Engineering the synergistic effect of carbon dots-stabilized atomic and subnanometric ruthenium as highly efficient electrocatalysts for robust hydrogen evolution

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Abstract
Currently, the most efficient electrocatalyst for the hydrogen evolution reaction (HER) in water dissociation is Pt-based catalyst. Unfortunately, the high cost and less than perfect efficiency hinder wide-range industrial/technological applications. Here, by controlling the treatment temperature of tris (2,2-bipyridine) ruthenium dichloride hexahydrate, synthesis of compounds with novel ruthenium single/dual atoms (Ru S/DAs) mixed with Ru nanoclusters (Ru S/DAs + Ru NCs) and supported by carbon dots is demonstrated. These compounds are shown to be highly efficient and competitive catalysts for hydrogen evolution. Ru S/DAs + Ru NCs exhibit very high activity, with overpotentials of 15 and 40 mV at a current density of 10 mA/cm² in 1.0 mol/L KOH and 0.5 mol/L H₂SO₄, respectively. Furthermore, the composites are found to possess outstanding stability and rapid HER kinetics. X-ray absorption fine structure analysis, supported by density functional theory calculations, shows charge rearrangement in single-atomic Ru, and the Ru dual sites promote active hydrogen adsorption and recombination. Ru S/DAs and Ru NCs demonstrate high electroactivity due to the electroactive Ru 4d orbitals. The introduction of Ru NCs activates the carbon support, providing a high electronic conductivity to transfer electrons from Ru NCs to Ru S/DAs, and facilitates water dissociation for the HER process.

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KEYWORDS
carbon dots, hydrogen evolution reaction, nanoclusters, ruthenium, single/dual atoms

1 | INTRODUCTION

Hydrogen is an ideal energy source to replace limited fossil fuels to achieve a green energy blueprint.1 Electrocatalytic water splitting, with the advantages of zero carbon emission, satisfying efficiency, and high product purity, is one of the most promising routes for hydrogen generation.2–6 Pt-based electrocatalyst materials have been demonstrated to enhance electrolytic water splitting; however, Pt is expensive, and the catalysts are relatively unstable. In addition, considering the actual water-splitting application, the ideal electrocatalyst is expected to work well in wide pH values.7,8 The development of efficient and inexpensive electrocatalysts for cost-effective and high-purity hydrogen production is of paramount importance. Ruthenium (Ru), possessing a bond strength with hydrogen (≈65 kcal/mol) similar to that of Pt, is a widely used substitute.9 Ru is much less expensive than Pt, making it a promising alternative for catalyzing the hydrogen evolution reaction (HER). Some Ru-based electrocatalysts have displayed HER activity comparable or even superior to that of Pt/C.10–15 However, in most Ru-based electrocatalysts, Ru exists as Ru nanoparticles (NPs), leading to low utilization of the element.

Downsizing Ru metal to nanoclusters (NCs), even to the single atom (SA) scale, can maximize the utilization of Ru and markedly enhance the mass activity.16–18 However, SAs tend to aggregate during synthetic and catalytic processes due to the high surface energy.19,20 Preventing agglomeration of the SA catalyst during preparation and keeping the SA catalyst stable during the catalytic process is challenging. An often employed remedy is to load suitable amounts of active metals onto various supports with high surface areas and desired anchoring sites.21,22 Herein, we propose a new synthetic strategy to overcome the above problem.

Promising substrates for anchoring single Ru atoms and Ru NCs include carbon materials (CMs), such as carbon dots (CDs), biomass, and ultrathin nitrogen-doped holey carbon, which possess high electrical conductivity, good chemical stability, and unique edge sites and can potentially enhance the catalytic property.23–27 To prevent SAs aggregation in caustic media, we suggest loading single Ru atoms into carbon. This method has been widely used in various catalytic systems due to its ability to maintain high activity and stability. However, the traditional approaches to fabricating CMs rely greatly on complex procedures and specific precursors. In contrast, small organic metal molecules can be converted into functional CMs via a metal-assisted carbonization process by a simple, effective, and scalable method.28,29 Metals can promote the thermal stability of molecular precursors and assist in forming thermally stable polymeric intermediates during the carbonization process, which guarantees the successful preparation of carbons at a high yield. Furthermore, regulating the electronic structure of metal centers in single-atomic-site electrocatalysts has proven to be an efficient way to enhance the intrinsic activity of SAs.30–32 Alternatively, the electronic structure of Ru sites in Ru-N or Ru-C structures can be regulated by nearby Ru NCs to further improve the HER activity.33,34 Our previous work confirmed that the coexistence of CDs and Ru NPs significantly enhances hydrogen generation.35–38 Hence, introducing Ru single/dual atoms (Ru S/DAs) into Ru NCs will be very promising as a facile and effective method to optimize the electronic structure of Ru NCs to enhance the intrinsic activity for the HER.

In the following, we report the synthesis of CD-supported Ru NCs and atomically dispersed Ru catalysts. We found that Ru S/DAs and Ru NCs possess high activity and stability for hydrogen evolution over a wide pH range. The increased performance benefits from multicomponent synergistic effects and the unique structural feature. Ru S/DAs in conjunction with Ru NPs lead to the high HER activity of the catalyst. The dual (dimer) active sites in Ru S/DAs and Ru NCs exhibit superior catalytic activities arising from a strong synergistic effect. Theoretical calculations demonstrate that the high electroactivities in Ru S/DAs and Ru NCs derive from different origins. For acidic HER, Ru NCs act as an efficient electron reservoir guaranteeing electron transfer. For alkaline HER, the superior capability of Ru NCs for water dissociation enhances the performance. The promising results indicate a new perspective for the rational design and synthesis of economical and practical HER electrocatalysts.

2 | CHARACTERIZATION OF ELECTROCATALYSTS

The transmission electron microscopy (TEM) image of Ru S/DAs (Figure 1A) shows that Ru S/DAs are uniformly dispersed on the CDs. The high-resolution TEM (HRTEM) image of Ru S/DAs displays a lattice fringe spacing of 0.34 nm (Figure 1B), which can be indexed to the (002) plane of graphitic carbon and is consistent with the diffraction pattern (Figure 1C). No Ru NPs are observed based on HRTEM. The existence of Ru in the as-prepared Ru
S/DAs is confirmed by the high-angle annular dark-field scanning TEM (HAADF-STEM) image. The Ru is evidently atomically dispersed as SAs or atom pairs (Figure 1D). By increasing the pretreatment temperature, catalysts of nitrogen-containing CD-supported Ru S/DAs and ruthenium single/dual atoms mixed with Ru NCs (Ru S/DAs + Ru NCs) were obtained. The morphology of Ru S/DAs + Ru NCs was examined by TEM. As temperatures rise further, CDs cross link and form membrane-like structures. Figure 1E shows that the Ru S/DAs and Ru NCs are homogeneously distributed in the nitrogen-carbon matrix. The corresponding particle size distribution indicates that the Ru NCs have an average diameter of 2.31 nm (Figure S1). The HRTEM image of Ru S/DAs + Ru NCs displays a lattice fringe spacing of 0.23 nm (Figure 1G), indexed to the (100) plane of hexagonal Ru. The corresponding energy-dispersive X-ray spectroscopy mapping images show a homogenous distribution of C, N, and Ru over the entire structure (Figure 1H).

X-ray diffraction (XRD) was employed to characterize the structure and composition of Ru S/DAs and Ru S/DAs + Ru NCs. As shown in Figure S2, both samples show the typical carbon peak at approximately 22°. In Ru S/DAs + Ru NCs, the known (002) diffraction peak of hexagonal-close-packed (HCP) Ru is observed. In comparison, no characteristic peaks indicate crystalline Ru...
species in the XRD patterns of Ru-S/DAs, supporting the dispersion of atomic Ru due to the space-confinement effect and strong anchoring ability of the N functional groups. Three distinct Raman peaks are observed for these Ru-based samples at 1345, 1594, and 2680 cm\(^{-1}\), indicating the D-band of structurally disordered carbon, the G-band of graphitic carbon and the 2D band, respectively (Figure S3). The calculated \(I_D/I_G\) intensity ratios for Ru S/DAs and Ru S/DAs + Ru NCs are 0.98 and 1.03. These values confirm that the two samples are typical disordered graphitic carbons. The higher intensity ratio in Ru S/DAs + Ru NCs indicates an increase in structural defects, suggesting that the N of the precursor ratio in Ru S/DAs + Ru NCs indicates an increase in typical disordered graphitic carbons. 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The electrochemical behavior of the catalysts was measured by linear sweep voltammetry (LSV) using a three-electrode system with acidic and basic electrolytes. The HER performance of single Ru S/DA was first investigated in a 1 mol/L KOH solution. For comparison, the HER performances of CDs, commercial Ru powder and commercial Pt/C (20 wt. %) were also measured under the same conditions. As shown in Figure 3A, Ru S/DA shows a very small onset overpotential of 0 mV versus reversible hydrogen electrode (RHE), suggesting excellent electrocatalytic activity. Moreover, the applied HER overpotential for the Ru S/DA electrocatalyst at a current density of 10 mA/cm² (η10) is only 58 mV in 1 mol/L KOH. This value is higher than that of the commercial Pt/C catalyst (40 mV). The Tafel plots of electrocatalysts provide profound insight into the intrinsic HER kinetic process. As shown in Figure 3B, the Tafel slope of the Ru S/DA electrocatalyst is 90 mV/dec, which is higher than that of Pt/C (49 mV/dec). The electrocatalytic HER stability is another vital criterion for evaluating the performance of an electrocatalyst.39,40
1 mol/L KOH aqueous solution, which will be compared with those for Pt/C tested under the same conditions. After 5000 CV cycles, the HER overpotential of the Ru S/DA electrocatalyst at 10 mA/cm² increases to 73 mV, which is lower than that of the Pt/C catalyst of 119 mV. The HER performance of Ru S/DAs was further studied in a 0.5 mol/L H₂SO₄ solution. In this case, Ru S/DAs require an overpotential of 118 mV to achieve a current density of 10 mA/cm². The Tafel slope for Ru S/DAs is 76 mV/dec (Figure S8A,B). Additionally, in an acidic electrolyte, Ru S/DAs exhibit similar durability after 1000 CV cycles, as shown in Figure S8C.

As demonstrated above, strongly coupled Ru S/DAs and Ru NCs and the porous carbon support exhibit excellent HER performance. Ru S/DAs + Ru NCs are expected to have even more superior performance for the HER. We evaluated the HER catalytic properties of Ru S/DAs + Ru NCs in a 1 mol/L KOH solution using a three-electrode electrochemical system. Figure 3D shows the LSV polarization curve of Ru S/DAs + Ru NCs together with those of commercial Ru powder and Pt/C (20 wt. %) as references. Ru S/DAs + Ru NCs have an onset overpotential of nearly 0 mV, which is much lower than those of commercial Ru (24 mV) and commercial...
Pt/C (2 mV). At a current density of 10 mA/cm², a small overpotential (\(\eta\)) of 15 mV is achieved by Ru S/DAs + Ru NCs, compared with 40 and 104 mV achieved by commercial Pt/C and Ru powder, respectively. The excellent catalytic activity of Ru S/DAs + Ru NCs is validated by the Tafel plots (Figure 3E). The Tafel slope (40 mV/dec) of Ru S/DAs + Ru NCs is much lower than those of Pt/C (49 mV/dec) and Ru powder (92 mV/dec), ensuring the ability to obtain a large current at a small overpotential. The HER process can be described by the Volmer-Tafel or Volmer-Heyrovsky mechanism. The Volmer-Tafel mechanism suggests that the discharge reaction is fast and H\(_2\) is evolved by a rate-determining combination reaction. In contrast, the Volmer-Heyrovsky mechanism occurs when the discharge reaction is relatively slow, and a rate-determining ion-atom reaction evolves H\(_2\). To study the stability of the catalyst, we measured 5000 continuous CV cycles at an accelerated scan rate of 5 mV/s in 1 mol/L KOH. As shown in Figure S7B, after 5000 cycles, the overpotential at a current density of 10 mA/cm² for Ru S/DAs + Ru NCs only increases by 2 mV, confirming that the catalyst is highly stable.

The HER performance of Ru S/DAs + Ru NCs was studied further in a 0.5 mol/L H\(_2\)SO\(_4\) solution. Remarkably, only a relatively low overpotential of 40 mV was required for Ru S/DAs + Ru NCs to achieve a current density of 10 mA/cm². This value is comparable to that of Pt/C. Ru S/DAs + Ru NCs show a Tafel slope of 44 mV/dec, which is only slightly higher than that of Pt/C (35 mV/dec) (Figure S8D,E). Moreover, the Ru S/DAs + Ru NC catalyst also exhibits remarkable stability in 0.5 mol/L H\(_2\)SO\(_4\). According to Figure S8F, the HER polarization curves exhibit virtually no change after 5000 potential cycles.

Electrochemical impedance spectroscopy was used to study the interfacial electron transfer dynamics of Ru S/DAs and Ru S/DAs + Ru NCs in 1 mol/L KOH solutions. The related Nyquist plots and equivalent circuits are shown in Figure S9. The interfacial electron transfer kinetics follow the order of Ru S/DAs + Ru NCs > Ru S/DAs > Pt/C > Ru powder. This trend corresponds with the HER activity exactly. Among them, Ru S/DAs + Ru NCs exhibit the fastest interfacial electron transfer kinetics. This result reveals that alloying the composite structure can enhance the electrical conductivity and improve the interfacial electron transfer kinetics due to the synergistic effect between the N-doped Ru clusters and Ru S/DAs (Figure S9). To tentatively compare the number of available catalytically active sites, the capacitance of the catalyst-solution interface of Ru S/DAs and Ru S/DAs + Ru NCs was further examined. As shown in Figures S10 and S11, the current densities were measured from 5 to 40 mV/s in a potential window of 0.17–0.27 V (vs. RHE) and could be plotted as a function of the scan rate to study the effective surface area by evaluating the electrochemical double-layer capacitance (Cdl). The capacitance (Cdl) of Ru S/DAs + Ru NCs of 46.03 mF/cm² is much higher than that of Ru S/DAs.

4 UNDERSTANDING THE HER ACTIVE CENTER

Thiocyanate ions (SCN\(^-\)) are known to poison active metal centers due to their strong binding ability on metal atoms, while ethylenediaminetetraacetic acid (EDTA) could form coordination bonds with Ru-N/Ru-C. Therefore, EDTA and KSCN were used as poisoning species to help differentiate their contributions. According to Figure 3C, when 10 mmol/L EDTA was added to the solution, \(\eta_{10}\) shifted negatively by >55 mV. The shift was much smaller (ca. 12 mV) when 10 mmol/L SCN\(^-\) was added to the solution, indicating almost all S/DAs in Ru S/DAs. In comparison, as both Ru NCs and Ru S/DAs (likely in Ru-N/Ru-C) are present in the Ru S/DAs + Ru NC samples, the addition of 10 mmol/L KSCN shifts \(\eta_{10}\) negatively by >150 mV, but the initial potential remains small. When 10 mmol/L EDTA was added to the solution, the \(\eta_{10}\) shift was much smaller, and the initial potential increased, as shown in Figure 3F. We speculate that the reason for the high activity of Ru S/DAs + Ru NCs is the synergy of Ru S/DAs and Ru NCs. Ru NC sites facilitate water dissociation, while abundant Ru S/DAs sites help promote adsorption and recombination. The collaborative effect of Ru S/DAs and Ru NCs not only enhances the catalytic activity but also improves the stability compared to Ru S/DAs.

5 DENSITY FUNCTIONAL THEORY (DFT) CALCULATIONS

To analyze the superior electroactivity of Ru S/DAs and Ru NCs, we carried out theoretical calculations based on DFT. First, we demonstrate the electronic distributions of the three different materials. In Ru SAs, we note that the anchoring Ru atom dominates the electroactive region. Meanwhile, the neighboring N and C sites show strong coupling with the Ru sites (Figure 4A). When a second Ru atom is introduced, the local electronic structure is perturbed, where the second Ru site shows higher electroactivity. Moreover, the electronic distribution of the neighboring C and N sites becomes uneven. The C2 sites become more electron-rich, while the C1 sites are less electroactive (Figure 4B). Ru NCs have a highly uneven...
electronic distribution and strong coupling with the local CDs. The increased electroactive region indicates the potential water dissociation capability for the HER (Figure 4C). The calculated projected partial density of states (PDOS) was used to analyze contributions to the electronic structures. Notably, the Ru 4d orbitals dominate the Fermi level (E_F), supporting the high electroactivity for electron transfer to the adsorbates. The s and p orbitals at both C and N sites are found to overlap significantly with the Ru 4d orbitals, confirming the strong electronic coupling (Figure 4D). When a second Ru atom is introduced, strong interactions between the Ru atoms lead to e_g – t_{2g} splitting in the Ru 4d band. The small energy difference indicates high electroactivity as...
the energy barrier for electron transfer decreases. Moreover, the overall electronic structure of the carbon nanodots is not affected, supporting the stable electronic structures for both Ru SAs and Ru DAs to achieve high durability for the HER (Figure 4E). In comparison, Ru NCs show distinctively different electronic structures. The sharp peaks of Ru 4d become a broad band covering $E_V - 8.0 \text{ eV}$ to $E_V + 4.0 \text{ V}$ and crossing $E_F$. This lowers the barycenter of the Ru 4d band and supplies electrons to the nearby Ru S/DAs. The results are consistent with the downshift of binding energies in Ru S/DAs + Ru NCs observed in the XPS spectra (Figure 4F). Since the CDs show similar electronic structures in Ru DAs and Ru SAs, we studied the Ru SAs to investigate the C sites. For C1–C3 sites, the s and p orbitals of carbon still display small gaps near $E_F$. Comparatively, the splitting of s and p orbitals of C4 is much larger than that of C1–C3 sites, leading to a lower electron transfer efficiency due to the larger barrier (Figure 4G). After the introduction of Ru NCs, the electronic environment of carbon is modulated. Notably, the s and p orbitals of C1–C3 sites are activated since the energy gap for electron transfer disappears. These results support the much-enhanced electron transfer capability of the CDs, facilitating the HER performance (Figure 4H). The calculations also explain the site-dependent electroactivity in the Ru cluster. Due to the strong interaction between the activated CDs and the Ru cluster, the interfacial Ru atoms alleviate the electron transfer activation barrier. Concomitantly, the bulk and middle layer Ru sites inside the Ru cluster show a larger splitting, which supports a relatively weak electron transfer. In comparison, $e_p - t_{2g}$ splitting is substantially suppressed at the surface Ru sites, boosting the electroactivity for the HER (Figure 4I).

Energy level diagrams are shown (Figure 4J,L) to compare the thermodynamic behaviors. For hydrogen atom adsorption, Ru NCs show a stronger binding strength than Ru DAs. We note a continuous downhill trend for the acidic HER process in Ru DAs. In comparison, Ru NCs show a subtle energy barrier from 2H* to H$_2$ of 0.16 eV in the acidic HER (Figure 4I). In the alkaline HER, both Ru DAs and Ru NCs show an exothermal trend with energy releases of 1.00 and 0.70 eV, respectively. The initial water adsorption is the key step to enable an efficient HER process. We note a significant energy drop for water dissociation in Ru NCs than that in Ru DAs (Figure 4K). Comparing the activation barriers for the crucial water dissociation step, Ru NCs have a lower activation energy of 0.15 eV, which is 0.50 eV lower than that in Ru DAs. The enhanced HER performance in the KOH solution can be attributed to the improved water dissociation efficiency in Ru S/DAs + Ru NCs (Figure 4L). Therefore, the synergistic effect between the Ru clusters and Ru single/dual atoms is confirmed in Ru S/DAs + Ru NCs.

According to the aforementioned experimental and DFT analysis, the design principle and water splitting mechanism of Ru S/DAs + Ru NCs are illustrated in Figure 5, indicating the multicomponent synergistic effects.

6 | CONCLUSIONS

For the first time, we demonstrated that nitrogen-doped CD-supported ruthenium single/dual atoms (Ru S/DAs) and ruthenium single/dual atoms mixed with ruthenium clusters (Ru S/DAs + Ru NCs) catalyzed the HER better than commercial Pt-based catalysts. The activity of Ru S/DAs + Ru NCs is higher than that of Ru S/DAs. Ru S/DAs + Ru NCs exhibit high HER activity that requires only a 15 mV overpotential in alkaline solution and a 40 mV overpotential in acidic solution to drive a current density of 10 mA/cm$^2$. These catalysts are among the best HER electrocatalysts ever reported. DFT calculations have shown that strong couplings between Ru NCs and the carbon support enable efficient electron transfer to the neighboring Ru S/DAs and effective dissociation of water molecules. The optimized electronic structure leads to remarkable HER performances in both acidic and alkaline solutions. The anchoring of Ru S/DAs on Ru clusters improves the intrinsic activity and enhances the operational stability compared to Ru SA or commercial powder catalysts. We advocate that the pair site configuration of Ru clusters and S/DAs has a strong collaborative effect that enhances the catalytic activity. The findings reported here help open up a new opportunity to explore cost-effective and high-performance electrocatalysts for energy conversion applications.
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CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

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