

Short Communication

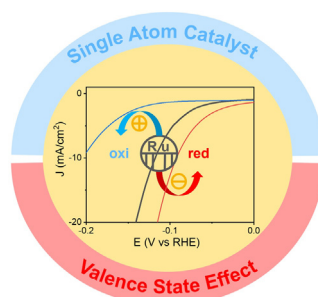
Impacts of ruthenium valence state on the electrocatalytic activity of ruthenium ion-complexed graphitic carbon nitride/reduced graphene oxide nanosheets towards hydrogen evolution reaction

Dingjie Pan^a, Qiming Liu^a, Forrest Nichols^a, Rene Mercado^a, Han-Lin Kuo^b, Jennifer Q. Lu^b, Frank Bridges^c, Shaowei Chen^{a,*}^aDepartment of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, CA 95064, USA^bSchool of Engineering, University of California, 5200 North Lake Road, Merced, CA 95343, USA^cDepartment of Physics, University of California, 1156 High Street, Santa Cruz, CA 95064, USA

HIGHLIGHTS

- Ruthenium atomically dispersed within C₃N₄/rGO nanosheets.
- Valence states manipulated by chemical reduction/oxidation.
- HER activity increases/decreases with electron-enrichment/depletion of Ru centers.
- Contribution of Ru 3d electrons to the density of states near the Fermi level.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 August 2022

Revised 12 September 2022

Accepted 14 September 2022

Available online 24 September 2022

Keywords:

Ruthenium

Carbon nitride

Graphene nanosheet

Hydrogen evolution reaction

Valence state

ABSTRACT

Design and engineering of effective electrode catalysts represents a critical first step for hydrogen production by electrochemical water splitting. Nanocomposites based on ruthenium atomically dispersed within a carbon scaffold have emerged as viable candidates. In the present study, ruthenium metal centers are atomically embedded within graphitic carbon nitride/reduced graphene oxide nanosheets by thermal refluxing. Subsequent chemical reduction/oxidation leads to ready manipulation of the ruthenium valence state, as evidenced in microscopic and spectroscopic measurements, and hence enhancement/diminishment of the electrocatalytic activity towards hydrogen evolution reaction in both acidic and alkaline media. This is largely ascribed to the increased/reduced contribution of the Ru valence electrons to the density of state near the Fermi level which dictates the binding and reduction of hydrogen. Results from this study highlight the significance of the valence state of metal centers in the manipulation and optimization of the catalytic performance of single atom catalysts.

© 2022 Elsevier Inc. All rights reserved.

1. Introduction

Hydrogen has been attracting extensive interest as a viable substitution of fossil fuels due to its remarkably high energy density

(120 MJ kg⁻¹); yet, currently the commercial production of hydrogen is mostly based on catalytic reforming of natural gas, where CO₂ emissions are inevitable during the hydrogen generation process [1,2]. Producing hydrogen via electrochemical water splitting has emerged as an efficient and sustainable solution, which entails two half-reactions, hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode, where effi-

* Corresponding author.

E-mail address: shaowei@ucsc.edu (S. Chen).

cient electrocatalysts are required to reduce the activation energy and overpotentials at both electrodes [3]. For an ideal HER catalyst, the Gibbs free energy of hydrogen adsorption (ΔG_H) should be close to 0 eV, since weak hydrogen binding to the catalyst surface would limit the adsorption rate while strong binding would impede the desorption of the final product [4]. At present, platinum with a nearly thermo-neutral ΔG_H is considered as the catalyst of choice for HER. However, the natural scarcity and high cost of platinum renders it unsustainable to produce H_2 from water splitting based on platinum catalysts [5–7]. This has fuelled substantial research efforts of the development of cost-effective alternatives [8–13]. Within this context, ruthenium has been attracting extensive interest, due largely to a ΔG_H comparable to that of Pt but at ca. 60 % of the cost [14,15]. Remarkably, when ruthenium is atomically dispersed into a N-doped carbon matrix forming $Ru_{x_1}N_{y_1}$ moieties, the resulting composites exhibit a significant HER activity, as compared to commercial Pt/C [16–18]. For instance, in a previous study [16], refluxing of $RuCl_3$ with graphitic carbon nitride ($g-C_3N_4$) nanosheets led to the formation of RuN_2 moieties whereby Ru(III) was reduced to Ru(II) and chelated to the pyridinic N of two neighboring tri-s-triazine units (Ru-N). This intimate interaction between the Ru centers and the carbon scaffold led to substantial charge redistribution around the metal centers, where the adjacent Ru, N, and C atomic sites all exhibited a markedly reduced $|\Delta G_H|$ and collectively contributed to the binding and reduction of hydrogen. Further charge transfer from the metal centers could be achieved by the incorporation of reduced graphene oxide (rGO) nanosheets forming a stacked structure with the $Ru-C_3N_4$ composites ($Ru-C_3N_4/rGO$) [17]. Indeed, recent studies based on density functional theory (DFT) calculations have shown that the formation of $g-C_3N_4/rGO$ heterostructures results in a reduced material bandgap [19–21]. Therefore, the strong electronic interactions among Ru, $g-C_3N_4$, and rGO improved the electrical conductivity and charge carrier density, and lowered the charge-transfer resistance, leading to additional enhancement of the HER performance [17]. This suggests that the valence state of the metal centers plays a critical role in dictating the HER activity.

Notably, the valence state of such single atom catalysts (SACs) has been recognized to exert a great impact on the electrocatalytic activity, since the adsorbate binding would be weakened with a decreasing density of valence-filling electrons [22–24]. This has been manifested in the manipulation of electrocatalytic activity towards a range of important reactions, such as HER, OER, and ORR (oxygen reduction reaction) [22,25–31]. For instant, Nichols et al. [28] embedded platinum centers into $g-C_3N_4$ nanosheets by refluxing with two different precursors ($PtCl_2$ and $PtCl_4$), and observed that the HER activity increased with increasing Pt^{4+} concentration, with a low overpotential (η_{10}) of only -7.7 mV to reach the current density of 10 mA cm^{-2} for the optimized sample. In another study [29], the valence state of the doping elements (Ir, Pt, and Ru) was found to impact the electrocatalytic activity of nickel-iron layer double hydroxide (NiFe-LDH). Specifically, compared to tetravalent iridium (Ir^{4+}), trivalent iridium ions (Ir^{3+}) showed a higher HER and OER activity, because the neighboring O atoms were electron-rich with the lower-valence Ir^{3+} ion, which facilitated water dissociation and hydrogen desorption. A similar effect was also found with Ru and Pt ions, where Pt^{2+} and Ru^{3+} doped NiFe-LDH exhibited a better catalyst performance than that with Pt^{4+} and Ru^{4+} . In another study [30], an enhanced HER performance was observed with high valence state Mo (i.e., Mo^{4+} , Mo^{5+} , and Mo^{6+}) in molybdenum carbide (Mo_xC), where oxidation of Mo_xC nanoparticles by controlled air treatment led to improved HER activity in both acidic ($\eta_{10} = -130$ mV) and alkaline media ($\eta_{10} = -116$ mV). For Fe,N-codoped carbon composites [31], markedly better ORR and OER catalytic activities were observed at the Fe^{2+}/Fe^{3+} ratio of 1.15 than at 1.5 and 0.92. Mechanistically, this

was accounted for by the synergistic interactions between the metal centers, where Fe^{2+} facilitated oxygen adsorption and Fe^{3+} was beneficial to the conduction of valence electrons of oxygen ions.

In this study, the ruthenium valence state of $Ru-C_3N_4/rGO$ composites was manipulated by chemical reduction/oxidation, as manifested in X-ray spectroscopic measurements. The reduced sample was found to exhibit an enhanced HER activity in both acidic and alkaline media, whereas the performance diminished with the oxidized sample, as compared to the as-prepared composite. This was ascribed to the enhanced/diminished contribution of the Ru valence electrons for the reduced/oxidized nanocomposites to the density of state (DOS) near the Fermi level, which played a critical role in determining the energetics of hydrogen adsorption.

2. Experiment section

2.1. Chemicals

Melamine (99 %, Acros), ruthenium(III) chloride hydrate ($RuCl_3 \cdot xH_2O$, 35–40 % Ru, Acros), graphite flakes (Fisher Chemicals), sulfuric acid (H_2SO_4 , 98 %, Fisher Chemicals), potassium hydroxide (KOH, 99 %, Acros), sodium nitrate ($NaNO_3$, 99 %, Acros), potassium permanganate ($KMnO_4$, 99 %, Fisher Chemicals), sodium borohydride ($NaBH_4$, 99 %, Acros), and ascorbic acid (99 %, Fisher Chemicals) were used as received without further purification. Deionized water was supplied with a Barnstead Nanopure Waster System ($18.2 \text{ M}\Omega \text{ cm}$).

2.2. Sample preparation

The synthesis of $Ru-C_3N_4/rGO$ nanocomposites was detailed previously [17]. In brief, 10 g of melamine was heated in a muffle oven at 600°C for 3 h in a covered crucible. The obtained $g-C_3N_4$ sample was then ground to a fine powder.

The modified Hummers method was used in the synthesis of graphene oxide (GO) nanosheets. Experimentally, 2 g of graphite and 1 g of $NaNO_3$ were ground and transferred to a 1000 mL round-bottom flask in an ice bath. 46 mL of concentrated H_2SO_4 and 6 g of $KMnO_4$ were added slowly into the flask under magnetic stirring for 3 h. The flask was then heated at 35°C in an oil bath under stirring with the addition of 92 mL of H_2O , and further heated at 95°C for 30 min. After the solution was cooled down to ambient temperature, 150 mL of H_2O and 20 mL of H_2O_2 were added slowly into the flask, followed by 50 mL of concentrated HCl and 300 mL of H_2O before centrifugation. The supernatant was collected and neutralized with $NaHCO_3$ to $pH \approx 7$ before being dialyzed for 7 d (with a daily change of water) and finally freeze-dried.

To prepare $g-C_3N_4/rGO$ composites, 100 mg of the $g-C_3N_4$ powders prepared above was dispersed into 100 mL of Nanopure water under sonication in a round-bottom flask for 1 h, into which was then added 100 mg of the above-obtained GO nanosheets. After sonication for 1 h, 352 mg of ascorbic acid was added into the solution, which was refluxed in an oil bath at 100°C for 2 h. The resultant $g-C_3N_4/rGO$ composites were collected by centrifugation for 10 min and dried overnight.

To incorporate Ru centers into $g-C_3N_4/rGO$, the $g-C_3N_4/rGO$ hybrids prepared above were dispersed in 100 mL of Nanopure water under sonication for 1 h, into which was then added 56 mg of $RuCl_3$. The mixture was refluxed at 100°C in an oil bath for 2 h. The $Ru-C_3N_4/rGO$ composites were collected by centrifugation for 10 min and rinsed with H_2O and ethanol two times.

The valence state of Ru in the $Ru-C_3N_4/rGO$ composites was further manipulated by chemical reduction/oxidation. In the reduc-

tion process, 20 mg of Ru-C₃N₄/rGO was dispersed into 4 mL of H₂O, into which was added freshly prepared 1 mL of a NaBH₄ solution (3 mg mL⁻¹). The mixture was under magnetic stirring for 30 min before the solid was collected by centrifugation and dried overnight. The resulting sample was denoted as Ru-C₃N₄/rGO_{red}. The oxidation treatment was carried out in a similar fashion except that 1 mL of a KMnO₄ solution (8.8 mg mL⁻¹) was used instead, and the resulting sample was referred to as Ru-C₃N₄/rGO_{ox}.

2.3. Characterization

Transmission electron microscopy (TEM) measurements were carried out with an FEI Tecnai G2 200 kV TEM. Elemental mapping analyses based on energy-dispersive X-ray spectroscopy (EDS) were carried out with a Talos F200C G2 TEM. Scanning electron microscopic (SEM) studies, along with element mapping analysis, were conducted with a Thermo Fisher Scientific Apreo S LoVac electron microscope. X-ray photoelectron spectroscopic (XPS) studies were performed with a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer. X-ray diffraction (XRD) patterns were acquired with a Rigaku Smartlab Diffractometer. X-ray absorption spectroscopy (XAS) measurements were carried out at 10 K at beamline 4-1 of the Stanford Synchrotron Radiation Light source using an Oxford liquid helium cryostat.

2.4. Electrochemistry

Electrochemical measurements were carried out with a CHI 710 electrochemical workstation, while electrochemical impedance spectroscopy (EIS) and Mott-Schottky tests were conducted with a Gamry Reference 600 instrument. A glassy carbon rotating disk electrode (RDE, surface area 0.196 cm²) and a graphite rod were used as the working electrode and counter electrode, respectively. The Ag/AgCl reference electrode (in 3 M KCl) was calibrated against a reversible hydrogen electrode (RHE), and all potentials in the present study were referenced to this RHE. To prepare catalyst inks, 2 mg of the nanocomposite catalysts obtained above and 3 mg of Vulcan XC72 carbon black were dispersed in a mixture of H₂O (200 μ L), ethanol (790 μ L) and Nafion (10 μ L). After sonication for 30 min, 15 μ L of the ink was dropcast evenly onto the RDE surface. The electrode was dried at ambient temperature before being immersed into an electrolyte solution for electrochemical measurements. All measurements were repeated at least 2 times and the deviations were typically under 5 %.

3. Results and discussion

Experimentally, g-C₃N₄ nanosheets were derived thermally from melamine, and GO from chemical exfoliation of graphite flakes. The stacked structure of g-C₃N₄/rGO hybrids was then prepared by refluxing the g-C₃N₄ and GO mixture in the presence of ascorbic acid [32,33]. A second thermal refluxing with RuCl₃ led to the incorporation of ruthenium centers via chelation to the pyridinic nitrogen of the tri-s-triazine units of the g-C₃N₄/rGO scaffold, forming Ru-C₃N₄/rGO nanocomposites [16,17]. The valence state of the Ru centers was further manipulated by NaBH₄ reduction or KMnO₄ oxidation, producing Ru-C₃N₄/rGO_{red} and Ru-C₃N₄/rGO_{ox}, respectively.

The sample structures were first characterized by TEM measurements. From Fig. 1a, the as-prepared Ru-C₃N₄/rGO sample can be seen to exhibit a flaky nanosheet morphology [17]. In high-resolution TEM measurements (Fig. 1b), one can see that the sample consisted of arrays of nanocrystalline domains (ca. 2 nm) with a slightly darker contrast against a largely amorphous (light grey) background, and exhibited well-defined lattice fringes

with an interplanar distance of 0.237 nm that can be ascribed to the (110) crystalline planes of g-C₃N₄ [34], indicative of successful stacking of C₃N₄ onto rGO nanosheets, mostly due to π - π interactions between the two-dimensional nanosheets [17]. No obvious lattice fringes can be assigned to either metallic Ru or RuO₂, suggesting atomically dispersed Ru within the C₃N₄/rGO scaffold (further confirmation by XPS and XAS measurements, vide infra). Consistent results were obtained from EDS-based elemental mapping analysis. From Fig. 1c, the element of Ru can be readily identified, yet only discretely within the sample matrix, consistent with the atomic dispersion of ruthenium within the carbon matrix [17]. Notably, no apparent variation of the sample structure and elemental distributions was observed after chemical reduction or oxidation (Figure S1 and S2). Similar results were obtained from SEM and EDS measurements. From Figure S3-S5, one can see a rather consistent distribution pattern for C, N, and O, although it was apparently different from that of Ru, in agreement with the stacking interaction between g-C₃N₄ and rGO nanosheets (and the absence of RuO₂).

The corresponding XRD patterns are shown in Figure S6. The main diffraction peak at $2\theta = 27.5^\circ$ can be ascribed to the combined contributions of C₃N₄ (002) and rGO (002) facets [16,35–38]. It should be noted that no peaks can be resolved for metallic Ru or RuO_x nanoparticles, consistent with the atomic dispersion of Ru in the sample [17].

The chemical composition and valence states of the composites were determined by XPS measurements. From the survey spectra in Figure S7a, the C 1 s/Ru 3d, N 1 s, Ru 3p, and O 1 s electrons can be readily identified at ca. 284, 400, 475, and 532 eV for the sample series. On the basis of the integrated peak areas, the elemental contents of Ru-C₃N₄/rGO were estimated to be 69.48 at.% for C, 13.21 at.% for N, 15.10 at.% for O, and 2.22 at.% for Ru [17]. The high-resolution scans of the Ru 3p electrons are shown in Fig. 2a (the right panel is the zoom in of the Ru 3p_{3/2} peaks). Deconvolution yields two doublets for all three samples (Table S1). For Ru-C₃N₄/rGO, the doublet at 463.30/485.50 eV can be assigned to the 3p_{3/2}/3p_{1/2} electrons of Ru(II), and the other at 465.81/488.01 eV to Ru(III). The binding energies diminished slightly for the Ru-C₃N₄/rGO_{red}, Ru(II) at 462.98/485.24 eV and Ru(III) at 465.14/487.30 eV, whereas a small increase was observed with Ru-C₃N₄/rGO_{ox}, Ru(II) at 463.52/485.65 eV and Ru(III) at 465.93/487.83 eV [16,17]. This suggests effective electron-enrichment/depletion of the Ru centers by postsynthesis chemical reduction/oxidation. In addition, the fact that no metallic Ru was detected in the samples was consistent with atomic dispersion of Ru into the carbon scaffold, as suggested in the above TEM and XRD measurements.

The corresponding C 1 s and Ru 3d spectra are shown in Figure S7b, where a rather appreciable change of the Ru 3d_{5/2} binding energy can also be observed, Ru-C₃N₄/rGO_{red} (281.73 eV) < Ru-C₃N₄/rGO (281.85 eV) < Ru-C₃N₄/rGO_{ox} (282.09 eV), in good agreement with the trend of the Ru 3p electrons. In addition, the N-C=N and C=C peaks can be identified at ca. 288.0 and 284.5 eV, respectively [16,17], and remained virtually unchanged after chemical reduction/oxidation, suggesting minimal impacts on the carbon scaffold. Similar behaviors were observed in the relevant N 1 s and O 1 s spectra (Figure S7c-d and Table S1). The fact that no peak below 530 eV can be resolved in the O 1 s spectra suggests the absence of Ru-O species in the samples, and Ru was most likely chelated to N (and C), in good agreement with results from XAS measurements, as shown below.

Further structural insights were obtained from XAS measurements. From the Ru K-edge X-ray absorption near-edge structure (XANES) spectra in Fig. 2b, one can see that the absorption edges of the samples all lie in the intermediate between those of Ru foil and RuO₂, suggesting a valence state between 0 and + 4, which is

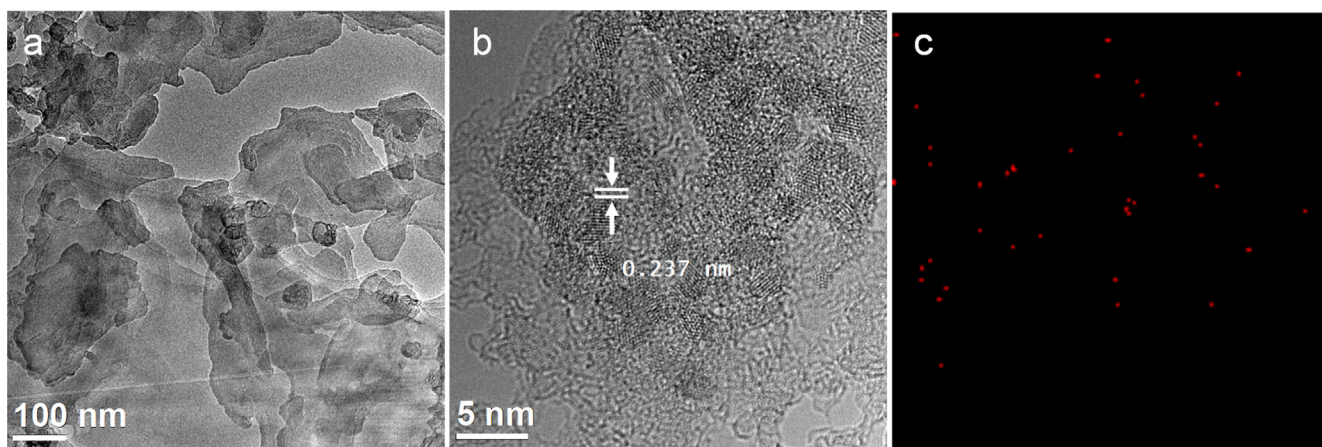


Fig. 1. (a,b) TEM images of Ru-C₃N₄/rGO at different magnifications. Scale bars are (a) 100 nm and (b) 5 nm. (c) The corresponding elemental map of Ru.

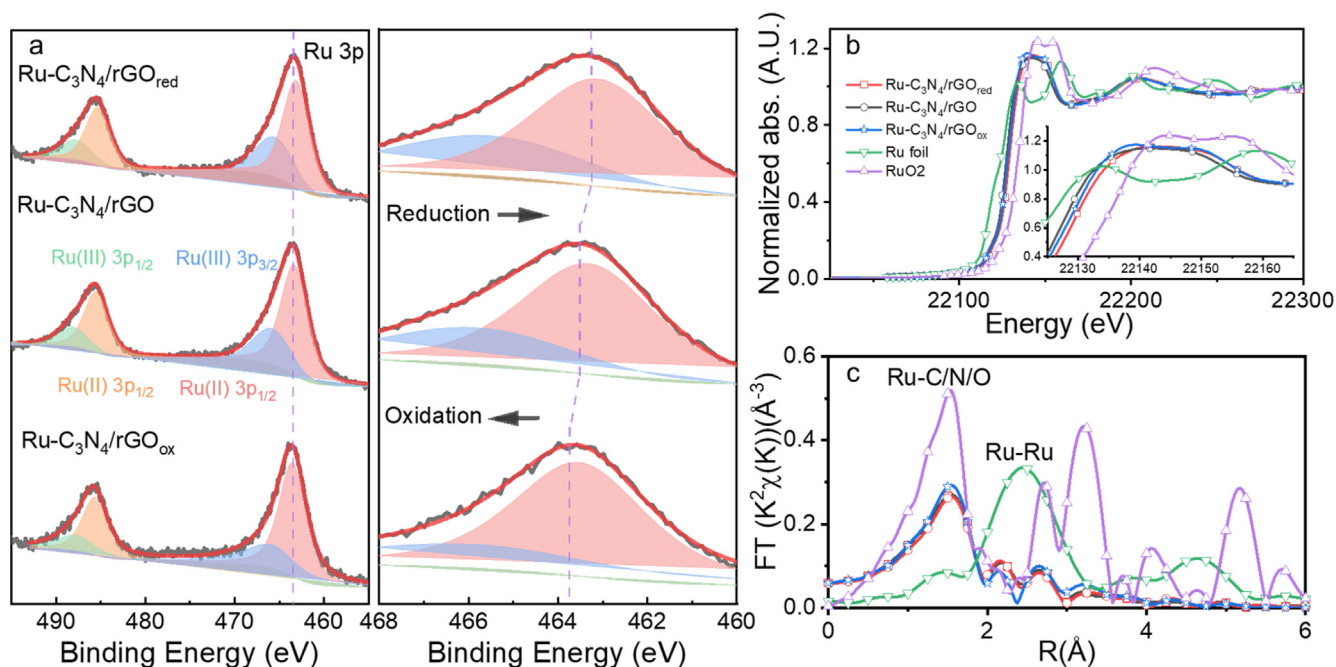


Fig. 2. (a) (left panel) XPS spectra of Ru 3p electrons of Ru-C₃N₄/rGO_{red}, Ru-C₃N₄/rGO, and Ru-C₃N₄/rGO_{ox}, with the sp_{3/2} peaks magnified in the right panel to highlight the shift of the binding energy. (b) Normalized Ru K-edge XANES spectra of Ru-C₃N₄/rGO_{red}, Ru-C₃N₄/rGO, Ru-C₃N₄/rGO_{ox}, and the standard Ru foil and RuO₂. Inset is the zoom in of the area near the absorption edge. (c) Ru K-edge R-space EXAFS data for the corresponding samples within the Fourier transformation range of 3.5 to 11 Å⁻¹.

consistent with the atomic dispersion of Ru(II)/Ru(III) centers within the carbon skeleton. In addition, from the inset to Fig. 2b, one can see that the absorption edge energy varied in the order of Ru-C₃N₄/rGO_{red} ≈ Ru-C₃N₄/rGO < Ru-C₃N₄/rGO_{ox}, in agreement with results from the XPS measurements where chemical reduction/oxidation led to electron-enrichment/depletion of the Ru centers.

Notably, the extended X-ray absorption fine structures (EXAFS) of the composite samples also exhibited a clear deviation from those of Ru foil and RuO₂, further confirming the absence of metal Ru and RuO₂ nanoparticles in the samples; and the almost identical oscillation patterns suggest a consistent atomic configuration that was retained during chemical reduction/oxidation.

The corresponding R-space EXAFS data are depicted in Fig. 2c (the k-space plot is shown in Figure S8), where the nanocomposites of Ru-C₃N₄/rGO_{red}, Ru-C₃N₄/rGO and Ru-C₃N₄/rGO_{ox} all exhibited only a major peak at 1.5 Å, which is characteristic of the Ru-C/

N/O bonds [18]. However, as no Ru-O linkage was identified in XPS measurements (Figure S7 and Table S1), the Ru centers were embedded within the carbon scaffold most likely via the Ru-C/N bonds only. Note that this peak (1.5 Å) is very prominent with the RuO₂ reference, which also included a series of additional peaks above 2.5 Å for the Ru-Ru paths. The fact that the latter can not be found in the nanocomposites suggests the absence of RuO₂ nanoparticles in the samples. In addition, the Ru foil exhibited a major peak at 2.3 Å for the Ru-Ru bond, which is also absent in the nanocomposites. Taken together, these observations are in excellent agreement with results from TEM, XPS, and XRD measurements that no Ru or RuO_x nanoparticles were produced in the nanocomposites and ruthenium was atomically dispersed into the matrix forming RuC_xN_y moieties. Furthermore, the Ru-C/N configuration was determined by fitting of the EXAFS data (Fig. 2c and S8), which featured an almost identical bond length and coordination number among the three samples, 2.03 Å and 5.56 for Ru-

$\text{C}_3\text{N}_4/\text{rGO}_{\text{red}}$, 2.03 Å and 5.00 for $\text{Ru-C}_3\text{N}_4/\text{rGO}$, and 2.02 Å and 6.31 for $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{ox}}$ (Table S2) [39–41]. That is, the coordination environment of the Ru centers remained largely invariant before and after chemical reduction/oxidation of the samples.

The HER performance of the sample series was then examined and compared in 0.5 M H_2SO_4 . From the polarization curves in Fig. 3a, one can see that in comparison to the as-prepared $\text{Ru-C}_3\text{N}_4/\text{rGO}$, chemical reduction (oxidation) drastically enhanced (diminished) the HER activity, as manifested by the significant variation of the corresponding η_{10} , in the order of $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{ox}}$ (−205 mV) < $\text{Ru-C}_3\text{N}_4/\text{rGO}$ (−130 mV) < $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{red}}$ (−93 mV). The Tafel plots are depicted in Fig. 3b, where the Tafel slope varied in the order of $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{ox}}$ (99.08 mV dec^{−1}) > $\text{Ru-C}_3\text{N}_4/\text{rGO}$ (75.78 mV dec^{−1}) ≥ $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{red}}$ (75.64 mV dec^{−1}), suggesting enhanced (impeded) electron-transfer kinetics by chemical reduction (oxidation), although the performance remained subpar as compared to commercial Pt/C, which featured an η_{10} of −34 mV and a Tafel slope of 17.35 mV dec^{−1}. This is also confirmed in electrochemical impedance spectroscopy measurements. From the Nyquist plots acquired at −100 mV (Fig. 3c), the charge-transfer resistance (R_{ct} , Table S3) can be found to decrease markedly in the order of $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{ox}}$ (678 Ω) > $\text{Ru-C}_3\text{N}_4/\text{rGO}$ (39 Ω) > $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{red}}$ (18 Ω). Notably, similar results were obtained in 1 M KOH, in terms of η_{10} , Tafel slope and R_{ct} (Figure S9 and Table S3).

Mechanistically, results from first principles calculations [16] have shown that the incorporation of Ru centers within g- C_3N_4 led to an apparent redistribution of electrons within the composite, and hence an enhanced density of states (DOS) at the Fermi level, which dictates the adsorption and reduction of hydrogen, as compared to the pristine g- C_3N_4 , with the Ru 4d and 5 s orbitals being

the major contributors. This will be strengthened (weakened) when the ruthenium centers are chemically reduced (oxidized), as manifested in the change of valence state by XPS measurements, electrical conductivity by electrochemical impedance measurements, and HER activity in both acidic and alkaline media by electrochemical measurements.

Remarkably, the $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{red}}$ sample also exhibited excellent stability. From the chronoamperometric tests conducted at −125 mV in Fig. 3d, one can see that the voltametric currents were highly reproducible for up to 9 h when the hydrogen bubbles were removed every 3 h from the RDE surface.

4. Conclusions

In summary, $\text{Ru-C}_3\text{N}_4/\text{rGO}$ ternary nanocomposites were prepared by a facile wet-chemistry procedure. Chemical reduction/oxidation led to a ready variation of the valence state of the ruthenium metal centers, whereas the carbon scaffolds remained largely intact, as manifested in microscopic and spectroscopic measurements. Remarkably, the HER performances in both acidic and alkaline media were found to enhance (diminish) drastically after chemical reduction (oxidation), in comparison to the as-produced sample. The correlation of electron-enriched (-deficient) Ru centers with markedly enhanced (diminished) HER activity suggested an increased (reduced) contribution of Ru valence electrons to the DOS near the Fermi level that dictated the energetics of hydrogen adsorption. Results from this study may be exploited as a unique strategy for the deliberate structural

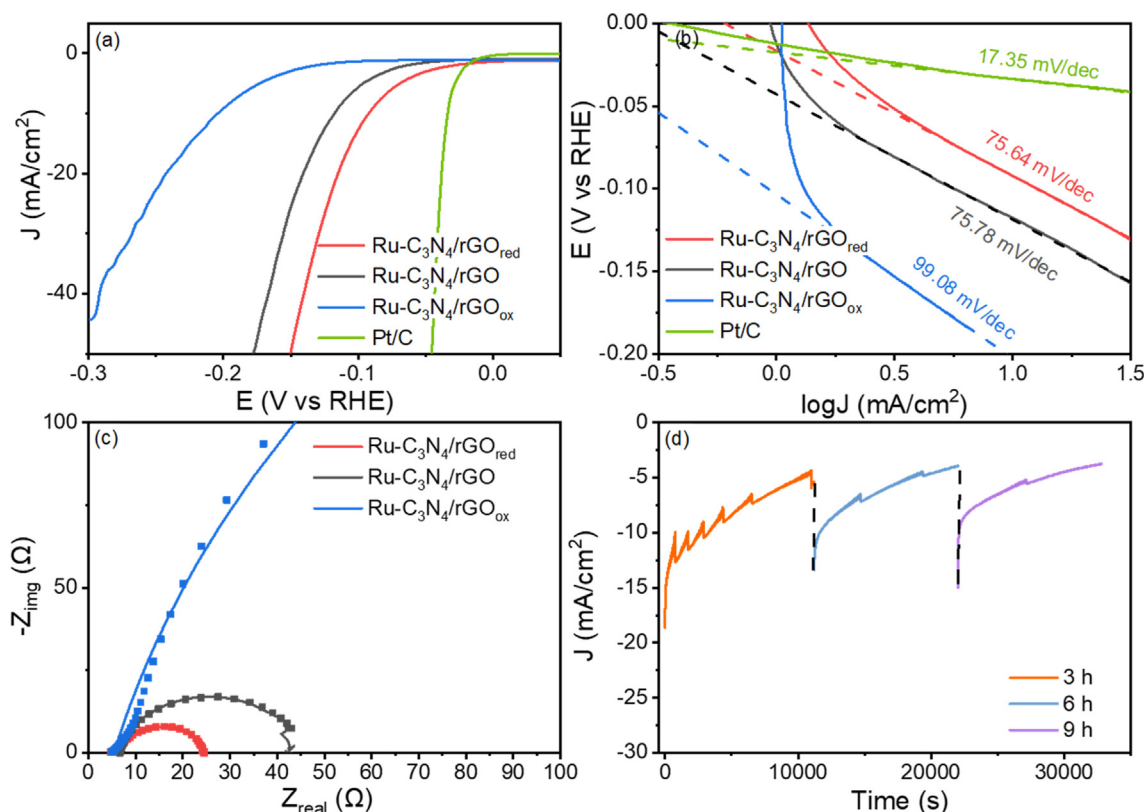


Fig. 3. (a) HER polarization curves of $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{red}}$, $\text{Ru-C}_3\text{N}_4/\text{rGO}$, $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{ox}}$ and commercial Pt/C in 0.5 M H_2SO_4 , and (b) the Corresponding Tafel plots. (c) Nyquist plots of the samples without carbon black at −100 mV in 0.5 M H_2SO_4 . Inset is the equivalent circuit where R_s is the serial resistance, CPE is the constant phase element and R_{ct} is the charge-transfer resistance. (d) Chronoamperometric measurements of $\text{Ru-C}_3\text{N}_4/\text{rGO}_{\text{red}}$ applying −125 mV in 0.5 M H_2SO_4 for 9 h, where hydrogen bubbles are removed from the RDE surface every 3 h.

engineering of single atom catalysts and ultimate optimization of their electrocatalytic activity [23].

CRedit authorship contribution statement

Dingjie Pan: Data curation, Formal analysis, Methodology, Writing – original draft. **Qiming Liu:** Data curation, Formal analysis. **Forrest Nichols:** Data curation. **Rene Mercado:** Data curation. **Han-Lin Kuo:** Data curation. **Jennifer Q. Lu:** Data curation. **Frank Bridges:** Data curation, Formal analysis, Funding acquisition. **Shaowei Chen:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Project administration, Funding acquisition, Writing – review & editing.

Data availability

Data will be made available on request.

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.

Acknowledgments

This work was supported by grants from the National Science Foundation (CHE-1900235 and CHE-2003685) and NASA (NNH18ZHA008CMIROG6R). TEM and XPS work was carried out as part of a user project at the National Center for Electron Microscopy and Molecular Foundry, Lawrence Berkeley National Laboratory, which was supported by the US Department of Energy under contract No. DE-AC02-05CH11231. The XAS experiments were performed at the Stanford Synchrotron Radiation Lightsource (SSRL), which is also supported by the US Department of Energy under contract No. DE-AC02-76SF00515. We thank Mr. J. Barnett for the assistance in XRD sample preparation and data acquisition and the X-ray Facility at University of California Santa Cruz for use of the Rigaku Smartlab Diffractometer, funded by the National Science Foundation (MRI-1126845).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2022.09.080>.

References

- [1] F. Dawood, M. Anda, G.M. Shafiuallah, Hydrogen production for energy: An overview, *Int J Hydrog Energy* 45 (7) (2020) 3847–3869.
- [2] J. Yu, Q. He, G. Yang, W. Zhou, Z. Shao, M. Ni, Recent Advances and Prospective in Ruthenium-Based Materials for Electrochemical Water Splitting, *ACS Catal* 9 (11) (2019) 9973–10011.
- [3] B. Xiong, L. Chen, J. Shi, Anion-containing noble-metal-free bifunctional electrocatalysts for overall water splitting, *ACS Catal* 8 (4) (2018) 3688–3707.
- [4] Z.W. Seh, J. Kibsgaard, C.F. Dickens, I.b. Chorkendorff, J.K. Nørskov, T.F. Jaramillo, Combining theory and experiment in electrocatalysis: Insights into materials design, *Science* 355 (6321) (2017).
- [5] P. Du, R. Eisenberg, Catalysts made of earth-abundant elements (Co, Ni, Fe) for water splitting: Recent progress and future challenges, *Energy, Environ Sci* 5 (2012) 6012–6021.
- [6] C.C.L. McCrory, S. Jung, I.M. Ferrer, S.M. Chatman, J.C. Peters, T.F. Jaramillo, Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices, *J Am Chem Soc* 137 (13) (2015) 4347–4357.
- [7] S.J.A. Moniz, S.A. Shevlin, D.J. Martin, Z.-X. Guo, J. Tang, Visible-light driven heterojunction photocatalysts for water splitting—a critical review, *Energy, Environ Sci* 8 (3) (2015) 731–759.
- [8] H.I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J.R. Long, C.J. Chang, A molecular MoS₂ edge site mimic for catalytic hydrogen generation, *Science* 335 (6069) (2012) 698–702.
- [9] J. Kibsgaard, Z. Chen, B.N. Reinecke, T.F. Jaramillo, Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis, *Nat Mater* 11 (2012) 963–969.
- [10] B. Cao, G.M. Veith, J.C. Neufeld, R.R. Adzic, P.G. Khalifah, Mixed close-packed cobalt molybdenum nitrides as non-noble metal electrocatalysts for the hydrogen evolution reaction, *J Am Chem Soc* 135 (51) (2013) 19186–19192.
- [11] X. Hu, B.S. Brunschwig, J.C. Peters, Electrocatalytic hydrogen evolution at low overpotentials by cobalt macrocyclic glyoxime and tetraimine complexes, *J Am Chem Soc* 129 (29) (2007) 8988–8998.
- [12] P.-A. Jacques, V. Artero, J. Pécaut, M. Fontecave, Cobalt and nickel diimine-dioxime complexes as molecular electrocatalysts for hydrogen evolution with low overvoltages, *Proc Natl Acad Sci* 106 (49) (2009) 20627–20632.
- [13] S.W. Kohl, L. Weiner, L. Schwartzburd, L. Konstantinovski, L.J.W. Shimon, Y. Ben-David, M.A. Iron, D. Milstein, Consecutive thermal H₂ and light-induced O₂ evolution from water promoted by a metal complex, *Science* 324 (5923) (2009) 74–77.
- [14] N. Wang, S.L. Ning, X.L. Yu, D. Chen, Z.L. Li, J.C. Xu, H. Meng, D.K. Zhao, L.G. Li, Q. M. Liu, B.Z. Lu, S.W. Chen, Graphene composites with Ru-RuO₂ heterostructures: Highly efficient Mott-Schottky-type electrocatalysts for pH-universal water splitting and flexible zinc-air batteries, *Appl Catal B-Environ*, 302 (2022) 120838.
- [15] Q. Liu, B. Lu, F. Nichols, J. Ko, R. Mercado, F. Bridges, S. Chen, Rapid preparation of carbon-supported ruthenium nanoparticles by magnetic induction heating for efficient hydrogen evolution reaction in both acidic and alkaline media, *SusMat* 2 (3) (2022) 335–346.
- [16] Y.i. Peng, B. Lu, L. Chen, N. Wang, J.E. Lu, Y. Ping, S. Chen, Hydrogen evolution reaction catalyzed by ruthenium ion-complexed graphitic carbon nitride nanosheets, *J Mater Chem A* 5 (34) (2017) 18261–18269.
- [17] Y.i. Peng, W. Pan, N. Wang, J.-E. Lu, S. Chen, Ruthenium Ion-Complexed Graphitic Carbon Nitride Nanosheets Supported on Reduced Graphene Oxide as High-Performance Catalysts for Electrochemical Hydrogen Evolution, *ChemSuschem* 11 (1) (2018) 130–136.
- [18] B.Z. Lu, L. Guo, F. Wu, Y. Peng, J.E. Lu, T.J. Smart, N. Wang, Y.Z. Finck, D. Morris, P. Zhang, N. Li, P. Gao, Y. Ping, S.W. Chen, Ruthenium atomically dispersed in carbon outperforms platinum toward hydrogen evolution in alkaline media, *Nat Commun* 10 (2019) 631.
- [19] M. Yan, Q. Jiang, L. Yang, H. He, H. Huang, Three-Dimensional Ternary Hybrid Architectures Constructed from Graphene, MoS₂, and Graphitic Carbon Nitride Nanosheets as Efficient Electrocatalysts for Hydrogen Evolution, *ACS Appl Energy Mater* 3 (7) (2020) 6880–6888.
- [20] H. He, Y. Chen, C. Yang, L. Yang, Q. Jiang, H. Huang, Constructing 3D interweaved MXene/graphitic carbon nitride nanosheets/graphene nanoarchitectures for promoted electrocatalytic hydrogen evolution, *J Energy Chem* 67 (2022) 483–491.
- [21] H. Huang, M. Yan, C. Yang, H. He, Q. Jiang, L. Yang, Z. Lu, Z. Sun, X. Xu, Y. Bando, Y. Yamauchi, Graphene Nanoarchitectonics: Recent Advances in Graphene-Based Electrocatalysts for Hydrogen Evolution Reaction, *Adv Mater* 31 (2019) 1903415.
- [22] S. Kim, C. Choi, J. Hwang, J. Park, J. Jeong, H. Jun, S. Lee, S.-K. Kim, J.H. Jang, Y. Jung, Interaction mediator assisted synthesis of mesoporous molybdenum carbide: Mo-valence state adjustment for optimizing hydrogen evolution, *ACS nano* 14 (2020) 4988–4999.
- [23] B.Z. Lu, Q.M. Liu, S.W. Chen, Electrocatalysis of Single-Atom Sites: Impacts of Atomic Coordination, *ACS Catal* 10 (2020) 7584–7618.
- [24] Y.X. Wang, H.Y. Su, Y.H. He, L.G. Li, S.Q. Zhu, H. Shen, P.F. Xie, X.B. Fu, G.Y. Zhou, C. Feng, D.K. Zhao, F. Xiao, X.J. Zhu, Y.C. Zeng, M.H. Shao, S.W. Chen, G. Wu, J. Zeng, C. Wang, Advanced Electrocatalysts with Single-Metal-Atom Active Sites, *Chem Rev* 120 (2020) 12217–12314.
- [25] Y. Tian, L. Cao, P. Qin, Bimetal–Organic Framework Derived High-Valence-State Cu-Doped Co₃O₄ Porous Nanosheet Arrays for Efficient Oxygen Evolution and Water Splitting, *ChemCatChem* 11 (2019) 4420–4426.
- [26] P. Guo, Z. Wang, T. Zhang, C. Chen, Y. Chen, H. Liu, M. Hua, S. Wei, X. Lu, Initiating an efficient electrocatalyst for water splitting via valence configuration of cobalt-iron oxide, *Appl Catal B: Environ* 258 (2019) 117968.
- [27] Q. Liu, H. Wang, X. Wang, R. Tong, X. Zhou, X. Peng, H. Wang, H. Tao, Z. Zhang, Bifunctional Ni_{1-x}Fe_x layered double hydroxides/Ni foam electrodes for high-efficient overall water splitting: A study on compositional tuning and valence state evolution, *Int J Hydrog Energy* 42 (2017) 5560–5568.
- [28] F. Nichols, J.E. Lu, R. Mercado, R. Dudschus, F. Bridges, S.W. Chen, Platinum Oxide Nanoparticles for Electrochemical Hydrogen Evolution: Influence of Platinum Valence State, *Chem-Eur J* 26 (2020) 4136–4142.
- [29] M. Wang, J.Q. Wang, C. Xi, C.Q. Cheng, C.G. Kuai, X.L. Zheng, R. Zhang, Y.M. Xie, C.K. Dong, Y.J. Chen, Valence-State Effect of Iridium Dopant in NiFe (OH)₂ Catalyst for Hydrogen Evolution Reaction, *Small* 17 (2021) 2100203.
- [30] P. Wang, J. Qi, X. Chen, C. Li, T. Wang, C. Liang, New insights into high-valence state Mo in molybdenum carbide nanobelts for hydrogen evolution reaction, *Int J Hydrog Energy* 42 (2017) 10880–10890.
- [31] X.-T. Wu, L.-J. Peng, K. Xiao, N. Li, Z.-Q. Liu, Rational design and synthesis of hollow Fe–N/C electrocatalysts for enhanced oxygen reduction reaction, *Chem Commun* 57 (2021) 5258–5261.
- [32] Y. Zhao, F. Zhao, X. Wang, C. Xu, Z. Zhang, G. Shi, L. Qu, Graphitic carbon nitride nanoribbons: graphene-assisted formation and synergic function for highly efficient hydrogen evolution, *Angew Chem Int Ed* 53 (2014) 13934–13939.
- [33] Y. Zheng, Y. Jiao, Y. Zhu, L.H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S.Z. Qiao, Hydrogen evolution by a metal-free electrocatalyst, *Nat Commun* 5 (2014) 3783.

- [34] F. Zhen-Yi, L. Yu-Xian, Effective Route to Graphitic carbon Nitride from Ball-Milled Amorphous carbon in NH₃ Atmosphere Under Annealing, *Chin Phys Lett* 20 (2003) 1554–1557.
- [35] I. Boukhoubza, M. Khenfouch, M. Achehboune, B.M. Mothudi, I. Zorkani, A. Jorio, X-ray diffraction investigations of nanostructured ZnO coated with reduced graphene oxide, *J. Phys.: Conf. Ser.*, 1292 (2019) 012011.
- [36] H.S. Maharana, P.K. Rai, A. Basu, Surface-mechanical and electrical properties of pulse electrodeposited Cu-graphene oxide composite coating for electrical contacts, *J Mater Sci* 52 (2017) 1089–1105.
- [37] A. Kumar, A.M. Sadanandhan, S.L. Jain, Silver doped reduced graphene oxide as a promising plasmonic photocatalyst for oxidative coupling of benzylamines under visible light irradiation, *New J Chem* 43 (2019) 9116–9122.
- [38] A. Jabbar, G. Yasin, W.Q. Khan, M.Y. Anwar, R.M. Korai, M.N. Nizam, G. Muhyodin, Electrochemical deposition of nickel graphene composite coatings: effect of deposition temperature on its surface morphology and corrosion resistance, *RSC Adv* 7 (2017) 31100–31109.
- [39] F. Nichols, Q.M. Liu, J. Sandhu, Z. Azhar, R. Cazares, R. Mercado, F. Bridges, S.W. Chen, Platinum-complexed phosphorous-doped carbon nitride for electrocatalytic hydrogen evolution, *J Mater Chem A* 10 (2022) 5962–5970.
- [40] C.H. Zhang, J.W. Sha, H.L. Fei, M.J. Liu, S. Yazdi, J.B. Zhang, Q.F. Zhong, X.L. Zou, N.Q. Zhao, H.S. Yu, Z. Jiang, E. Ringe, B.I. Yakobson, J.C. Dong, D.L. Chen, J.M. Tour, Single-Atomic Ruthenium Catalytic Sites on Nitrogen-Doped Graphene for Oxygen Reduction Reaction in Acidic Medium, *Acs Nano* 11 (2017) 6930–6941.
- [41] J. Yang, D. He, W. Chen, W. Zhu, H. Zhang, S. Ren, X. Wang, Q. Yang, Y. Wu, Y. Li, Bimetallic Ru-Co Clusters Derived from a Confined Alloying Process within Zeolite-Imidazolate Frameworks for Efficient NH₃ Decomposition and Synthesis, *Acs Appl Mater Interfaces* 9 (45) (2017) 39450–39455.