Simple construction of ruthenium single atoms on electrospun nanofibers for superior alkaline hydrogen evolution: A dynamic transformation from clusters to single atoms

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HIGHLIGHTS

- Ru SAs were in situ synthesized by the dynamic transformation from clusters.
- The formation of Ru–N–C bonds plays an important role for anchoring the Ru SAs.
- The transformation can be controlled by the treatment time and temperatures.
- Ru SAs exhibit superior HER activity with overpotential of 34 mV (20 mA cm⁻²).

GRAPHICAL ABSTRACT

ABSTRACT

The challenges for preparing metal single atoms (MSAs) catalysts are facile synthesis approaches and the suitable supports with strong coordination to stabilize MSAs. Herein, we reported a facile strategy to synthesize the Ru single atoms (Ru SAs) through the dynamic transformation from clusters to single atoms by combining the electrospun technology and NH₃-assisted graphitization process. The small Ru nanoclusters (NCs) supported on carbon nanofibers (CNFs) were in situ converted into Ru SAs in N-doped CNFs under the NH₃ treatment. Through controlling the NH₃ treatment time and graphitization temperatures, the Ru nanocrystals exhibit a dynamic transformation from nanoclusters to single atoms. The results indicate that the Ru NCs with larger amounts of Ru SAs exhibit superior HER activity in alkaline media with low overpotential of 34 mV at 20 mA cm⁻², which is even significantly better than commercial Pt/C catalysts. The mass activity of Ru SAs/NCNFs is about 390 A g⁻¹ at an overpotential of 100 mV, which is ~3.5 times higher than that of commercial Pt/C (110 A g⁻¹). This strategy will provide a new way for the large-scale production of MSAs transformed from different metal nanoparticles or nanoclusters.

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1. Introduction

Hydrogen, a carbon-free and high-density energy, is a promising candidate for efficient and environmental energy conversion to replace the traditional fossil fuels [1, 2]. As a sustainable technology to produce hydrogen, electrochemical water splitting has drawn increasing attention owing to its high-efficiency and satisfactory product purity [3, 4]. Although there are numerous researches about water electrolysis in acidic electrolytes have been reported, considering the high cost and sluggish kinetics of counter electrode catalysts for oxygen evolution reaction (OER) in acidic solutions, the hydrogen evolution reaction (HER) in alkaline media deserves detailed study to accelerate the industrialization process of overall water splitting [5–7]. Platinum (Pt)-based materials are considered as the best electrocatalysts for HER [8]. Unfortunately, the expensive price and unsatisfactory stability in alkaline media will restrict their large-scale applications [9]. Therefore, design and synthesis of efficient and low-cost catalysts to replace Pt-based materials has great significance. To date, a number of low cost and competitive performance alternatives for water splitting in alkaline solutions have been reported, including Co-based catalysts [10–12], Mo-based catalysts [13–15], Cu-based catalysts [16–18]. However, these catalysts still show higher overpotentials and Tafel slopes in comparison with commercial Pt/C electrocatalysts.

To overcome the challenges of the high cost of precious metal and unsatisfactory activity of transition metal, it’s very important to decrease the loading dosage and increase the efficiency of noble metal electrocatalysts. Metal single atoms (MSAs) catalysts have emerged as a new frontier catalyst because of the maximum atom-utilization efficiency and incredible performance in catalysis [19, 20]. However, the synthesis of MSAs remains challenging due to the high surface free energy caused by their ultra-small size. The high reactivity would result in metal aggregation to nanoclusters and nanoparticles during synthesis and catalysis process, which would limit the large-scale applications of MSAs. An effective strategy to overcome aggregation is to introduce a high-surface-area support material to interact with the metal atoms [21–23]. Recently, several technologies, such as atomic layer deposition [24], wet impregnation [25], co-precipitation [26] and photochemical deposition [27] are being utilized for the fabrication of MSAs. Metal oxides [28], carbon with defects [29], metal-organic frameworks [30], were widely used as supports to anchor the isolated metal atoms. They are still two major challenges and one is the complicated synthesis methods, and the as-synthesized MSAs suffered from low loading due to the limited surface defect density of the substrate [31, 32]. The other one is the weak metal-support interaction, resulting in the aggregation of MSAs caused by the migration of atomic metal species [33]. Therefore, developing facile approach and building the suitable support to stabilize MSAs is important for enhancing the metal-support interactions and preparing high-loading MSAs.

Herein, we reported a facile strategy for the in situ synthesis of Ru single atoms (Ru SAs) through the dynamic transformation from clusters to single atoms by combining the electrospun technology and NH3-assisted graphitization process. The small Ru nanoclusters (NCs) supported on carbon nanofibers (CNFs) were in situ converted into Ru SAs in N-doped CNFs under the NH3 treatment. By controlling the NH3 treatment time and graphitization temperatures, the Ru nanocrystals exhibit a dynamic transformation from nanoclusters to single atoms. The experimental and theoretical methods were used to study the formation process and catalytic properties of N-doped CNFs supported Ru SAs (Ru SAs/CNFs). The electrocatalytic hydrogen evolution reaction (HER) was performed to understand the effect of Ru SAs on the catalytic properties. The results indicate that the Ru SAs/CNFs electrocatalyst with larger amounts of Ru SAs exhibit superior HER activity in alkaline media with a low overpotential of 34 mV at the current density of 20 mA cm−2, which is even significantly better than commercial Pt/C catalysts. The mass activity of Ru SAs/CNFs is about 390 A gRu−1 at an overpotential of 100 mV, which is ~3.5 times higher than that of commercial Pt/C (110 A gPt−1). This strategy will provide a new way for the large-scale production of MSAs transformed from different metal nanoparticles or nanoclusters.

2. Experimental section

2.1. Synthesis of Ru nanoclusters supported on electrospun carbon nanofibers (Ru NCs/CNFs)

In a typical procedure, 1 g polyvinyl alcohol (PVA) and 0.05 g ruthenium chloride (RuCl3) were dissolved in deionized water and stirred under magnetic force for 12 h to get homogenous solution. Then, the precursor solution was transferred to a 10 mL syringe with the needle diameter of 0.7 mm. The applied voltage connected to the needle tip was 15 kV and the distance from tip to collector was 15 cm. The feeding rate of the PVA solution was 0.2 mL h−1 at ambient temperature of 30 °C ± 2 °C.

The as-prepared RuCl3/PVA precursor nanofibers were firstly drying at 80 °C for 12 h to remove the residual moisture, and then, the electrospun precursor nanofibers were placed in the home-built chemical vapor deposition (CVD) system. The samples were directly heated to 800 °C at a heating rate of 5 °C min−1 under Ar atmosphere and maintained constant for 3 h. The Ru NCs/CNFs were obtained after the above graphitization. In addition, the Ru NCs/CNFs prepared at different graphitization temperatures (800, 1000 and 1200 °C) were synthesized in the same way.

2.2. Synthesis of Ru single atoms supported on electrospun N-doped carbon nanofibers (Ru SAs/CNFs)

During the graphitization process, the as-prepared samples were directly heated to the design temperatures (800, 1000, 1200 °C) with a heating rate of 5 °C min−1 under NH3/Ar atmosphere. The NH3 were introduced into the furnace at the 800, 1000 and 1200 °C and maintained constant for 0.5, 1, 2 h, respectively. The Ru SAs/CNFs with different morphologies were obtained after the above graphitization.

2.3. Materials characterization

The morphologies and crystal structures of the samples were investigated by field-emission scanning electron microscope (FE-SEM, HITACHI S-4800) at an acceleration voltage of 3 kV and transmission electron microscope (TEM, JEM-2100 plus) at an acceleration voltage of 200 kV. Spherical aberration corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) measurements were carried out with a modified FEI Temis TEM operated at an acceleration voltage of 300 kV with a HAADF detector. X-ray diffraction (XRD) patterns were acquired by a Bruker AXS D8 instrument using Cu-Kα (λ = 0.154 nm) in the scan range of 5°–90°. X-ray photoelectron spectroscopy (XPS, Kratos Axis supra) analyses were acquired with an aluminum (mono) Kα source (1486.6 eV). Raman spectra were collected with a confocal Raman microscope using 532 nm laser excitation. The atomic concentration of Ru in catalysts was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an ICAP-7400 spectrometer. The X-ray absorption fine structure (XAFS) spectra for the Ru-edge was performed in fluorescence mode on beamline 20-BM-B with electron energy of 7 GeV and an average current of 100 mA which is located in the Advanced Photon Source at Argonne National Laboratory. The radiation was monochromatized by a Si (1 1 1) double-crystal monochromator. All XAFS measurements were conducted at room temperature under ambient pressure. XANES and EXAFS data reduction and analysis were processed by Athena software.
2.4. Electrochemical measurements

All electrochemical experiments were performed on AutoLab electrochemical workstation with a standard three-electrode system at room temperature. The as-prepared self-supporting spinning membrane, a saturated calomel electrode (SCE) and a graphite rod were used as the working electrode, reference electrode and counter electrode in 1.0 M KOH, respectively. The hydrogen evolution reaction (HER) activity was evaluated by linear sweep voltammetry (LSV) with a sweep rate of 5 mV s⁻¹ and the long-term activity were evaluated by chronocoulometry measurements. Cyclic voltammetry (CV) curves were collected at different scan rates to measure the electrochemically active surface area (ECSA). Electrochemical impedance spectroscopy (EIS) was tested at open circuit voltage from 0.01 Hz to 100 kHz with an amplitude of 5 mV. All potentials were converted to reversible hydrogen electrode (RHE) by the Nernst equation (\( E_{RHE} = E_{SCE} + 0.0591pH + 0.244 \)), and all polarization curves were corrected by the iR compensation. For the calibration of reference electrodes, the new standard calomel electrode and the working calomel electrode were used as the count electrode and working electrode in saturated KCl solution to measure the potential changes before electrochemical measurement. All the reference electrodes were calibrated at each electrochemical measurement.

3. Results and discussion

Single atom electrocatalysts usually feature high activity and however, it is highly desirable for the development of facile construction and durable utilization. In this work, the Ru single atoms (Ru SAs) were in situ synthesized in the electrospun N-doped carbon nanofibers (NCNFs) via the carbon trapping and nitrogen anchoring. As shown in Scheme 1, in a typical procedure, the RuCl₃ within the PVA nano fibers were firstly prepared through the electrospinning process. After the carbonization process at 800 °C in Ar atmosphere, the RuCl₃/PVA precursor nanofibers were converted to the Ru nanoalusters/carbon nanofiber (Ru NCs/CNFs). When the as-synthesized Ru NCs/CNFs were treated by the NH₃, the substrate CNFs were in situ converted into N-doped carbon. The N-doped carbon can catch the Ru SAs from the Ru NCs due to the strong Ru-N coordination effects. In addition, controlling the NH₃ treatment time and high graphitization temperature can tailor the sizes of the Ru NCs, suggesting the dynamic transformation of Ru SAs from Ru NCs.

The morphologies and structures of the obtained Ru NCs/CNFs-800, Ru SAs/CNFs-800, Ru NPs/CNFs-1000 were investigated by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). As shown in Fig. 1a, the Ru NCs/CNFs-800 exhibits the distinct nanofiber morphology with random distribution. The average diameter of Ru NCs/CNFs-800 is about 170 ± 10 nm. The random assembled nanofibers has a unique three-dimensional (3D) networks with porous structures and high specific surface area, which is beneficial for the sufficient contact with electrolyte and desorption of hydrogen on catalyst surfaces. As shown in Fig. 1b, larger amounts of the Ru nanoclusters are densely and homogeneously in situ synthesized in the electrospun CNFs. HRTEM image in Fig. 1c and the inset indicates that the average diameter of the Ru NCs is about 1.88 ± 0.12 nm. The electrospun CNFs served as hosts and anchoring sites for the growth of Ru NCs and due to the confined effects of carbon, the Ru nanocrystals could be restricted to small nanoclusters. After the 1 h NH₃ treatment during the graphitization process, as shown in Fig. 1d, the as-prepared Ru SAs/CNFs-800 exhibit the similar 3D nanofiber assembled networks. TEM images in Fig. 1e clearly indicate the in situ synthesized Ru NCs embedded in N-doped CNFs. Due to the NH₃ treatment, the average diameter of Ru NCs in NCNFs decreases to 1.59 ± 0.10 nm, suggesting that the introduce of N into carbon matrix could lead to the small size of Ru NCs. Compared with the Ru NCs in NCNFs, the average diameter of the Ru NPs in Ru NPs/CNFs-1000 prepared at 1000 °C significantly increases to 9.94 ± 0.43 nm, demonstrating that the high graphitization temperature would result in the aggregation and growth of Ru nanocrystals (Fig. 1g–i).

Spherical aberration corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) were used to investigate the crystal structures of Ru NCs/CNFs and Ru SAs/CNFs at atomic scale. As shown in Fig. 2a, the Ru NCs with size of 1.88 nm were densely and uniformly dispersed in the PVA derived CNFs without any aggregation. AC-HAADF-HRTEM image of a single Ru NC clearly displays the lattice fringe with d spacing of 2.1 Å, corresponding to the (1 0 0) planes of the Ru phase. Ru single atoms cannot be observed in the PVA derived CNFs without N element, indicating that the carbon trapping cannot generate the single atom structures of Ru. The STEM-EDX mapping images of the Ru NCs/CNFs (Fig. 2b) clearly indicate the well distribution of carbon and ruthenium elements, confirming the formation of Ru NCs in CNFs. For the Ru SAs/CNFs prepared with 1 h NH₃ treatment at high temperature, as shown in Fig. 2c, besides the Ru NCs in NCNFs, there are tremendous Ru single atoms formed throughout the whole NCNFs. The Ru single atoms are formed around Ru nanoclusters.

In addition, the above hexagonal-like Ru NCs in CNFs become irregular and unconsolidated in NCNFs after the NH₃ treatment of Ru SAs/CNFs (Fig. 2c). It seems that the initial Ru NCs in CNFs are converted into the Ru single atoms by the NH₃ treatment. In the transformation process, the NH₃ could promote the trapping and anchoring of Ru atoms by forming the Ru–N bonds. The inset in Fig. 2c exhibits the HRTEM image of Ru NCs and shows the lattice fringe with d spacing of 2.1 Å, corresponding to the (1 0 0) planes of the Ru phase. As shown in STEM-EDX mapping image in Fig. 2d, the carbon, nitrogen and ruthenium all exist in the NCNFs, demonstrating that the nitrogen...
plays an important role in the formation of Ru single atoms.

The crystallinity and phase structures of Ru NCs/CNFs and Ru SAs/NCNFs were investigated by the powder X-ray diffraction (XRD). As shown in Fig. 3a, the XRD pattern of Ru NCs/CNFs exhibits two small peaks with 2θ at 42° and 44°, which can be ascribed to the (0 0 2) and (1 0 1) planes of Ru phase (PDF: 06-0663). The XRD pattern of the Ru SAs/NCNFs only exhibits the broad peaks for carbon but no characteristic peaks for Ru crystals. It is reported that the ultra-small Ru clusters or Ru single atoms may not show the diffraction peaks in XRD patterns [34]. X-ray photoelectron spectroscopy (XPS) was further used to investigate the chemical states and composition of Ru NCs/CNFs and Ru SAs/NCNFs (Fig. 3b, c). The Ru 3p high-resolution XPS spectrum of the Ru NCs/CNFs demonstrates two peaks with binding energies (BEs) at ~462.6 and ~484.8 eV, corresponding to the Ru 3p3/2 and Ru 3p1/2 spin–orbit peaks of metallic Ru (Ru0 3p3/2 and Ru0 3p1/2) [35]. For the Ru 3p XPS spectra of Ru SAs/NCNFs, the BEs for peaks of Ru 3p3/2 and Ru 3p1/2 shift to lower energy at ~462.1 and ~484.3 eV, suggesting the formation of Ru–N bonds. The shifts in BEs is attributed to the strong electron transfer from N to the anchored Ru SAs.

The N 1s XPS spectra of Ru NCs/CNFs do not display the chemical states of N, which is according with the STEM-EDX mapping results. The results indicate that the pure carbon may not anchor the Ru SAs. Due to the NH3 treatment, the N 1s XPS spectra of the as-prepared Ru SAs/NCNFs nanomaterials exhibit the distinct characteristic peaks with BEs at ~399.0, ~400.9, ~402.1 and ~403.4 eV, which can be ascribed to the N1 (pyridinic N), N2 (pyrrolic N), N3 (graphitic N) and N4 (oxidized N), respectively [36]. The pyridinic N would coordinate with the Ru single atoms, forming the Ru-N bonds. The results demonstrate that the Ru-N interaction is strong than the Ru-C interaction. Therefore, the nitrogen plays an essential role in the formation of Ru single atoms.

To further verify the transformation from Ru NCs to Ru SAs, the electronic and coordination structures were investigated by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies. Fig. 3d shows the normalized Ru K-edge XANES spectra of Ru NCs/CNFs and Ru SAs/NCNFs. The absorption edge of Ru NCs/CNFs is close to that of Ru foil, confirming that the Ru NCs are mainly metallic Ru nanocrystals. While the profile of Ru SAs/NCNFs is drastically different from those of Ru foil and RuO2, which shows an almost flat feature around the range of 22130–22150 eV, attributing to the co-existence of Ru nanoclusters and Ru single atoms [37].

As shown in Fig. 3e, only one prominent peak at 2.35 Å can be observed in the EXAFS spectra of Ru NCs/CNFs, corresponding to the Ru-Ru metallic bond. In contrast, the low-intensity of the Ru-Ru peak for Ru SAs/NCNFs confirms the presence of smaller and lower loading Ru nanoclusters in Ru SAs/NCNFs samples [38], which is consistent with the TEM results (Fig. 1c, f). Besides, there is another coordination peak around 1.5 Å of Ru SAs/NCNFs, which can be ascribed to the Ru–N coordination. The considerable weak of the Ru–Ru bond and significant intensity of Ru–N bond in Ru SAs/NCNFs indicate the successful transformation from clusters to single atoms.

The XAFS characterization combining with the HAADF-STEM images...
confirm that the formation of Ru SAs coordinated with N doped carbon and the Ru NCs can be converted into Ru SAs with the assistance of NH₃ in carbonization process.

The Raman spectra was further used to investigate the Ru NCs/CNFs and Ru SAs/NCNFs (Fig. S2). The D band and G band at 1350 and 1600 cm⁻¹ are ascribed to the disoriented carbon and graphitic carbon, respectively. The results suggest that the incorporation of NH₃ into the CNFs would accelerate the process of graphitization, leading to the high ratio of IG/ID. As shown in Fig. S2b, the vibrational bands around 450 cm⁻¹ could be ascribed to the Ru–C stretching [39], and the weak in the intensity indicates that the Ru cooperated with carbon is partially substituted by the Ru–N bonds, suggesting the formation of Ru single atoms.

The above results indicate that the NH₃ treatment and graphitization temperatures could influence the formation of Ru NCs and Ru SAs. We further designed a series of Ru nanocrystals synthesized in CNFs and NCNFs to investigate the influence of NH₃ treatment and graphitization temperature on the size of Ru nanocrystals. Fig. 4a–c exhibits the Ru SAs/NCNFs prepared at 800 °C with different time for NH₃ treatment. With the NH₃ treatment time increasing from 0.5 to 2 h, the size of the Ru NCs become bigger, indicating that excess NH₃ treatment would lead to the increased size of Ru nanocrystals. The high temperatures only lead to increased sizes of Ru NCs from 1.59 to 10.47 nm without seriously erosion of CNFs. The obtained Ru nanocrystals in CNFs prepared at 1000 and 1200 °C are smaller than those of the Ru nanocrystals in NCNFs prepared 1000 and 1200 °C, suggesting the substrate can restrict the growth of Ru nanocrystal. Therefore, excess NH₃ treatment time and high temperatures would destroy the anchoring sites, resulting in the increased Ru nanoparticles and vanished of Ru SAs. The XRD patterns in Fig. S4 indicates that the high temperatures would result in the strong intensity for the diffraction peaks of Ru, demonstrating increased size and better crystallinity of Ru crystals. The best conditions of NH₃ treatment time and graphitization temperatures are 1 h and 800 °C.

The electrochemical performance of the as-prepared electrocatalysts for alkaline HER were carried out by using a standard three-electrode electrochemical system in 1 M KOH electrolyte. The Ru nanocrystals/CNFs prepared at different graphitization temperatures (800, 1000 and 1200 °C) are denoted as Ru NCs/CNFs-800, Ru NCs/CNFs-1000 and Ru NPs/CNFs-1200. The Ru nanocrystals/NCNFs prepared at different times with NH₃ (0.5 h, 1 h and 2 h) at the graphitization temperatures of 800, 1000 and 1200 °C with the NH₃ treatment time of 1 h are denoted as Ru SAs/CNFs-800-0.5, Ru SAs/CNFs-800-1, Ru SAs/CNFs-800-2 and Ru SAs/NCNFs-800, Ru NPs/NCNFs-1000, Ru NPs/NCNFs-1200.

As shown in Fig. 5a, the commercial Pt/C (20 wt%) catalyst need an overpotential of 89 mV to acquire the current density of 20 mA cm⁻². The Ru NCs/CNFs-800 exhibits an overpotential of 86 mV.
which is smaller than that of the commercial Pt/C (20 wt%), suggesting the small Ru nanoclusters has a superior HER activity. For the Ru SAs/NCNFs prepared at different NH3 treatment time, the Ru SAs/NCNF-800-0.5, Ru SAs/NCNFs-800-1 and Ru SAs/NCNFs-800-2 required the overpotentials of 48, 34 and 86 mV to achieve the current density of 20 mA cm$^{-2}$. The increased size of Ru NCs and decreased content of Ru SAs result from excess NH3 treatment would cause the increased overpotentials. Note that the atomic concentration of metal Ru in Ru SAs/NCNFs-800-1 is 2.96 wt% determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Table S2). As shown in Fig. 5b, the mass activity of Ru SAs/NCNFs-800-1 is about 390 A g$^{-1}$Ru at an overpotential of 100 mV, which is ~3.5 times higher than that of commercial Pt/C (110 A g$^{-1}$Pt). The Tafel slope of Ru SAs/NCNF-800-1 is 71 mV decade$^{-1}$ around the current density of 20 mA cm$^{-2}$, which is smaller than those of Ru NCs/NCNFs-800 (132 mV decade$^{-1}$), Ru SAs/NCNFs-800-0.5 (101 mV decade$^{-1}$), Ru SAs/NCNFs-800-2 (135 mV decade$^{-1}$) and Pt/C (171 mV decade$^{-1}$). Based on the overpotential, Tafel slope and mass activity, the Ru single atoms exhibit the best HER activity in alkaline solution. Besides, The HER properties of Ru-based nanomaterials is summarized in Table S3, the Ru SAs/NCNFs obtained in this work shows competitive HER performance. Such superior HER activity indicate that the low-cost Ru SAs catalysts have a good potential for realizing the large-scale applications and replacing the Pt-based catalysts.

The electrochemically active surface area (ECSA) of Ru NCs/NCNFs-800, Ru SAs/NCNFs-800-0.5, Ru SAs/NCNFs-800-1 and Ru SAs/NCNFs-800-2 were estimated by the double-layer capacitance ($C_{dl}$) using the cyclic voltammetry (CV) technique at different scan rates. As shown in Fig. 5e, the Ru SAs/NCNFs-800-1 shows a much larger $C_{dl}$ of 3266 mF cm$^{-2}$ than those of Ru NCs/NCNFs-800 (249 mF cm$^{-2}$), Ru SAs/NCNFs-800-0.5 (606 mF cm$^{-2}$) and Ru SAs/NCNFs-800-2 (400 mF cm$^{-2}$). The results confirm that the Ru SAs possess more active sites, which is beneficial for the HER activity. Furthermore, the electrochemical impedance spectroscopy (EIS) analysis was carried out to investigate the electrocatalytic kinetics during HER. As shown in Fig. S5, the Nyquist plots of Ru SAs/NCNFs-800-1 has the smallest charge-transfer resistance ($R_{ct}$) of 0.86 Ω, demonstrating the intrinsic fast electron transfers.
Meanwhile, the electrocatalytic stability of commercial 20 wt% Pt/C and Ru SAs/NCNFs-800-1 was also investigated using chronocoulometry method at a static overpotential of 20 mV. As shown in Fig. 5f, the current density of commercial 20 wt% Pt/C decreases drastically with increased reaction time, indicating the inferior stability. Meanwhile, the Ru SAs/NCNFs-800-1 exhibits superior durability with slight deterioration after continuous HER process for 20 h. And a typical serrate shape is observed due to the accumulation and release process of H2 bubbles. As shown in the inset in Fig. S6, the overpotential of Ru SAs/NCNFs-800-1 after the 20 h stability test only exhibit a small increase of 26 mV at 20 mA cm\(^{-2}\). The morphology after long-term durability test display no observed changes in comparison with the initial catalysts (Fig. S7). In addition, the UV–vis spectrum (Fig. S8) of Ru SAs/NCNFs-800-1 electrolyte after long-term durability test shows no absorption peak with Ru, and there is no Ru\(^0\) or Ru\(^{n+}\) ions dissolved in electrolyte, suggesting the superior stability of Ru SAs protected by the NCNFs.

Moreover, to further investigate the active sites of HER in the presence of both Ru NCs and Ru SAs atoms in Ru SAs/NCNFs-800-1, the KSCN and ethylene diamine tetraacetic acid (EDTA) were used to poison the active metal centers and Ru-N/Ru-C sites. The strong binding ability with metal atoms would help to identify their contributions on the HER activity (Fig. 5g). It is obvious that with the addition of EDTA (10 mM) to the 1 M KOH electrolyte, the current density at the overpotential of 100 mV decreased from 82 to 51 mA cm\(^{-2}\) due to the formation of coordination bonds between EDTA and Ru-N/Ru-C. Besides, the current density exhibits a decrease about 62 mA cm\(^{-2}\) at 100 mV after adding KSCN, which would adsorb onto active Ru NCs centers and Ru-N/Ru-C sites. The results indicated that both Ru SAs and Ru NCs play vital roles on the HER activity.

The superior HER performance of Ru SAs/NCNFs arises from the following aspect. Firstly, the uniform dispersion and small size of Ru single atoms and Ru nanoclusters provide large amounts of active sites for HER. The poison for the Ru SAs/NCNFs by EDTA and KSCN strongly indicate that the Ru SAs significantly enhanced the HER activity (Fig. 5g). Secondly, the 3D nanoﬁbers networks with porous structures possess high speciﬁc surface area, which is beneﬁcial for the sufﬁcient contact with electrolyte and desorption of hydrogen on catalyst surfaces. And the strong interactions of Ru nanocrystals with N-doped carbon nanoﬁbers prevent its aggregation and dissolution during synthesis and long term reacting. The UV–vis spectrum (Fig. S8) of Ru SAs/NCNFs-800-1 electrolyte after long-term durability test indicate that there is no Ru\(^0\) or Ru\(^{n+}\) ions dissolved in electrolyte, suggesting the superior stability of Ru SAs protected by the NCNFs. At last, the synergistic effect of Ru nanoclusters and large amounts of Ru single atoms could promote the intrinsic activity and maximize the atom-utilization efficiency.

The HER performance of Ru nanocrystals/NCNFs and Ru NPs/CNFs prepared at different temperatures were investigated. As shown in Fig. 5h, with the temperature increasing from 800 °C to 1000 °C and 1200 °C, the Ru NPs/NCNFs-1000 and Ru NPs/NCNFs-1200 exhibit inferior HER performance than Ru SAs/NCNFs-800 due to the vanished single atoms and eroded structure of carbon nanofibers. Interestingly, Ru nanocrystals/CNFs shows the inverse result attributing to the high electric conductivity and intact carbon nanofibers (Fig. 5i). The results indicate that the protection of carbon nanofibers would promote the
HER performance by restricting Ru nanocrystals. Moreover, to further investigate the influence of NH3 treatment time calcined at high temperature, the polarization curves of Ru NPs/NCNFs-1000, Ru NPs/NCNFs-1000-0.5, Ru NPs/NCNFs-1000-1, Ru NPs/NCNFs-1000-2, and commercial 20 wt% Pt/C in 1 M KOH. (b) Polarization curves of mass activities for Ru SAs/NCNFs-800-1 and 20 wt% Pt/C. (c) The corresponding Tafel plots of the as-prepared electrocatalysts. (d) The summarized Tafel slopes and overpotentials at 20 mA cm$^{-2}$. (e) Capacitive currents at different scan rates of Ru NCs/CNFs-800, Ru SAs/NCNFs-800-0.5, Ru SAs/NCNFs-800-1, and Ru SAs/NCNFs-800-2. (f) The potentiostatic curve of commercial 20 wt% Pt/C and Ru SAs/NCNFs-800-1 at a static overpotential of 20 mV for 20 h. (g) Polarization curves of Ru SAs/NCNFs-800 electrocatalyst with the addition of 10 mM EDTA or 10 mM KSCN in 1 M KOH. (h) Polarization curves of Ru NCs/CNFs-800, Ru NPs/NCNFs-1000 and Ru NPs/NCNFs-1200. (i) Polarization curves of Ru NCs/CNFs-800, Ru NPs/NCNFs-1000 and Ru NPs/NCNFs-1200.

4. Conclusion

In summary, we reported a facile strategy to in situ synthesize the Ru single atoms through the dynamic transformation from clusters to single atoms by combining the electrospun and NH3-assisted graphitization process. The small Ru NCs supported on PVA derived CNFs were in situ converted into Ru SAs in N-doped CNFs under the NH3 treatment. By controlling the NH3 treatment time and graphitization temperatures, the Ru nanocrystals exhibit a dynamic transformation from nanoclusters to single atoms. The AC-HAADF-STEM, XPS and XAFS characterizations confirm that the formation of Ru SAs coordinated with N-doped carbon and the Ru NCs can be converted into Ru single atoms. The excessive NH3 treatment would result in the serious irregularity of NCNFs, which cause the weak metal-support interaction and lead to poor capability for protecting the Ru SAs from aggregation. The obtained Ru SAs/NCNFs-800-1 exhibits superior HER performance than commercial Pt/C in alkaline solution with the overpotential of only 34 mV at 20 mA cm$^{-2}$ and lower Tafel slope. The excellent electroactivity of Ru-SAs/NCNFs-800-1 is due to the large electrochemically active surface area, small charge-transfer resistance, synergistic effect of Ru NCs and Ru SAs, protection of carbon nanofibers and 3D networks of nanofibers. This strategy will provide a new way for the larger scale production of MSAs transformed from different metal nanoparticle or nanocluster.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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