precursors are employed (heavy doping), some new peaks appear (Figure S1b), which are attributed to the diffraction peaks of AlO(OH), as indexed to PDF 21-1307. In this stage, this material becomes a composite of Ru and AlO(OH) rather than the formation of pure Ru-Al alloys. The energy-dispersive X-ray (EDX) measurements illustrate that the atomic ratios between Al and Ru are 0.18, 0.30, and 1.03 for Ru₅Al, Ru₃Al, and RuAl, respectively (Figure S2). Therefore, controlling the amount of Al intercalation is pivotal to achieving ideal alloy materials with enhanced catalytic behavior.

Transmission electron microscope (TEM) characterizations were performed to unravel the morphology of the Ru_3Al catalyst (Figure 2a,b). Flat nanosheet structures without any significant strips and crimps are found in these TEM images. Most of the nanosheets are dozens of nanometers in size and are stacked on each other. Interestingly, some holes are observed on the nanosheet surface, which are beneficial for more active sites exposed on the basal plane. Meanwhile, these generated holes can facilitate the diffusion of reactants and products and thus accelerate the HER process. For comparison, pristine Ru, Ru_5Al , and RuAl are also measured, with their TEM images given in Figures S3 and S4, respectively. Generally, pure Ru exhibits a larger sheetlike structure, while Ru_5Al and RuAl display relatively smaller



Figure 2. Characteristics of Ru_3Al : (a and b) TEM images; (c) HRTEM image; (d) SAED pattern; (e) STEM image and corresponding elemental mapping images.

nanoflake morphology. Moreover, holey structures are also obtained on Ru_3Al and RuAl, in association with that observed on Ru_3Al , suggesting that these holes are generated by Al dopants. Al is a typical amphoteric material, with radii (118 pm) comparable to that of Ru (125 pm); thus, it can partially substitute Ru and act as a holey building block during the solvothermal reaction.

To acquire the microstructural information, high-resolution TEM (HRTEM) measurements were carried out. Figure 2c reveals a lattice distance of 0.208 nm on Ru₃Al, which is ascribed to the (002) crystal plane of the Ru crystal. The decreased d-space distance compared to the pristine Ru(002) plane (Figure S3c,d) can be explained by Al intercalation. Furthermore, Figure 2d illustrates the selected-area electron diffraction (SAED) pattern, where two diffraction rings are observed, demonstrating its polycrystalline feature.¹⁴ The two measured rings indicate 0.206 and 0.135 nm lattice distances, corresponding to the (002) and (110) crystal planes of Ru, respectively, which are also observed as diffraction peaks in the XRD pattern. Moreover, the well distributions of Al and Ru on the nanosheet are observed from the scanning TEM (STEM)-EDX mapping analysis (Figure 2e), verifying the successful Al incorporation on Ru nanosheets. Atomic force microscopy (AFM) measurement discloses the height profile of about 1.6 nm for these nanosheets, corresponding to 6-8 atomic layers stacking along the c axis with the (001) planes as the basal planes (Figure S5).

X-ray photoelectron spectroscopy (XPS) spectra have been applied to investigate the surface chemical states and elemental compositions. As shown in Figure S6a, two distinct peaks around 461.7 and 483.6 eV are attributed to Ru $3p_{1/2}$ and Ru $3p_{3/2}$, respectively, and both can be seen on pristine Ru and Ru₃Al.¹⁵ After Al incorporation, these two peaks move 0.4 eV toward the lower-energy direction, suggesting its modulation essence on Ru nanosheets. Figure S6b displays the highresolution Ru $3p_{3/2}$ spectra, and they are deconvoluted into Ru⁰ and Ru^{IV}, located at 461.3 and 463.3 eV, respectively.¹⁶ The intensity ratio of Ru⁰ to Ru^{IV} will change from 3.22 to 4.15, implying that more reduced Ru states are induced via Al doping, in line with the negative shifts for the above Ru 3p peaks. This could be explained by their difference in electronegativity. Because Ru ($\chi = 2.2$) has a larger electronegativity than Al ($\chi = 1.5$), more electrons will transfer from Al to Ru after its incorporation. Additionally, the Al 2p peak around 74 eV is obtained on Ru₃Al in Figure S6c, further confirming the successful synthesis of an Al-doped Ru catalyst.^{17,18} The 3+ state of Al may be caused by the transferred electrons to Ru and partial oxidation on the surface.

After that, the electrocatalytic performance is evaluated using a three-electrode system in 0.5 M $\rm H_2SO_4.^{19,20}$ Figure 3a



Figure 3. Electrochemical characterizations: (a) LSV curves; (b) required overpotentials for 10 and 50 mA cm⁻²; (c) Tafel slopes; (d) EIS at an overpotential of 150 mV; (e) CO stripping measurement; (f) LSV curves for the durability evaluation. Inset: Overpotentials for 10 mA cm⁻² recorded at each 500 cycles.

shows the recorded linear-sweep voltammetry (LSV) curves measured on these prepared samples. Meanwhile, commercial Pt/C and bare glass carbon are also performed for comparison (Figure S7). Pristine Ru nanosheets exhibit relatively moderate activity toward hydrogen generation. With an increase in the amount of the Al component, the measured current density will gradually increase. However, when too much Al is employed, its catalytic performance will significantly decrease. Among them, Ru₃Al shows the highest HER activity with a small onset overpotential of 10 mV. To reach a 10 mA cm⁻² current density, Ru₂Al needs an overpotential of 79 mV, much smaller than the 164, 200, and 234 mV required for Ru₅Al, pristine Ru, and RuAl, respectively (Figure 3b). In addition, the current densities of 20 and 50 mA $\rm cm^{-2}$ can be obtained at the overpotentials of 109 and 142 mV, respectively. After that, the kinetics of HER is studied by calculating the Tafel slope. In general, the rate-determining step consists of three basic steps; (1) the Volmer reaction step $H^+ + e^- \rightarrow H_{ads}$; (2) the Heyrovsky reaction step $H_{ads} + H^+ + e^- \rightarrow H_2$; (3) the Tafel reaction step $H_{ads} + H_{ads} \rightarrow H_2$.²¹ The linear Tafel plots are obtained from the low overpotential region of the polarization curves. As shown in Figure 3c, Ru₃Al owns a Tafel slope of 81 mV dec⁻¹, smaller than pristine Ru (94 mV dec⁻¹), Ru_5Al (89 mV dec⁻¹), and RuAl (98 mV dec⁻¹). This indicates that moderate Al doping can effectively accelerate the HER process of Ru, without changing the Volmer-Heyrovsky reaction mechanism. Meanwhile, this enhancement is also supported by the electrochemical impedance spectroscopy (EIS) measurement. Figure 3d illustrates their corresponding Nyquist plots, with a dramatic declined charge-transfer resistance of 59.7 Ω for Ru₃Al relative to others, suggesting the enhanced interfacial resistance and improved conductivity caused by moderate Al

incorporation. The elecrochemical surface area is determined by CO stripping measurement, with the oxidation peak area for the preadsorbed CO molecules shown in Figures 3e and S8. Ru₃Al possesses a larger electrochemically active area than pristine Ru, about 1.22 times that for the pristine counterpart, confirming that more active sites are generated by Al. When normalized by an electrochemically active surface area, the area-specific HER current density of Ru₃Al is calculated to be 5.1 and 7.2 times those of pristine Ru, at -0.05 and -0.10 V versus reversible hydrogen electrode, respectively, verifying the enhanced HER kinetics via Al modulation. In addition, the durability is also estimated. There is a negligible difference between the LSV curves measured initially and after 3000 cycles, and the overpotential recorded at 10 mA cm⁻² exhibits a slight change during the stability measurement (Figure 3f). TEM image of Ru₃Al after the durability test also shows a holey nanosheet structure as before (Figure S9a). Moreover, the EDX measurement, XRD pattern, and elemental mapping images shown in Figure S9b-d also indicate the good stability of the Al-modulated Ru catalyst.

In summary, on the basis of the combination of DFT calculations and experimental measurements, we find that Al engineering can effectively regulate the electronic structure of Ru nanosheets and further improve their HER activity. The enhanced catalytic performance should be ascribed to (1) the induced more delocalized electrons caused by Al incorporation, (2) the optimized hydrogen adsorption Gibbs free energy, and (3) the formed holey structure with more exposed active sites. The synthesis of Al-incorporated Ru nanosheets is facial and adds a new component to the modulation strategies for obtaining high-performance functional materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01150.

Experimental and calculated methods, XRD patterns, EDX spectra, TEM images, AFM characterizations, XPS data, LSV measurements, and CV curves (PDF)

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Notes

The authors declare no competing financial interest.

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