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Yi Peng,<sup>a</sup> Bingzhang Lu,<sup>a</sup> Limei Chen,<sup>a</sup> Nan Wang,<sup>b</sup> Jia En Lu,<sup>a</sup> Yuan Ping,<sup>a\*</sup> and Shaowei Chen<sup>a\*</sup>

Development of cost-effective, high-performance electrocatalysts for hydrogen evolution reaction (HER) is urgently needed. In the present study, a new type of HER catalysts was developed where ruthenium ions were embedded into the molecular skeletons of graphitic-like carbon nitride ( $C_3N_4$ ) nanosheets of 2.0 ± 0.4 nm in thickness by refluxing  $C_3N_4$  and RuCl<sub>3</sub> in water. This took advantage of the strong affinity of ruthenium ions to pyridinic nitrogen of the tri-s-triazine units of  $C_3N_4$ . The formation of  $C_3N_4$ -Ru nanocomposites was confirmed in optical and X-ray photoelectron spectroscopic measurements, which suggested charge transfer from the  $C_3N_4$  scaffold to the ruthenium centers. Significantly, the hybrid materials were readily dispsersible in water, exhibited apparent electrocatalytic activity towards HER in acid and the activity increased with the loading of ruthenium metal centers in the  $C_3N_4$  matrix. Within the present experimental context, the sample saturated with ruthenium ion complexation at the atomic ratio of ruthenium to pyridinic nitrogen of a low Tafel slope of 57 mV/dec, and a large exchange current density of 0.072 mA/cm<sup>2</sup>. The activity was markedly lower when  $C_3N_4$  nanosheets to the HER activity, and the activity was most likely due to the formation of Ru-N moieties where the synergistic interactions between the carbon nitride and ruthenium metal centers facilitated the adsorption of hydrogen. This was strongly supported by results from density functional theory calculations.

## Introduction

Electrochemical water splitting for hydrogen generation represents an attractive technology for electrochemical energy storage and conversion.<sup>1-3</sup> Mechanistically, hydrogen evolution reaction (HER) involves multiple electron-transfer processes and requires appropriate catalysts to achieve a fast hydrogen evolution rate.4-7 Up to now, carbon-supported Pt has been recognized as the leading catalyst for HER with a high exchange-current density and small Tafel slope.<sup>8</sup> However, the high costs of Pt have severely hampered the wide-spread applications. Thus, development of non-platinum HER catalysts as cost-effective alternatives has been attracting a great deal of attention. For instance, transition metal sulfides, nitrides, phosphides, carbides and oxides (MX, with M = Mo, Fe, Co, Ni, etc) have been found to exhibit apparent activity towards HER.<sup>9-17</sup> However, because of low dispersibility in water, the catalytic activity is limited by the accessibility of the active centers. In addition, the durability may be compromised due to structural instability of the catalysts at low pH, a typical

#### condition for HER.

In contrast, for homogeneous catalysts based on organometallic complexes, such as cobalt macrocyclic glyoxime and tetraimine complexes,<sup>18</sup> cobalt and nickel diimine-dioxime complexes,<sup>19</sup> copper phthalocyanine complexes,<sup>20</sup> and ruthenium complexes,<sup>21</sup> surface accessibility is markedly enhanced. In these catalysts, the metal centers are coordinated to nitrogen-containing organic ligands, and the resulting M-N<sub>x</sub> moieties are generally believed to serve as the active sites for HER catalysis. Yet, despite much progress, the HER performance has remained largely subpar as compared to that of state-of-the art platinum catalysts.<sup>22</sup>

This is the primary motivation of the present study. Herein, by taking advantage of the abundant pyridinic nitrogen moieties in graphitic-like carbon nitride ( $C_3N_4$ ) nanosheets, we embedded ruthenium ions within the  $C_3N_4$  molecular skeleton forming Ru-N<sub>x</sub> moieties that may serve as effective active sites for HER, analogous to conventional organometallic complexes. With high chemical/thermal stability,<sup>23-34</sup>  $C_3N_4$  has been explored as advanced metal-free catalysts for a variety of energy conversion/storage processes.<sup>35, 36</sup> For instance,  $C_3N_4$ -based materials have been used as effective photocatalysts where the electronic band gap structure may be readily manipulated by doping with non-metal elements.<sup>37-42</sup> However, applications of  $C_3N_4$  in electrocatalysis, such as HER, have been limited by the low electrical conductivity. This may be mitigated by the incorporation of metal ions into the  $C_3N_4$ 



<sup>&</sup>lt;sup>a.</sup> Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, CA 95064, USA.

<sup>&</sup>lt;sup>b.</sup> New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou High Education Mega Centre, Guangzhou, Guangdong 510006, China.

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molecular skeleton by taking advantage of the tri-s-triazine units of  $C_3N_4$  that readily chelate transition metal ions.

Experimentally, the successful incorporation of ruthenium metal ions into the C<sub>3</sub>N<sub>4</sub> matrix was manifested by the emergence of unique metal-ligand charge transfer (MLCT) in UV-vis and photoluminescence (PL) measurements. XPS measurements suggested electron transfer from the C<sub>3</sub>N<sub>4</sub> skeleton to the ruthenium metal centers. Remarkably, the  $C_3N_4$ -Ru nanocomposites were found to be readily dispersed in water and exhibit apparent HER activity in acid, which increased with increasing loading of the ruthenium metal centers. Within the present experimental context, the sample saturated with ruthenium complexation at a ruthenium to pyridinic nitrogen ratio of ca. 1:2 displayed the best performance, with a low overpotential of only 140 mV to achieve the current density of 10 mA/cm<sup>2</sup>, a small Tafel slope of 57 mV/dec, and a large exchange current density of 0.072 mA/cm<sup>2</sup>, which was superior/comparable to results reported recently with  $C_3N_4$ -based HER catalysts. This remarkable performance was due to the formation of Ru-N moieties where the synergistic interactions between pyridinic nitrogen and ruthenium metal centers facilitated the adsorption of protons with a decrease of the Gibbs free energy. In fact, control experiments with other transition metal ions such as Fe<sup>3+</sup>, Co<sup>3+</sup>, Ni<sup>3+</sup> and Cu<sup>2+</sup> showed only minimal contributions from the C<sub>3</sub>N<sub>4</sub> nanosheets to the HER activity, and studies based on DFT calculations showed a downshift of the valence and conduction bands of  $C_3N_4$  and enhancement of electron mobility after embedment of ruthenium ions into the  $C_3N_4$ matrix. This led to optimized proton adsorption and reduction of the Gibbs free energies due to delocalized electrons from the ruthenium centers.

## **Experimental Section**

Chemicals. Melamine (99%, Acros), ruthenium(III) chloride (RuCl<sub>3</sub>, 35-40% Ru, Acros), ruthenium(IV) oxide (RuO<sub>2</sub>, 99.5%, anhydrous, ACROS), copper(II) acetate monohydrate  $(Cu(OAc)_2 \cdot H_2O)$ +98%, Alfa Aesar), cobalt(II) acetate tetrahydrate (Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, +99%, Matheson Coleman & Bell), nickel(II) acetate tetrahydrate, (Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, +99%, Matheson Coleman & Bell), iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O, +99%, Fisher Scientific), and sulfuric acid (98%, Fisher Chemicals) were used as received. All solvents were obtained from typical commercial sources and used without further treatment. Water was supplied by a Barnstead Nanopure water system (18.3 M $\Omega$  cm).

**Material preparation**. Graphitic  $C_3N_4$  nanosheets were synthesized by thermal treatment of melamine in air, as detailed previously.<sup>43, 44</sup> Briefly, 10 g of melamine was placed in a ceramic crucible with a cover and heated to 600 °C at a heating rate of 2.3 °C/min. The sample was heated at this temperature for 3 h before being cooled down to room temperature, yielding a yellow product that was grounded to fine powders. To synthesize ruthenium ion-complexed carbon nitride ( $C_3N_4$ -Ru), 50 mg of the  $C_3N_4$  powders synthesized

above were first dispersed into 50 mL of Nanopure H<sub>2</sub>O under sonication overnight to produce C<sub>3</sub>N<sub>4</sub> thin layers. 56 mg of RuCl<sub>3</sub> was then added into the mixture, which was refluxed for 4 h. The product was collected by centrifugation at 4500 rpm for 10 min and washed with Nanopure  $H_2O$  and ethanol to remove excess ruthenium ions. Note that in this synthesis, the supernatant showed a light brown color, indicating that there was a small excess of ruthenium ions in the solution and C<sub>3</sub>N<sub>4</sub> saturated with ruthenium complexation. The was corresponding sample was referred to as C<sub>3</sub>N<sub>4</sub>-Ru-F. Another sample was prepared in the same manner except the amount of RuCl<sub>3</sub> added was reduced by half to 28 mg. After centrifugation, the supernatant was colorless, indicating that all ruthenium ions were incorporated into C<sub>3</sub>N<sub>4</sub>. The product was denoted as C<sub>3</sub>N<sub>4</sub>-Ru-P.

 $C_3N_4$  complexed with other transition-metal ions (i.e., Fe<sup>3+</sup>, Co<sup>3+</sup>, Ni<sup>3+</sup> and Cu<sup>2+</sup>) was also prepared in a similar fashion where an equivalent amount of the salt precursors was used instead of RuCl<sub>3</sub>, and the corresponding products were referred to as  $C_3N_4$ -Fe,  $C_3N_4$ -Co,  $C_3N_4$ -Ni, and  $C_3N_4$ -Cu. For these samples, the supernatants after centrifugation showed the same colors as those of the original metal salts, suggesting that the metal ions were in excess and  $C_3N_4$  was saturated with the respective metal ions.

**Characterization**. Transmission electron microscopic (TEM) measurements were performed with a JOEL JEM 2100F microscope. Atomic force microscopic (AFM) measurements were carried out with a Molecular Imaging PicoLE SPM instrument. X-ray diffraction (XRD) patterns were acquired with a Rigaku Americas Miniflex Plus powder diffractometer operated at the voltage of 40 kV and current of 30 mA. XPS measurements were carried out with a PHI 5400/XPS instrument equipped with an AI K<sub>a</sub> source operated at 350 W and 10<sup>-9</sup> Torr. UV-vis spectra were collected with a Perkin Elmer Lambda 35 UV-vis spectrometer, and PL measurements were performed with a PTI fluorospectrometer. Inductively coupled plasma mass spectrometric (ICP-MS) analysis was carried out with an Agilent 1260-7700e instrument.

Electrochemistry. Electrochemical tests were performed using a CHI710 workstation and electrochemical impedance measurements were carried out with a Gamry Reference 600 instrument. A Ag/AgCl electrode (saturated KCl) and Pt wire were used as the reference electrode and counter electrode, respectively, while a glassy carbon electrode (5 mm in diameter, 0.196 cm<sup>2</sup>) was used as the working electrode. The Ag/AgCl electrode was calibrated against a reversible hydrogen electrode (RHE) and all the potentials were referred to this RHE electrode. To prepare catalyst inks, 2 mg of the C<sub>3</sub>N<sub>4</sub>-M powders obtained above and 3 mg of carbon black were dispersed in 1 mL of a 1:4 (v:v) water/ethanol mixed solvents along with 10 µL of a Nafion solution, and the mixture was sonicated for 30 min to achieve good dispersion of the materials. Then 15 µL of the above inks was dropcast onto the surface of the glassy carbon electrode and dried at room temperature, corresponding to a mass loading of 0.153 mg/cm<sup>2</sup> for the catalysts.

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Full water splitting was carried out with C<sub>3</sub>N<sub>4</sub>-Ru-F as the HER catalyst and commercial RuO<sub>2</sub> as the catalyst for oxygen evolution reaction (OER), along with a Ag/AgCl reference electrode. To prepare the electrodes, the catalysts were dispersed in ethanol at a concentration of 2 mg/mL under sonication for 0.5 h; then 0.5 mL of the catalyst inks was dropcast onto a piece of carbon cloth (1 cm × 2 cm) yielding a mass coverage of 0.5 mg/cm<sup>2</sup>. Water splitting tests were performed with an applied potential of 2 V in 1 M KOH, and the amounts of hydrogen and oxygen generated were quantified by water displacement measurements.

DFT calculations. The calculations of the electronic structures of C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub>-Ru were carried out by using open-source planewave code, Quantum Espresso.45 The two-dimensional unit cell was built with two chemical formula of C<sub>3</sub>N<sub>4</sub> and one Ru atom. The interlayer distance was set at 20 Å so that there was no interaction between the layers. The ultrasoft pseudopotential<sup>46</sup> was adopted with the wavefunction cutoff of 40 Ry (charge density cutoff 200 Ry), the energy threshold at  $10^{-8}$  Ry, and the force converged to  $10^{-4}$  a.u. The Marzari-Vanderbilt smearing<sup>47</sup> was adopted with 0.01 Ry for C<sub>3</sub>N<sub>4</sub>-Ru since the system became metal-like. The K point was set at 4 imes 4 imes 1. The vibration frequencies of surface species and zero-point energy (ZPE) and entropy contribution were evaluated by density functional perturbation theory (DFPT).48 All atoms were initiated with spin polarization. The structural model details and Gibbs free-energy calculations were included in the Supporting Information.

## **Results and discussions**

C<sub>3</sub>N<sub>4</sub> nanosheets were synthesized by thermal treatment of melamine in air,<sup>43, 44</sup> and refluxing with RuCl<sub>3</sub> in water led to effective incorporation of ruthenium metal ions into the C<sub>3</sub>N<sub>4</sub> scaffolds, most likely forming Ru-N<sub>x</sub> moieties through the pyridinic nitrogen, as schematically shown in Figure 1A. Figure 1B depicts a typical TEM image of the C<sub>3</sub>N<sub>4</sub>-Ru-F sample where nanosheet structures of a few tens of nm can be readily identified, rather consistent with the as-prepared C<sub>3</sub>N<sub>4</sub> (Figure S1). In XRD measurements (Figure S2), both C<sub>3</sub>N<sub>4</sub>-Ru-F and asprepared C<sub>3</sub>N<sub>4</sub> nanosheets displayed a single diffraction peak centered at 27.2°, corresponding to an interplanar spacing of 0.326 nm that is characteristic of the  $C_3N_4$  (002) planes.  $^{37,\,41,\,49}$ Energy dispersive x-ray (EDX) measurements confirmed that indeed Ru ions were incorporated into the  $C_3N_4$  matrix, as manifested in the elemental maps of C, N, Ru and Cl in Figure 1C-F, which were all distributed rather evenly across the sample.

A representative AFM topograph was depicted in Figure 1G, and the height profile of a line scan is shown in Figure 1H, where the thickness of the C<sub>3</sub>N<sub>4</sub>-Ru nanosheets was found to be rather consistent at ca. 2 nm. In fact, statistical analysis based on more than 100 nanosheets showed that the average thickness was 2.0  $\pm$  0.4 nm, as manifested in the thickness histogram (Figure 1I), identical to that of the as-produced C<sub>3</sub>N<sub>4</sub> nanosheets (Figure S3).

(E) (G) H 100 nm **L6 Figure 1.** (A) Schematic structure of  $C_2N_4$ -Ru nanosheets. (B) Representative TEM image of  $C_3N_4$ -Ru-F. EDX images of various elements in  $C_3N_4$ -Ru-F (scale bars all 50 nm): (C) C, (D) N, (E) Ru, (F) Cl. (G) Representative AFM topograph of  $C_3N_4$ -Ru-F (scale bar 200 nm). (H) Height profile of the line scan in panel (G). (I) Histogram of the thickness of  $C_3N_4$ -Ru-F nanosheets based on the AFM topographic macromote.

measurements.

XPS measurements were then carried out to determine the chemical composition and valence states of the composites. Figure 2A depicts the survey spectra of (i) C<sub>3</sub>N<sub>4</sub>, (ii) C<sub>3</sub>N<sub>4</sub>-Ru-P and (iii) C<sub>3</sub>N<sub>4</sub>-Ru-F, where the C 1s and N 1s electrons can be readily identified at ca. 285 eV and ca. 399 eV for all samples, and both C<sub>3</sub>N<sub>4</sub>-Ru-F and C<sub>3</sub>N<sub>4</sub>-Ru-P also exhibited two additional peaks at ca. 282 eV and ca. 199 eV, due to Ru 3d and Cl 2p electrons, respectively. The high-resolution scan of the Cl 2p electrons is depicted in Figure 2B where the binding energy was found to peak at 197.50 (Cl 2p<sub>3/2</sub>) and 199.00 eV (Cl 2p<sub>1/2</sub>) for C<sub>3</sub>N<sub>4</sub>-Ru-P and 197.70 (Cl 2p<sub>3/2</sub>) and 199.20 eV (Cl 2p<sub>1/2</sub>) for C<sub>3</sub>N<sub>4</sub>-Ru-F, consistent with those of Cl<sup>-</sup> ions in outersphere.<sup>50, 51</sup> The C 1s and Ru 3d spectra were depicted in Figure 2C. For the as-prepared  $C_3N_4$ , the C 1s spectrum can be deconvoluted into two peaks, a major one at 287.31 eV and a minor one 284.06 eV. The former may be assigned to the sp<sup>2</sup>hybridized carbon in N-C=N of the C<sub>3</sub>N<sub>4</sub> matrix, while the latter likely arose from defective carbon in sp $^3$  C-C bonds. $^{31, 32}$ Interestingly, the binding energy of C 1s in N-C=N blue-shifted somewhat to 287.57 eV for C<sub>3</sub>N<sub>4</sub>-Ru-P and even further to 287.93 eV for C<sub>3</sub>N<sub>4</sub>-Ru-F, likely due to the binding of (positively charged) ruthenium ions to the nitrogen moiety. For the Ru 3d electrons, the doublet can be resolved at 281.67 eV (Ru  $3d_{5/2}$ ) and 285.77 eV (Ru 3d<sub>3/2</sub>) for C<sub>3</sub>N<sub>4</sub>-Ru-P, and slightly lower at 281.30 eV (Ru 3d<sub>5/2</sub>) and 285.40 eV (Ru 3d<sub>3/2</sub>) for C<sub>3</sub>N<sub>4</sub>-Ru-F. Note that these binding energies are actually close to those of Ru(II) 3d electrons in ruthenium tris-bipyridine complex,<sup>52</sup>



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indicating that ruthenium was reduced to +2 from the original +3 charge state likely by hydroxide species, as observed previously by Creutz and Sutin,53 and incorporated into the C<sub>3</sub>N<sub>4</sub> matrix by Ru-N coordination bonds that enhanced electron-withdrawing of the nitrogen atoms. In fact, consistent results can be obtained in the high-resolution scans of the N 1s electros (Figure 2D). For the C<sub>3</sub>N<sub>4</sub> nanosheets, two peaks were resolved, a major one at 397.80 eV that may be attributed to the sp<sup>2</sup>-hybridized pyridinic nitrogen (C-N=C) and a minor one at 399.58 eV that can be assigned to the sp<sup>3</sup>-hybridized tertiary nitrogen (N-(C)<sub>3</sub>). After ruthenium ion complexation, the C-N=C peak blue-shifted to 398.08 eV for C<sub>3</sub>N<sub>4</sub>-Ru-P and 398.48 eV for  $C_3N_4$ -Ru-F (whereas the N-(C)<sub>3</sub> peak remained almost invariant). Note that in a previous study,<sup>54</sup> the N 1s binding energy of a polypyridyle ligand was also found to exhibit a positive shift of ca. 0.3 eV upon complexation with Ru(II) ions. These observations suggest charge transfer from the C<sub>3</sub>N<sub>4</sub> skeleton to the Ru d-orbital. Such MLCT may have significant implication in the electrocatalytic activity (vide infra).



Furthermore, based on the integrated peak areas, the elemental compositions of the samples were then analyzed. First, the atomic ratio of C(N-C=N):N was estimated to be 1:1.27 for C<sub>3</sub>N<sub>4</sub>, 1:1.20 for C<sub>3</sub>N<sub>4</sub>-Ru-P, and 1:1.18 for C<sub>3</sub>N<sub>4</sub>-Ru-F, in good agreement with the expected value of 1:1.33. In addition, the Ru to pyridinic N (C=N-C) ratio was estimated to be 1:4.7 for C<sub>3</sub>N<sub>4</sub>-Ru-P and almost doubled to 1:2.0 for C<sub>3</sub>N<sub>4</sub>-Ru-F (Table S1) — consistent results were obtained in ICP-MS measurements where the ruthenium content was found to increase with the amount of RuCl<sub>3</sub> added (Figure S4). This suggested that in the saturated structure, each Ru center was coordinated to two pyridinic nitrogen sites, as shown in the

schematic diagram of Figure 1A. In addition, the Ru:Cl ratios in both samples were very close at 1:0.5. Obviously, the Ru centers were not fully coordinated, which might be advantageous for catalytic reactions (vide infra).

Further structural insights were obtained in UV-vis and PL measurements. From Figure 3A, one can see that the asprepared  $C_3N_4$  nanosheets (black curve) exhibited an absorption peak at around 320 nm, similar to that observed with graphene quantum dots,<sup>55, 56</sup> and a weak, broad peak at ca. 390 nm which can be assigned to  $\pi$ - $\pi$ \* transitions that are commonly observed in conjugated ring systems including heterocyclic aromatics.<sup>57</sup> Similar optical characteristics can be seen with  $C_3N_4$ -Ru-F (red curve). However, the difference between these two spectra shows a new absorption band between 350 nm and 550 nm, where the peak at ca. 431 nm (green curve) is likely due to MLCT transitions, as observed previously with ruthenium-bipyridine complexes.<sup>58, 59</sup>





Furthermore, both the C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub>-Ru-F exhibited rather consistent PL profiles, with the emission peak ( $\lambda_{em}$ ) at 436 nm under the excitation ( $\lambda_{ex}$ ) of 330 nm at room temperature (Figure 3B).<sup>25, 60</sup> However, it can be seen that the emission intensity of C<sub>3</sub>N<sub>4</sub>-Ru-F decreased by about 91% as compared to that of C<sub>3</sub>N<sub>4</sub>, most likely because the emission coincided with the MLCT absorption of the Ru-N moieties (panel A) as well as because of marked diminishment of the C<sub>3</sub>N<sub>4</sub> bandgap upon ruthenium ion complexation, as suggested in DFT calculations

(vide infra). This is also manifested in the photographs of  $C_3N_4$ and  $C_3N_4$ -Ru-F solutions under photoirradiation at 365 nm (Figure 3B inset). The substantial quenching of the PL emission of  $C_3N_4$ -Ru-F, as compared to  $C_3N_4$ , suggested that ruthenium ion complexation suppressed radiative recombination of the photo-generated electron-hole pairs.<sup>61, 62</sup>



**Figure 4.** (A) Polarization curves of HER on various electrocatalysts in 0.5 M  $H_2SO_4$ . (B) Corresponding Tafel plots derived from panel (A). (C) Cyclic voltammograms within the range of +0.1 to +0.2 V where no faradaic reaction occurred at difference scan rates. (D) Variation of the double-layer charging currents at +0.15 V versus scan rate. (E) Nyquist plots collected at the overpotential of -50 mV. Inset is the equivalent circuit of the electrocatalystmodified electrode, where R<sub>s</sub> is (uncompensated) resistance, R<sub>ct</sub> is charge-transfer resistance and CPE is constant-phase element (equivalent to C<sub>al</sub>). (F) The 1<sup>st</sup> and 1000th cycle of HER polarization curves on C<sub>3</sub>N<sub>4</sub>-Ru-F in the stability test.

The electrocatalytic activities of the samples towards HER were then evaluated by electrochemical measurements in a  $N_2$ -saturated 0.5 M  $H_2SO_4$  solution. Figure 4A depicts the polarization curves of the various electrocatalysts loaded onto a glassy carbon electrode. One can see that at increasingly negative potentials, nonzero currents started to emerge with  $C_3N_4$ ,  $C_3N_4$ -Ru-P and  $C_3N_4$ -Ru-F, in comparison to the electrocatalytically inactive carbon black, indicating effective HER activity of the materials. Yet the activity varied markedly among the series. For instance, the overpotential  $(\eta_{10})$ required to achieve the current density of 10 mA/cm<sup>2</sup> was only -140 mV for C<sub>3</sub>N<sub>4</sub>-Ru-F, markedly lower than those for C<sub>3</sub>N<sub>4</sub>-Ru-P (–189 mV) and C<sub>3</sub>N<sub>4</sub> (–296 mV). For comparison,  $\eta_{10}$  for Ru nanoparticles was -233 mV,<sup>63</sup> signifying limited activity of ruthenium nanoparticles towards (metallic) hydrogen evolution. This indicates that it is the incorporation of ruthenium metal ions into the C<sub>3</sub>N<sub>4</sub> matrix that significantly enhanced the HER activity, which increased with increasing loading of the metal centers (Figure S4). Also, at the same overpotential of -200 mV, the current densities were the highest at 33.32 mA/cm<sup>2</sup> for C<sub>3</sub>N<sub>4</sub>-Ru-F, as compared to 12.73 mA/cm<sup>2</sup> for  $C_3N_4$ -Ru-P and 2.84 mA/cm<sup>2</sup> for  $C_3N_4$  (Figure S5).

That is, the HER activity of  $C_3N_4$ -Ru-F is 2.6 times that of  $C_3N_4$ -Ru-P and 11.7 times that of  $C_3N_4$ . Notably, whereas the overall performance remains subpar as compared to that of state-of-the art Pt/C (which exhibited an  $\eta_{10}$  of only -38 mV), it is better than leading results of  $C_3N_4$ -based HER electrocatalysts reported in recent literature, and is comparable to those based on non-precious metals and compounds (Table S2).

Additionally, the linear portions of the polarization curves (Figure 4B) were fitted to the Tafel equation,  $\eta = a \log |j| + b$  (j is the current density, and a is the Tafel slope), and the Tafel slope was estimated to be 57 mV/dec for C<sub>3</sub>N<sub>4</sub>-Ru-F, much lower than those for C<sub>3</sub>N<sub>4</sub>-Ru-P (81 mV/dec) and C<sub>3</sub>N<sub>4</sub> (178 mV/dec). For comparison, the Tafel slope was ca. 31 mV/dec for commercial Pt/C, consistent with results of earlier studies,<sup>13, 64</sup> and markedly greater at 234 mV/dec for the poorly active carbon black.

Note that HER involves three major steps, each of which carries a specific Tafel slope:

(1) Volmer reaction (Tafel slope 120 mV/dec):  $H_3O^+ + e^- \rightarrow H^* + H_2O$ 

(2) Heyrovsky reaction (Tafel slope 40 mV/dec):  $H^* + H_3O^+ + e^- \rightarrow H_2 + H_2O$ 

(3) Tafel reaction (Tafel slope 30 mV/dec):  $2H^* \rightarrow H_2$ 

where the asterisks denote surface-adsorbed species. Based on the Tafel slopes obtained above, one can see that the ratedetermining step (RDS) of HER on Pt/C is most likely the Tafel reaction where molecular hydrogen (H<sub>2</sub>) is formed by adsorbed hydrogen (H\*) and released from the catalyst surface, due to the high activity of platinum in the reduction of proton to atomic hydrogen.<sup>65</sup> For the C<sub>3</sub>N<sub>4</sub>-Ru complexes, the HER activity was likely dictated by the combined Volmer and Heyrovsky reactions, where the RDS involves the formation of metal-hydride moieties. Furthermore, the exchange current density (J<sub>o</sub>) can be estimated by extrapolation of the Tafel plot to the x axis to be 0.072 mA/cm<sup>2</sup> for  $C_3N_4$ -Ru-F, which is also superior/comparable to results reported in recent literatures with relevant electrocatalysts (Table S2). For comparison, Jo was markedly lower at 0.014.5 mA/cm<sup>2</sup> for C<sub>3</sub>N<sub>4</sub>-Ru-P, and 0.00015 mA/cm<sup>2</sup> for  $C_3N_4$ , whereas much higher at 1.5 mA/cm<sup>2</sup> for Pt/C.

In the above electrochemical measurements, one can clearly see that the HER activity of the as-prepared  $C_3N_4$  nanosheets alone was very poor, markedly lower than those of the  $C_3N_4$ -Ru composites. This suggests minimal contributions of pyridinic nitrogen in  $C_3N_4$  to hydrogen reduction, in contradiction to results in prior studies where DFT calculations and experimental results suggested that hybrid materials based on carbon nitride and nitrogen-doped graphene might be active for HER electrocatalysis.<sup>66, 67</sup> In the present study, the remarkable HER performance of  $C_3N_4$ -Ru is most likely due to the ruthenium metal centers embedded within the  $C_3N_4$  matrix, where the Ru-N moieties behaved analogously to conventional metal complexes for HER.<sup>18, 21, 22</sup> In fact, when the ruthenium metal centers were replaced by other transition-metal ions, such as Fe(II), Co(II), Ni(II), and Cu(II), the

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HER performance of the resulting  $C_3N_4$ -M composites diminished substantially and became comparable to that of  $C_3N_4$  alone (Figure S6-S7 and Table S3), indicating the unique role of ruthenium centers in the electroreduction of protons to hydrogen. The HER activity of  $C_3N_4$ -Ru-F was also manifested in full water splitting with commercial RuO<sub>2</sub> as the OER catalyst, where the amount of hydrogen generated was 2.05 times that of oxygen (Figure S8).

Further insights into the interactions between ruthenium metal centers and C<sub>3</sub>N<sub>4</sub> matrix were obtained by guantitative analysis of the electrochemical active surface area (ECSA) and charge-transfer resistance (R<sub>ct</sub>). Figure 4C depicts the cyclic voltammograms of C<sub>3</sub>N<sub>4</sub>-Ru-F recorded at different scan rates (10 to 60 mV/s) in the potential range of +0.1 to +0.2 V vs. RHE, where no faradaic reaction occurred (the data of C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub>-Ru-P were shown in Figure S9). Figure 4D plotted the current density at +0.15 V versus potential scan rate and the double layer capacitance (C<sub>dl</sub>, which is proportional to ECSA) of  $C_3N_4$ -Ru-F was estimated to be 18.4 mF/cm<sup>2</sup>, which was 4.7 times that of C<sub>3</sub>N<sub>4</sub> (3.9 mF/cm<sup>2</sup>), and 1.7 times that of C<sub>3</sub>N<sub>4</sub>-Ru-P (10.7 mF/cm<sup>2</sup>). This may be ascribed to the enhanced electrical conductivity of the composites with the incorporation of metal centers into the  $C_3N_4$  molecular skeleton. Taking into consideration the low mass loading of 0.153 mg/cm<sup>2</sup> of the composites, the C<sub>dl</sub> values were also comparable to result reported in prior studies (Table S2).

Electrochemical impedance measurements were then carried out to quantify the corresponding  $R_{ct}$ . Figure S10 depicts the typical Nyquist plots of  $C_3N_4$ -Ru-F at various overpotentials, and  $R_{ct}$  was estimated by fitting the data to Randle's equivalent circuit (inset to Figure 4E). One can see that  $R_{ct}$  decreased significantly with increasing overpotentials. Figure 4E compares the Nyquist plots of the various electrocatalysts at the overpotential of -50 mV, where  $R_{ct}$  was estimated to be 285  $\Omega$  for  $C_3N_4$ -Ru-F, 658  $\Omega$  for  $C_3N_4$ -Ru-P and 1550  $\Omega$  for  $C_3N_4$ . Indeed, one can see that the embedment of ruthenium metal centers within the  $C_3N_4$  matrix greatly facilitated the electron-transfer kinetics, consistent with results from the above voltammetric measurements.

Besides excellent electrocatalytic activity, stability of the catalysts is also an important variable in practical applications. For C<sub>3</sub>N<sub>4</sub>-Ru-F, the polarization profiles remained almost invariant after 1,000 cycles of potential scans, with the  $\eta_{10}$  value increased by only 3 mV, suggesting long-term durability of the catalyst (Figure 4F). In fact, XPS measurements showed no variation of the C 1s and Ru 3d electrons after 1,000 electrochemical cycles (Figure S11).

To unravel the mechanistic insights involved, DFT calculations were conducted to examine the effect of the incorporation of ruthenium ions into the  $C_3N_4$  matrix on the band structures and Gibbs free energy of hydrogen adsorption and reduction. 2 × 2 cells of  $C_3N_4$  and  $C_3N_4$ -Ru were used for the calculations (Figure S12-S14), where a ruthenium ion was bonded to two nitrogen sites, as suggested by experimental results (Figure 2 and Table S1). The calculated band structure of  $C_3N_4$  (Figure 5A) suggests an indirect band gap of about 1.3 eV, which is in good agreement with the PDOS plot in Figure

5B and results from previous studies.<sup>68, 69</sup> In contrast with the semiconducting nature of  $C_3N_4$ , the band structure of  $C_3N_4$ -Ru (Figure 5C) shows no band gap, most probably because the embedment of ruthenium ions into the  $C_3N_4$  matrix caused a charge transfer between  $C_3N_4$  and ruthenium ions, as observed in XPS measurements (Figure 2).<sup>70</sup> Additionally, the PDOS profile of  $C_3N_4$ -Ru shows a large density of states at the Fermi level, with the primary contributions from the Ru 4d and 5s orbitals (Figure 5D). This indicates that the incorporation of ruthenium ions into  $C_3N_4$  led to redistribution of the electrons within the composite, crossing of the Fermi level with the conduction band, and hence enhanced charge mobility and electrical conductivity, consistent with electrochemical impedance measurements (Figure 4E). This may also explain the quenching of the  $C_3N_4$  PL emission (Figure 3).



**Figure 5.** (A) Band structures and (B) projected density of states of  $C_3N_4$ . (C) Band structures and (D) projected density of states of  $C_3N_4$ . Ru. Contributions of Ru 4d and 5s orbitals to the PDOS are labeled in different colors. (E) Calculated Gibbs free-energy ( $\Delta G_H^*$ ) of HER at the equilibrium potential for  $C_3N_4$  (blue) and  $C_3N_4$ -Ru. (red) at various bonding sites as labeled in the panel inset. (F) Schematic of interfacial charge transfer in C3N4-. Red signals are positive charge and blue signals are negative charge with an isosurface value of 0.003 e/au<sup>3</sup>.

Such a marked discrepancy of the electronic structures of C<sub>3</sub>N<sub>4</sub>-Ru, as compared to that of C<sub>3</sub>N<sub>4</sub>, is likely responsible for the much enhanced electrocatalytic activity of C<sub>3</sub>N<sub>4</sub>-Ru.<sup>66, 71, 72</sup> Notably, HER typically involves a three-state process, an initial  $H^{\star}$  state, an intermediate  $H^{\star}$  state, and  ${}^{1}\!\!{}^{2}_{2}H_{2}$  state as the final product (Figure 5E), and the Gibbs free-energy of the formation of the intermediate H<sup>\*</sup> state,  $|\Delta G_{H^*}|$ , can be used as the descriptor of the HER performance for different electrocatalysts.<sup>73</sup> For an ideal HER electrocatalyst,  $|\Delta G_{H^*}|$ should be zero. In the present study, C<sub>3</sub>N<sub>4</sub> was found to exhibit a Gibbs free energy of  $\Delta G_{H*}^{C}$  = +1.23 eV and  $\Delta G_{H*}^{N}$  = -0.63 eV for the carbon and nitrogen bonding sites (labeled in the left inset to Figure 5E and Figure S13), respectively. Yet, when ruthenium ions were incorporated into the C<sub>3</sub>N<sub>4</sub> matrix, the  $|\Delta G_{H^*}|$  values were found to be substantially lower at the Ru, C, and N binding sites (labeled in the right inset to Figure 5E and Figure S14),  $\Delta G^C_{H*}$  = -0.48 eV,  $\Delta G^{N1}_{H*}$  = +0.57 eV,  $\Delta G^{N2}_{H*}$  = +0.60 eV and  $\Delta G_{H*}^{Ru}$  = -0.49 eV (Table S4), suggesting enhanced

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hydrogen adsorption by ruthenium ion complexation to  $C_3N_4$ . This is also manifested in Figure 5F, which depicts the interfacial charge transfer between  $C_3N_4$  and ruthenium ions (by computing the charge density difference between  $C_3N_4$ -Ru and  $C_3N_4$  + isolated Ru atom) and the resulting charge redistribution among the entire cell. From these studies, one can see that the incorporation of ruthenium ions into the  $C_3N_4$  molecular skeleton drastically enhanced the electrical conductivity, and facilitated the adsorption of hydrogen to various binding sites in the composites, which is likely responsible for the enhanced HER performance (Figure S14).

#### Conclusions

In this study, a new type of HER electrocatalysts was designed and synthesized by thermal refluxing of graphitic  $C_3N_4$  nanosheets and RuCl<sub>3</sub> in water, leading to the formation of C<sub>3</sub>N<sub>4</sub>-Ru hybrids that exhibited apparent HER activity in acidic media. In fact, the HER activity was found to increase with increasing loading of the ruthenium ions in the  $C_3N_4$ matrix, and the best sample displayed an overpotential of only 140 mV to achieve the current density of 10 mA/cm<sup>2</sup>, a Tafel slope of 57 mV/dec and an exchange current density of 0.072 mA/cm<sup>2</sup>, which is comparable/superior to results reported in recent literatures with relevant HER electrocatalysts. Such a remarkable performance was ascribed to the formation of Ru- $N_{\rm 2}$  moieties that facilitated the adsorption of hydrogen, a critical step in HER catalysis, as confirmed by studies based on DFT calculations. Significantly, the results suggest that graphitic C<sub>3</sub>N<sub>4</sub> nanosheets may be exploited as a unique functional scaffold for the fabrication of a wide range of single atom-like catalysts for diverse applications.74,75

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TOC graph

