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Ruthenium-Nickel Atomic Cluster Supported on Carbon Black for Improving Hydrogen Evolution Reaction Electrocatalysis Performance in Acidic Solution

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Abstract: Research on high-performance and low-cost hydrogen evolution reaction (HER) catalysts is of great significance for the large-scale development and practical application of hydrogen energy. Using cheaper metals instead of platinum (Pt) to reduce catalyst costs while ensuring HER performance is a current challenge. In this work, we used a facile and controllable method, the spray-drying technique combined with thermal decomposition reduction, to synthesize the catalyst of ruthenium-nickel atomic cluster supported on carbon black (RuNi-ac/C) at a reduction temperature of 300 °C in H₂. The results show that as-synthesized RuNi atomic clusters are uniformly distributed on the carbon black, with the particle size distribution ranging from 0.5 nm to 2.5 nm. Electrochemical tests indicate that the HER overpotential of RuNi-ac/C is only 37 mV at a current density of 10 mA·cm⁻² in 0.5 mol/L H₂SO₄ electrolyte. The overpotential is increased by only 2 mV after 4000 cyclic voltammetry cycles in the stability test, demonstrating excellent electrochemical stability. Compared with synthesized Ru/C-300 °C, Ni/C-400 °C, and RuNi/C (200, 400, and 500 °C) catalysts, the RuNi-ac/C has the best HER performance. Furthermore, the RuNi-ac/C has better HRE activity as well as lower cost compared with the commercial Johnson Matthey Pt/C catalyst, providing a new idea for the industrial application of low-cost and high-efficiency HER catalysts.

Key words: Ru-Ni atomic cluster; spray drying with thermal decomposition reduction; HER electrocatalysis; hydrogen energy

1 Introduction

Hydrogen (H₂), as an excellent energy carrier, is regarded as a promising alternative to increasingly scarce traditional fossil fuels due to its high energy density and environmental friendliness. This prospect has attracted extensive research effort^[1-5]. Electrocatalytic water splitting is one of the most promising methods for H₂ production, and the hydrogen evolution reaction (HER) in electrochemical water splitting devices enables direct H₂ generation on the electrode surface^[6-8]. Therefore, developing efficient and stable HER catalysts is crucial for H₂ production. Currently, the primary HER catalysts are platinum (Pt) or Pt-based alloy nanomaterials,

as Pt consistently exhibits high activity and stability in hydrogen evolution electrocatalysis^[9-14]. Commercial HER catalysts are mainly Pt/C nanomaterials, which have been widely applied in various water electrolysis devices^[15-16]. However, the scarcity and high cost of Pt resources lead to extremely high HER catalyst costs, restricting the development of water electrolysis for H₂ production. Thus, developing low-cost non-Pt catalysts with performance comparable to that of Pt-based catalysts is of great significance. It has been found that ruthenium (Ru), a platinum-group metal with lower cost than that of Pt, also demonstrates excellent HER performance. Various Ru-based catalysts have been reported and have emerged as one of the

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important alternatives to Pt-based catalysts^[17–22]. Generally, two main strategies are employed to enhance the HER electrocatalytic activity of Ru-based nanomaterials. One strategy is to alloy Ru with other metals (such as Ni, Co, Fe, and Cu) to form Ru-based multimetallic nanoalloys, which can reduce Ru consumption while promoting the formation of polymetallic synergistic effects to improve electrocatalytic performance. For instance, RuCo/C^[17], Ru/C₂N^[23], Ru nanocluster catalysts (NCs)/N-doped carbon (NC)^[24], and RuP₂ nanoparticles^[25] have been reported to exhibit excellent HER performance. The other strategy is to load Ru-based nanoalloys onto carbon materials with a large specific surface area and minimize the size of Ru-based nanoalloys as much as possible. This approach not only reduces Ru loading but also increases the effective utilization efficiency of Ru and enhances electrocatalytic activity^[17,23–24,26–27]. Therefore, integrating these two strategies is expected to develop Ru-based HER catalysts with lower cost and superior performance.

Nowadays, the preparation of Ru-based nanoparticles with high dispersity and ultra-small size supported on carbon materials has also been reported. A ligand-controlled synthesis strategy was employed to prepare a series of Ru-based nanoparticles anchored on the surface of hollow porous carbon shells, including those with high dispersity and ultra-small size (denoted as u-Ru/C) and those in a sparse and aggregated state (denoted as a-Ru/C). These catalysts exhibit favorable HER performance^[28]. In addition, ultra-small RuNi nanoparticles were deposited on Ni-anchored defective carbon via the unipolar pulsed electrodeposition (UPED) technique. The optimized catalyst achieves HER overpotentials of 9 and 253 mV at current densities of 10 and 1000 mA·cm⁻², respectively, demonstrating exceptional catalytic performance^[29]. Furthermore, a microwave reduction method was developed to rapidly synthesize a series of ultra-small precious-metal-doped *M*-Ru nanoparticles (3–3.5 nm) supported on carbon nanotubes (CNTs), labeled as *M*-Ru/CNT (*M*=Pt, Rh, Pd, or Ir). This synthesis process takes less than 1 min, and electrochemical tests confirm that the catalysts display excellent HER activity in 0.5 mol/L H₂SO₄ electrolyte^[30]. Despite the progress made in the preparation of ultrafine Ru-based nanoparticles, it remains challenging to achieve their synthesis in a simple and controllable manner. Therefore, the development of techniques for fabricating high-performance ultrafine Ru-based nanoparticles supported on carbon materials for HER still requires further exploration.

In this study, a facile and controllable method, namely the spray drying combined with thermal decomposition reduction (SD-TDR) technique, was adopted to synthesize carbon black-supported RuNi atomic clusters (RuNi-ac/C). HER tests were performed in an acidic electrolyte. In addition, in our previous work, a series of noble metal-based nanocatalysts (including Pt-based nanoparticles/rGO, Pt/Pt-based alloy 3D nanoframeworks, and Ru/RuCo nanoparticles/C) have been successfully synthesized via the SD-TDR method. These catalysts displayed remarkable performance in fuel cell methanol electrooxidation, water electrolysis HER, and oxygen evolution reaction (OER),

which fully demonstrates the effectiveness and universality of the proposed SD-TDR strategy^[13,17,31–32].

2 Experiment

All reagents and solvents were used as received without further purification. Anhydrous ruthenium trichloride (RuCl₃, analytical grade) was purchased from Xi'an Kaili New Material Co., Ltd. (Xi'an, Shaanxi, P. R. China). Nickel chloride (NiCl₂, analytical grade) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Carbon black (ECP600JD, analytical grade) was purchased from Shanghai King Chemical Co., Ltd. (Shanghai, P. R. China). Commercial 20wt% Pt/C catalyst was supplied by Johnson Matthey (Shanghai) Chemicals Ltd. (Shanghai, P. R. China). Deionized water used in all experiments was purified using a Milli-Q system (Millipore, Bedford, MA, USA).

The synthesis procedure of RuNi-ac/C is as follows. Precursor salts (RuCl₃ and NiCl₂) were weighed at a Ru: Ni atomic ratio of 1:1, with the total metal content accounting for 10wt% of the final catalyst mass. These salts were dissolved in deionized water to prepare a mixed precursor solution with a total concentration of Ru and Ni of 0.01 mol/L. Subsequently, carbon black (ECP600JD, 90wt% of the final catalyst) was added to the RuCl₃-NiCl₂ precursor solution. The mixture was heated to 60 °C and subjected to ultrasonic stirring for 2 h to ensure uniform dispersion. The homogeneous precursor suspension was then spray-dried using a home-designed spray dryer to obtain well-blended precursor powders. The spray-drying parameters were set as follows: inlet temperature of 180 °C, feed rate of 200 mL/h, high-pressure gas flow rate of 1.3 L/s, and drying gas flow rate of 35 m³/h. The spray-dried precursors were thermally reduced under an H₂ atmosphere and subsequently cooled in a nitrogen (N₂) atmosphere. The thermal treatment protocol was controlled as follows: a heating rate of 3 °C/min from room temperature to the target temperatures (200, 300, 400, and 500 °C), an isothermal holding time of 30 min at each target temperature, and a cooling rate of 5–10 °C/min. Finally, RuNi-ac/C was successfully synthesized.

The synthesis procedure of Ru/C and Ni/C is as follows. Precursor salts (RuCl₃ and NiCl₂) were weighed with the total metal content accounting for 10wt% of the final catalyst mass. These salts were dissolved in deionized water to prepare a precursor solution with a total metal concentration of 0.01 mol/L. Subsequently, carbon black (90wt% of the final catalyst) was added to the precursor solution, and the mixture was heated to 60 °C and subjected to ultrasonic stirring for 2 h to achieve uniform dispersion. The homogeneous mixture was then spray-dried using a home-designed spray dryer to obtain precursor powders. The spray-drying parameters were set as follows: inlet temperature of 180 °C, feed rate of 200 mL/h, high-pressure gas flow rate of 1.3 L/s, and drying gas flow rate of 35 m³/h. The spray-dried precursors were thermally reduced under a H₂ atmosphere, followed by cooling in a N₂ atmosphere. The thermal treatment conditions were controlled as follows: a heating rate of 3 °C/min from room temperature to the target temperatures (300 or 400 °C), a constant-

temperature holding time of 30 min, and a cooling rate of 5–10 °C/min. Finally, carbon black-supported Ru and Ni nanoparticles was successfully obtained.

The microstructures of the as-synthesized samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) using a JEOL JEM-2100 microscope operated at an accelerating voltage of 200 kV. Atomic-scale characterization was performed using a JEM Grand ARM 300 microscope equipped with a cold field emission gun (cold-FEG), an accelerating voltage of 300 kV, and both probe and image correctors. X-ray diffraction (XRD) patterns of the synthesized powders were recorded using an Empyrean X-ray diffractometer (PANalytical, the Netherlands) with Cu K α radiation at 50 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a K-Alpha+XPS system (Thermo Fisher Scientific) with an Al K α X-ray source (photon energy: 1486.6 eV).

Electrochemical measurements were performed using a CHI760E electrochemical workstation (CH Instruments) in a conventional three-electrode configuration. The working electrode was fabricated by coating the catalyst onto a polished glassy carbon disk (diameter: 5 mm; geometric area: 0.196 cm²). Typically, 5 mg catalyst (RuNi-ac/C, Ru/C, Ni/C, or JM Pt/C) was dispersed in 5 mL mixed solvent consisting of deionized water, 2-propanol, and 5 vol% Nafion (volume ratio=1: 1: 0.010). The mixture was then sonicated for 15 min to prepare the catalyst ink. A 5 μ L aliquot of the catalyst ink was deposited onto the polished glassy carbon electrode, which was subsequently dried at room temperature to yield the working electrode. A saturated KCl Ag/AgCl electrode served as the reference electrode, and a graphite rod was used as the counter electrode. Linear sweep voltammetry (LSV) measurements were conducted at a scan rate of 5 mV·s⁻¹ and a rotating speed of 1600 r/min to evaluate the HER performance of the catalysts. All HER electrocatalytic activity tests were carried out in a N₂-saturated 0.5 mol/L H₂SO₄ electrolyte. Electrochemical stability was assessed via cyclic voltammetry

(CV) cycling for 4000 cycles within a potential range from -0.2 V to 0.1 V (vs. reversible hydrogen electrode, RHE) in the same N₂-saturated 0.5 mol/L H₂SO₄ electrolyte.

3 Results and Discussion

In this work, RuNi-ac/C was successfully synthesized via the SD-TDR method, and a detailed schematic illustration of the synthetic process is provided in Fig. 1. Two key steps dominate the synthesis procedure. The first is the spray-drying process, which enables sufficient mixing of Ru³⁺ and Ni²⁺ ions to form carbon black-supported RuNi precursor particles. Given that the complete drying of droplets takes less than 0.6 s^[28], Ru and Ni ions have no time to segregate and thus form homogeneously mixed RuNi precursor particles upon precipitation, which are uniformly dispersed on the carbon black surface. This process guarantees the atomic-level uniform mixing of Ru and Ni atoms in the resulting atomic clusters after thermal decomposition and reduction. The second key step is thermal decomposition and reduction. During this process, the carbon black-supported RuNi precursor particles with uniform mixing is reduced, accompanied by the release of HCl and H₂O gases, ultimately yielding RuNi-ac/C. Owing to the low reduction temperature of 300 °C, the newly generated Ru and Ni atoms lack sufficient energy for agglomeration and grain growth. Consequently, Ru and Ni atoms are primarily stacked in an atomic state without forming obvious crystalline structures. Fig. 2a presents SEM image of RuNi-ac/C reduced at 300 °C, revealing a spherical microscopic morphology with slight agglomeration. This phenomenon is attributed to the evaporation of solutes in the aqueous solution during droplet drying, which forms spherical precursors; the as-synthesized RuNi-ac/C retains the morphological features of the spray-dried precursors during the calcination process. To further elucidate the microscopic characteristics of RuNi-ac/C, TEM analysis was conducted, as displayed in Fig. 2b and 2c. Ultrafine nanoparticles are clearly observable and uniformly dispersed on the carbon black surface, with a particle size of

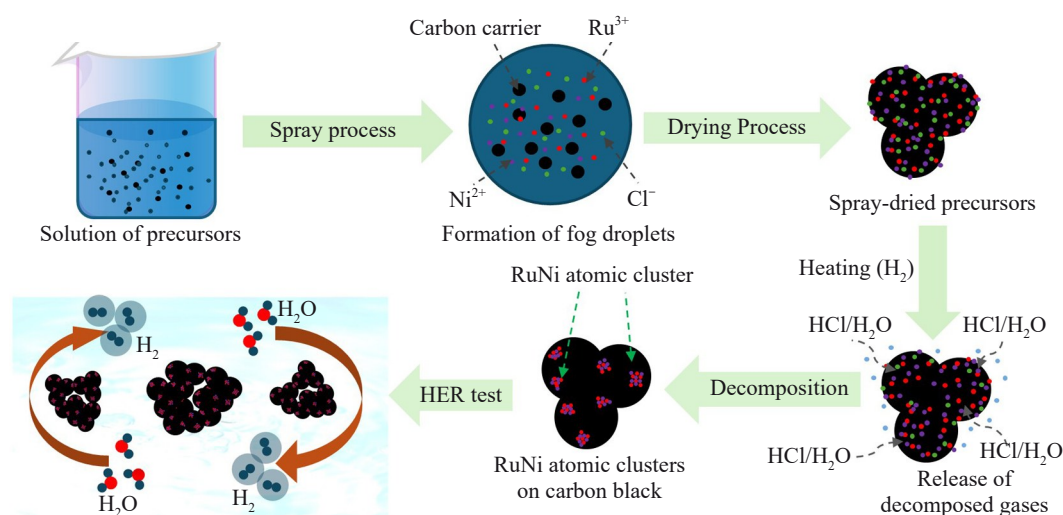


Fig.1 Schematic of the synthesis process of RuNi-ac/C

less than 2.5 nm and no apparent agglomeration. Additionally, HAADF-STEM characterization was performed, and the result is shown in Fig.2d. Fig.2e shows XRD pattern of RuNi-ac/C. No characteristic diffraction peaks corresponding to metallic phases are detected, whereas an amorphous phase feature is observed. Collectively, TEM and XRD analyses confirm that the RuNi species in this work are stacked in an atomic state, eventually forming RuNi atomic clusters supported on the carbon black surface.

In addition, the microstructures and morphologies of RuNi/C synthesized at different reduction temperatures were investigated, and the results are presented in Fig. 3. Fig. 3a shows the TEM image of RuNi/C prepared at 200 °C, where no obvious nanoparticles are observable. This is primarily attributed to the insufficient reduction of RuNi precursors at the low temperature of 200 °C. When the reduction temperature is increased to 300 °C (Fig. 3b), ultrafine RuNi nanoparticles with uniform dispersion are clearly observed on the carbon black surface. As illustrated in Fig. 3c, when the reduction temperature is elevated to 400 °C, the nanoparticles exhibit noticeable growth and local agglomeration. This phenomenon arises from the enhanced thermal energy at higher temperatures, which provides a driving force for the

growth and aggregation of nanoclusters. This trend is further exacerbated at 500 °C (Fig.3d), where the RuNi nanoparticles undergo dramatic growth and severe agglomeration. Consistent trends are also reflected in the XRD patterns of RuNi/C prepared at different reduction temperatures (Fig.3e). When the temperature is below 300 °C, the XRD pattern exhibits an amorphous structure, which is consistent with the TEM observations in Fig. 3a and 3b. At 400 °C, alloy diffraction peaks with a broad half-width appear in the XRD pattern, corresponding to the growth and crystallization of RuNi nanoparticles observed in the TEM images. When the reduction temperature reaches 500 °C, distinct and sharp XRD diffraction peaks are detected, which is in line with the rapid growth of RuNi nanoparticles at this temperature. Notably, the XRD pattern of RuNi/C prepared at 500 °C shows diffraction peaks that are consistent with neither pure Ru nor pure Ni but fall between the diffraction peaks of the two metals. This confirms the formation of a RuNi alloy at 500 °C. RuNi alloys typically exhibit two crystal structures: close-packed hexagonal (hcp) and face-centered cubic (fcc) ones. Collectively, these results demonstrate that the optimal reduction temperature for synthesizing RuNi atomic clusters is approximately 300 °C. Furthermore, the particle size distribution of the RuNi atomic

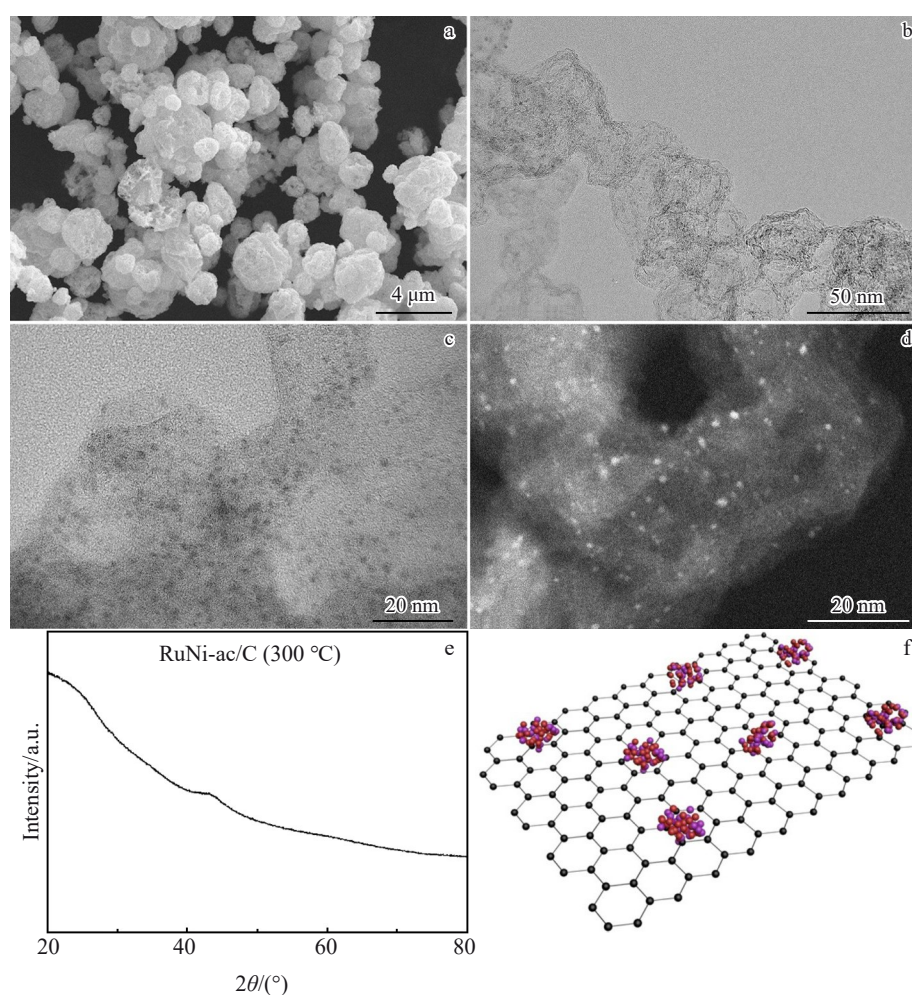


Fig.2 SEM (a), TEM (b–c), and HAADF-STEM (d) images as well as XRD pattern (e) of RuNi-ac/C obtained by reduction at 300 °C; schematic diagram of RuNi cluster particles distributed on the carbon black (f)

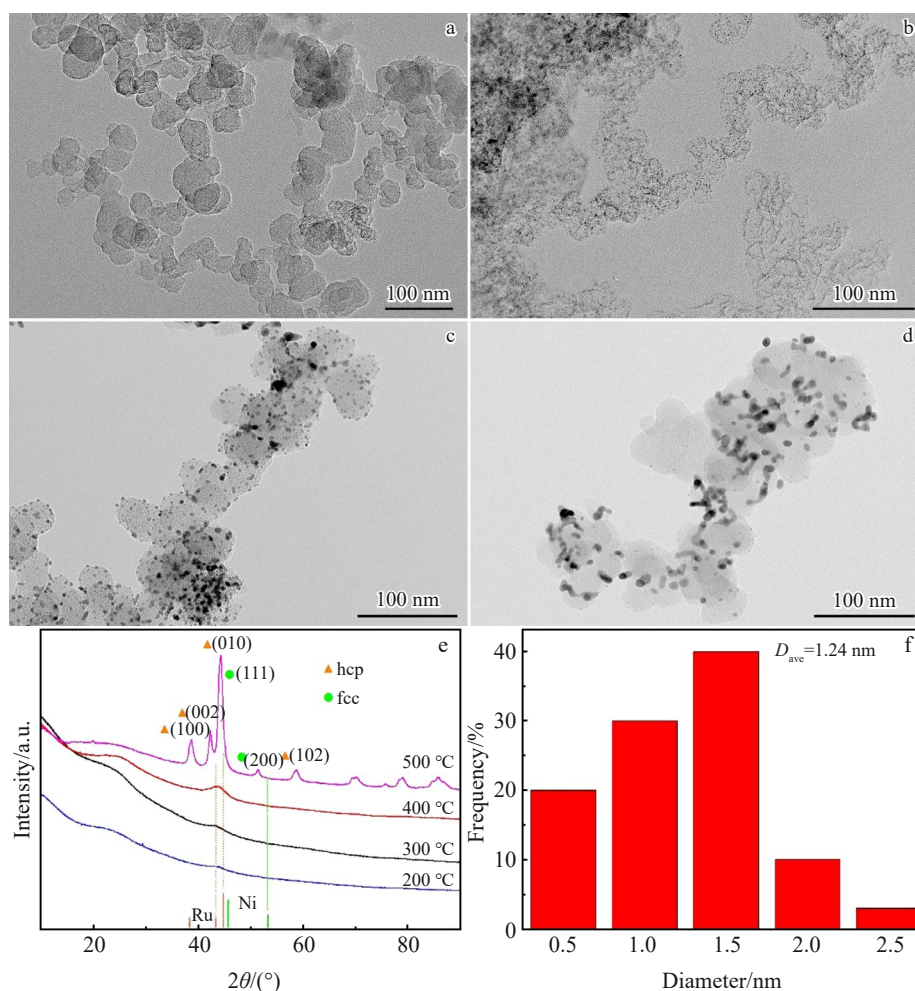


Fig.3 TEM images (a–d) and XRD patterns (e) of RuNi/C reduced at 200 °C (a), 300 °C (b), 400 °C (c), and 500 °C (d); particle size distribution of RuNi-ac/C obtained by reduction at 300 °C (f)

clusters was statistically analyzed by counting all particles in Fig. 4, and the result is shown in Fig. 3f. The RuNi atomic clusters exhibit a size distribution ranging from 0.5 nm to 2.5 nm, with an average particle size (D_{ave}) of 1.24 nm.

To compare the HER performance of RuNi-ac/C, Ru/C, and Ni/C, these catalysts were synthesized via the same method. Fig. 5a and 5b display the TEM images of Ru/C prepared at 300 °C; the particle size and dispersion of Ru nanoparticles are comparable to those of RuNi-ac/C. However, the particle size and dispersion of Ni nanoparticles differ significantly

from those of the above two catalysts. Since Ni ions cannot be effectively reduced at 300 °C, Ni/C was synthesized at 400 °C, and its microscopic morphology is presented in Fig. 5c and 5d. Severe agglomeration and large particle size are observed for Ni/C, suggesting that the introduction of Ru contributes to particle refinement and inhibits particle growth during the synthesis process. Furthermore, to clarify the element valence states of RuNi-ac/C prepared at 300 °C, XPS characterization was performed to analyze its chemical composition and electronic configuration, with the results shown in Fig. 6a. The

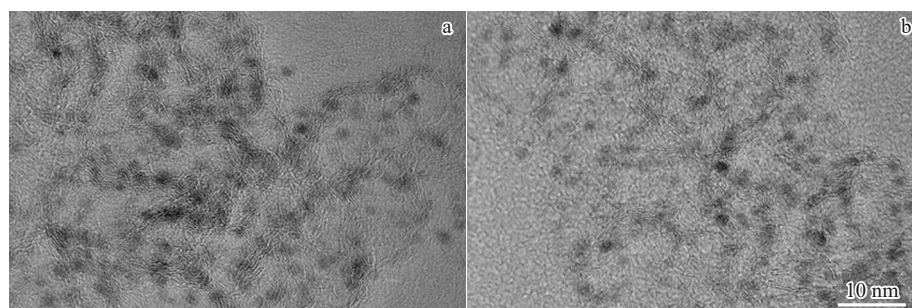


Fig.4 TEM images of RuNi-ac/C obtained by reduction at 300 °C

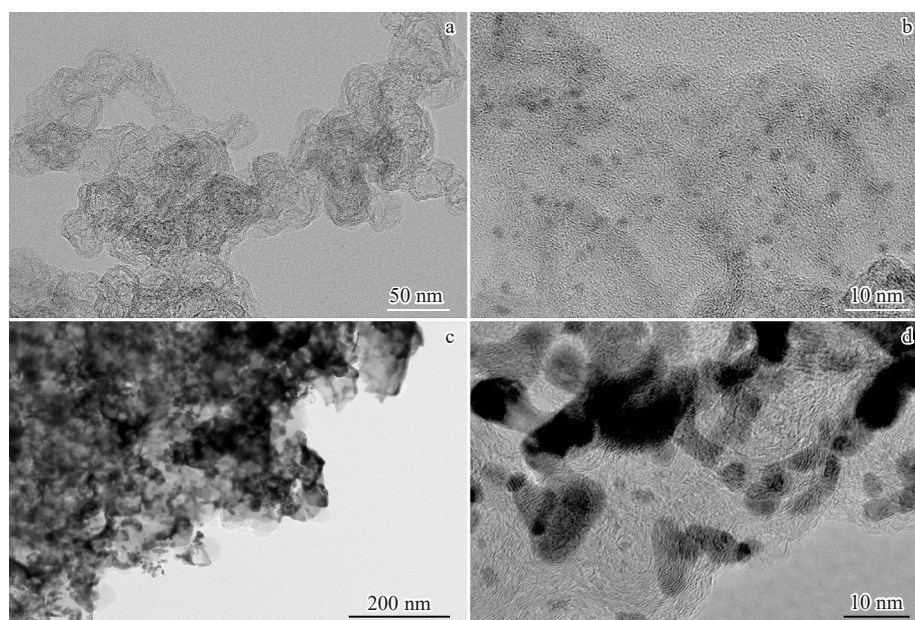


Fig.5 TEM images of Ru/C and Ni/C: (a–b) Ru/C after reduction at 300 °C; (c–d) Ni/C after reduction at 400 °C

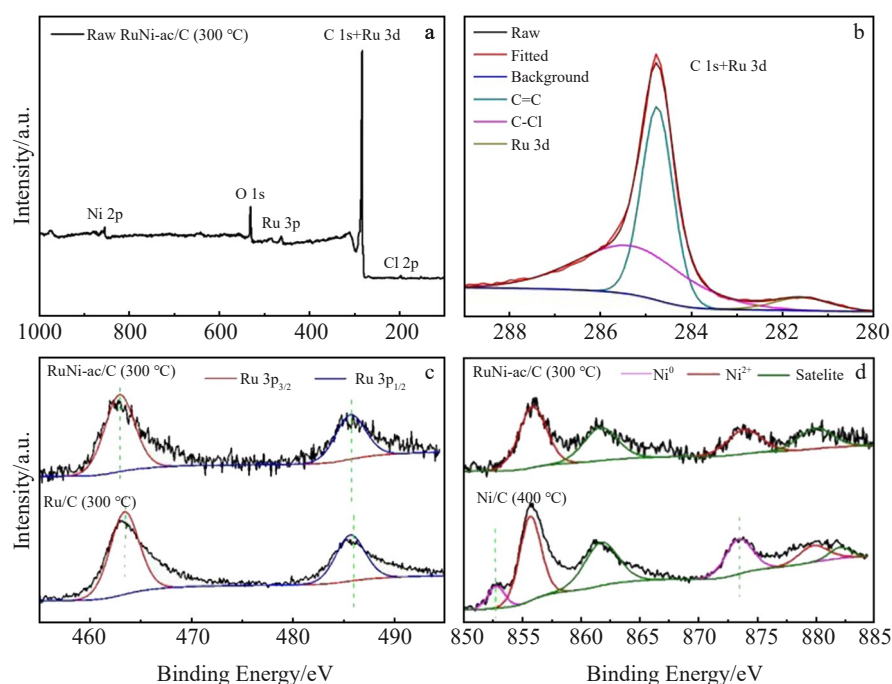


Fig.6 XPS spectrum of RuNi-ac/C scanned in the full range (a); XPS spectra of C 1s of RuNi-ac/C (b); XPS spectra of Ru (c) and Ni (d) of different catalysts

full-range XPS spectrum of RuNi-ac/C exhibits characteristic binding energies at 198.25, 281.4, 284.6, 462.5/485.7, 531.5, and 856.3 eV, which correspond to Cl 2p, Ru 3d, C 1s, Ru 3p, O 1s, and Ni 2p orbitals, respectively. It can be seen from Fig.6a that a small amount of Cl residue remains in the RuNi-ac/C sample, which is mainly attributed to the relatively low preparation temperature that inhibits complete removal of Cl-containing species. As shown in Fig.6b, the C 1s spectra of RuNi-ac/C show three characteristic peaks centered at approximately 284.8, 285.5, and 281.4 eV, which can be

deconvoluted into three sub-peaks corresponding to C=C, C-Cl, and Ru 3d orbitals, respectively. Notably, the Ru 3d peak is less affected by the C 1s signal interference, but Ru 3p was selected for valence state analysis to ensure accuracy. Fig.6c presents the Ru 3p spectra of RuNi-ac/C, which exhibit two distinct peaks at 463.2 and 485.53 eV, corresponding to the metallic Ru 3p_{3/2} and Ru 3p_{1/2} states, respectively. This confirms that Ru³⁺ ions are almost completely reduced to metallic Ru⁰ during the hydrogen reduction process. The Ni 2p spectra (Fig.6d) show Ni 2p_{3/2} and Ni 2p_{1/2} peaks at 856.3 and

875.5 eV, with corresponding satellite peaks at 860.8 and 880.7 eV, respectively. This indicates that Ni exists primarily in the Ni^{2+} oxidation state, because Ni, as a non-precious metal, is highly susceptible to surface oxidation. The synergistic effect between metallic Ru^0 and Ni^{2+} species in RuNi atomic clusters is hypothesized to modulate the H-M (hydrogen-metal) binding energy to an optimal range, thereby enhancing the HER catalytic performance.

In addition, XPS characterization was performed on Ru/C and Ni/C for comparison with RuNi-ac/C. As shown in Fig.6c, at the same reduction temperature (300 °C), the Ru binding energy of Ru/C exhibits a positive shift (shifting to the right) relative to that of RuNi-ac/C, though Ru exists in the metallic Ru^0 state in both catalysts. From the Ru XPS spectrum analysis, the Ru binding energy of RuNi-ac/C shows a negative shift (shifting to the left) compared to Ru/C. This phenomenon is mainly attributed to the introduction of Ni, which induces an electron transfer between Ru and Ni species. Notably, the negative shift of Ru binding energy indicates an increase in electron density around Ru atoms, which modulates the electronic structure of Ru. This further confirms that RuNi atomic clusters form a unique electronic configuration, which is favorable for promoting the HER process. The XPS spectra of Ni/C are presented in Fig.6d. In contrast to the Ni binding energy of RuNi-ac/C, a characteristic peak corresponding to metallic Ni^0 appears in the Ni/C spectrum. This is because Ni particles prepared at 400 °C undergo significant agglomeration and grain growth, and the surface oxidation of larger Ni particles in air is

relatively limited compared to ultrafine Ni species. Collectively, the XPS comparative analysis of RuNi-ac/C, Ru/C, and Ni/C demonstrates that RuNi atomic clusters possess a distinct surface electronic structure compared to the monometallic counterparts. This unique electronic structure is anticipated to endow RuNi-ac/C with superior potential HER catalytic performance.

In this work, the HER performance of the synthesized RuNi-ac/C, Ru/C, and Ni/C catalysts was evaluated in a 0.5 mol/L H_2SO_4 electrolyte, with commercial JM Pt/C (20wt% Pt) employed as a reference. Prior to testing, the catalyst-modified working electrodes were activated, followed by LSV measurements at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ and a rotating speed of 1600 r/min. Fig. 7a presents the LSV curves of RuNi-ac/C samples prepared at different reduction temperatures (200, 300, 400, and 500 °C) and commercial JM Pt/C. It is evident that RuNi-ac/C reduced at 300 °C exhibits exceptional HER performance, achieving an overpotential of only 37 mV at a current density (j) of $10 \text{ mA}\cdot\text{cm}^{-2}$, which is far superior to that of RuNi-ac/C prepared at other temperatures. In contrast, the overpotentials of RuNi-ac/C samples prepared at 200, 400, and 500 °C are 152, 100, and 175 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$, respectively. The inferior HER performance of RuNi-ac/C prepared at 200 °C is attributed to the incomplete reduction of RuNi precursors. For samples prepared at higher temperatures (400 and 500 °C), the RuNi atomic cluster structure is destroyed, accompanied by particle growth and severe agglomeration, which significantly deteriorate HER catalytic activity. Furthermore, the commercial JM Pt/C catalyst

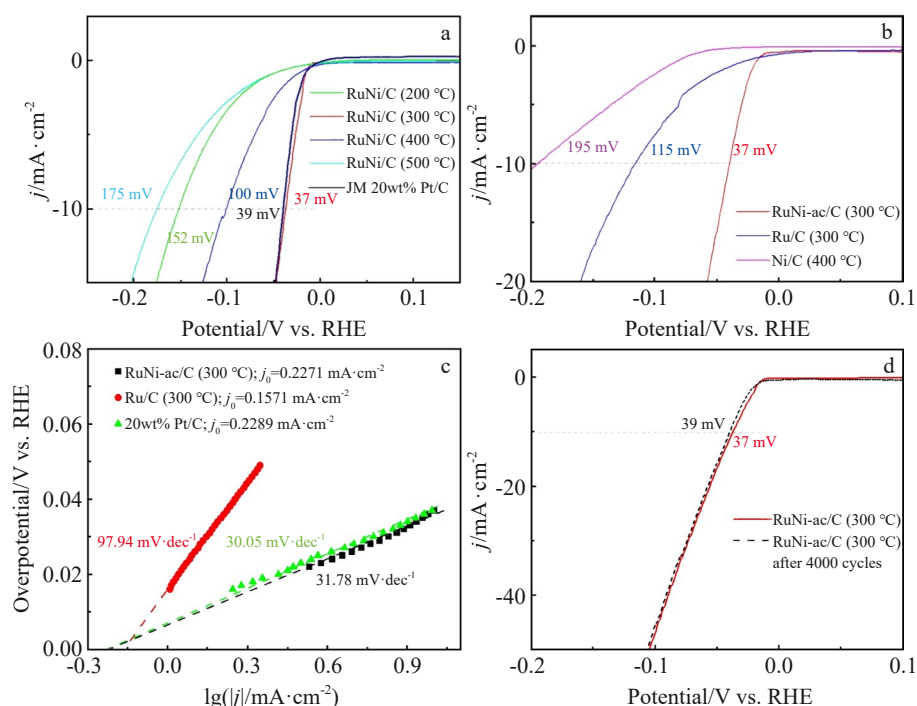


Fig.7 HER performance characterization of RuNi-ac/C, Ru/C, Ni/C, and JM Pt/C in 0.5 mol/L H_2SO_4 solution: (a) polarization curves of RuNi-ac/C and JM Pt/C with scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$; (b) polarization curves of RuNi-ac/C, Ru/C, and Ni/C with scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$; (c) Tafel slopes and exchange current densities of different catalysts; (d) polarization curves of RuNi-ac/C before and after 4000 CV cycles (the mass density of the catalyst during the test is $0.283 \text{ mg}\cdot\text{cm}^{-2}$)

exhibits an overpotential of 39 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$. These results demonstrate that the lab-synthesized RuNi-ac/C (300 °C) achieves HER performance comparable to that of the commercial Pt-based catalyst, while substantially reducing the cost of precious metals. Fig. 7b shows the LSV curves of Ru/C and Ni/C, with their overpotentials at $10 \text{ mA}\cdot\text{cm}^{-2}$ reaching 115 and 195 mV, respectively. These findings confirm that the introduction of Ni into Ru-based catalysts to form RuNi-ac/C can effectively enhance HER performance. This improvement is synergistically contributed by the electronic interaction between Ru and Ni species and the formation of highly dispersed RuNi atomic clusters.

To gain deeper insights into the HER performance of RuNi-ac/C, the Tafel slope and exchange current density (j_0) of RuNi-ac/C (300 °C), Ru/C (300 °C), and JM Pt/C were measured and compared. The Tafel slope is a critical parameter for evaluating the reaction kinetics on the electrode surface: at the same current density, a smaller Tafel slope corresponds to a lower overpotential for the catalytic reaction, indicating faster reaction kinetics. Meanwhile, the j_0 is another key indicator of electrocatalytic reaction kinetics. A higher j_0 value implies that the electrocatalytic reaction is more facile to initiate and proceeds with a lower activation energy. As presented in Fig. 7c, the Tafel slope of RuNi-ac/C is $31.78 \text{ mV}\cdot\text{dec}^{-1}$, which is comparable to that of JM Pt/C ($30.05 \text{ mV}\cdot\text{dec}^{-1}$) and significantly lower than that of Ru/C ($97.94 \text{ mV}\cdot\text{dec}^{-1}$). This result suggests that the hydrogen adsorption energy on the active sites of RuNi-ac/C is closer to the optimal value (near zero), which optimizes the HER pathway and accelerates the catalytic kinetics, making the HER process on RuNi-ac/C much faster than that on the other synthesized catalyst (Ru/C). Additionally, the j_0 of RuNi-ac/C, Ru/C, and JM Pt/C are 0.2271 , 0.1571 , and $0.2289 \text{ mA}\cdot\text{cm}^{-2}$, respectively. The j_0 value of RuNi-ac/C is nearly identical to that of JM Pt/C and higher than that of Ru/C, confirming that the electrocatalytic HER on RuNi-ac/C is more prone to occur with a lower reaction activation energy. Collectively, these kinetic parameters demonstrate that RuNi-ac/C possesses superior HER performance compared to Ru/C and comparable kinetics to commercial JM Pt/C.

In addition, catalyst stability is a crucial indicator for

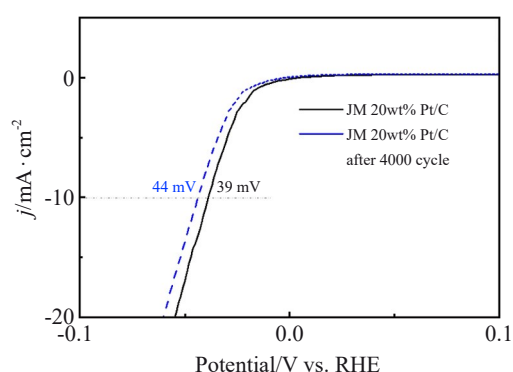


Fig.8 Long-term durability measurement of LSV curves of JM Pt/C before and after 4000 CV cycles

evaluating catalyst lifespan, which significantly affects the practical application potential of the catalyst. The stability of RuNi-ac/C was evaluated via CV cycling for 4000 cycles within the potential range from -0.2 V to 0.1 V (vs. RHE) in an N_2 -saturated $0.5 \text{ mol/L H}_2\text{SO}_4$ electrolyte. Fig. 7d displays the LSV curves of RuNi-ac/C before and after 4000 CV cycles. After the long-term durability test, the LSV curve of RuNi-ac/C shows no significant shift, with only a slight overpotential increment of 2 mV at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. For comparison, commercial JM Pt/C was subjected to the same durability test conditions, and the results are presented in Fig. 8. The commercial JM Pt/C exhibits a noticeable degradation in catalytic performance, with its overpotential increasing by 5 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ after cycling. This indicates that the commercial JM Pt/C has inferior stability compared to the lab-synthesized RuNi-ac/C. Collectively, these results confirm that RuNi-ac/C possesses excellent HER stability in acidic electrolytes, further supporting its potential for practical applications.

4 Conclusions

1) Carbon black-supported RuNi atomic clusters (RuNi-ac/C) could be successfully synthesized via the facile and controllable SD-TDR method. The as-synthesized RuNi atomic clusters are uniformly dispersed on the carbon black matrix, with a particle size distribution ranging from 0.5 nm to 2.5 nm.

2) To compare the HER performance with RuNi-ac/C, Ru/C (300 °C), Ni/C (400 °C), and RuNi/C samples prepared at different reduction temperatures (200, 400, and 500 °C) were also fabricated using the same SD-TDR strategy. Among all the synthesized catalysts, RuNi-ac/C exhibits the most superior HER performance: at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, the overpotentials of RuNi-ac/C, Ru/C (300 °C), Ni/C (400 °C), RuNi/C (200 °C), RuNi/C (400 °C), and RuNi/C (500 °C) are 37, 115, 195, 152, 100, and 175 mV, respectively. In the stability evaluation, after 4000 CV cycles, the overpotential of RuNi-ac/C at $10 \text{ mA}\cdot\text{cm}^{-2}$ only increases by 2 mV, demonstrating excellent electrochemical stability.

3) Compared with the commercial JM Pt/C catalyst, RuNi-ac/C achieves better HER activity and superior stability, while featuring a significantly lower precious metal cost, highlighting its great potential for practical hydrogen production applications.

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炭黑负载钌镍原子簇用于强化酸性体系下析氢反应电催化性能

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摘 要: 研发高性能、低成本析氢反应 (HER) 催化剂是推动氢能规模化开发与实际应用的关键瓶颈突破方向。当前的研究难点在于如何使用廉价金属替代铂 (Pt) 以在保障 HER 催化性能的同时降低催化剂成本。采用简单可控的喷雾干燥-热分解还原法, 在氢气中还原温度为 300 °C, 制备出炭黑负载钌镍原子簇催化剂 (RuNi-ac/C)。表征结果显示, 所制备的钌镍原子簇在炭黑载体表面实现均匀分散, 粒径分布集中于 0.5~2.5 nm。电化学测试表明, 该催化剂在 0.5 mol/L 硫酸电解液中, 电流密度在 10 mA·cm⁻² 时的 HER 过电位仅为 37 mV; 稳定性测试中, 经过 4000 圈循环伏安扫描后, 过电位增幅仅为 2 mV, 展现出优异的电化学稳定性。相较于同步制备的 Ru/C (300 °C)、Ni/C (400 °C) 催化剂, 以及在 200、400、500 °C 条件下合成的 RuNi/C 催化剂, RuNi-ac/C 的 HER 催化活性最优。更为重要的是, 与商用 Pt/C 催化剂相比, RuNi-ac/C 不仅具备更出色的 HER 活性, 同时拥有显著的成本优势, 为低成本高效 HER 催化剂的产业化应用提供了新思路。

关键词: 钌镍原子簇; 喷雾干燥-热分解还原法; 析氢反应电催化; 氢能

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