The Front Cover shows the production of hydrogen gas when electrons and protons meet on ruthenium ion-complexed graphitic carbon nitride nanosheets supported on graphene surface. The image is based on an ancient Chinese legend of Niulang (牛郎) and Zhinü (织女). Niulang was a human cowherd and Zhinü was a fairy from heaven. They fell in love with each other. Yet their love was banned by the fairy’s queen, who forcefully separated them by the Silver River. The lovers were only able to see each other once a year, on the 7th day of the 7th lunar month, with the help of a flock of magpies that formed a bridge. More information can be found in the Full Paper by Peng et al.
Ruthenium Ion-Complexed Graphitic Carbon Nitride Nanosheets Supported on Reduced Graphene Oxide as High-Performance Catalysts for Electrochemical Hydrogen Evolution


Carbon-based materials are promising, low-cost electrocatalysts toward hydrogen evolution reaction (HER), although the catalytic performance needs to be further improved before commercialization. In this study, ruthenium ions are incorporated into graphitic carbon nitride/reduced graphene oxide (rGO) hybrids to form Ru–C₃N₄/rGO composites through Ru–N coordination bonds. The incorporation of Ru ions, at a loading of 1.93 at.%, leads to electron redistribution within the materials and dramatically enhances the HER performance over those of C₃N₄, C₃N₄/rGO, and Ru–C₃N₄ with an overpotential of only −80 mV to reach a current density of 10 mA cm⁻², a Tafel slope of 55 mV dec⁻¹, and an exchange current density of 0.462 mA cm⁻². This performance is comparable to that of Pt/C, and ascribed to the positive shift of the conduction band of the composite, where the charge carrier density increases by a factor of about 250 over that of C₃N₄, leading to a lower energy barrier for hydrogen evolution. The results suggest a new strategy in the design and engineering of functional nanocomposites for effective HER electrocatalysis by embedding selective metal ions into carbon-based molecular skeletons.

Introduction

As a clean and environmentally friendly fuel, hydrogen has been hailed as one of the most promising energy sources of the future. Towards this end, it is imperative to develop efficient technologies for hydrogen storage and conversion.[1,2] Mechanistically, effective electrocatalysts are required to achieve a high hydrogen generation rate as the hydrogen evolution reaction (HER) involves multiple electron-transfer steps.[3,4] To date, platinum-based materials supported on carbon have exhibited the best electocatalytic performance for HER. However, widespread commercial applications are hindered by the low natural abundance and high costs of platinum.[5] In recent years, a variety of transition metal-based materials have been found to show apparent electrocatalytic activities towards HER. However, durability remains an issue because of corrosion of the catalysts in acidic electrolytes, a common medium for HER.[6–9] Carbon-based materials, such as graphene, carbon nanotubes, and amorphous carbon, have also been explored as viable catalysts for HER.[10–18] However, their activities have remained markedly lower than that of state-of-the-art Pt/C.

More recently, Chhetri et al. found that carbon-rich borocarbonitrides (BC₃N₄) had an apparent activity with an overpotential (η₁₀) of only −70 mV to reach a current density of 10 mA cm⁻², which was comparable to that of Pt/C. However, the Tafel slope was relatively high (100 mV dec⁻¹), indicative of increasing deviation from Pt/C at high overpotentials.[19] In another study,[20] carbon nitride (C₃N₄) and N-doped graphene (NG) were combined to form a hybrid structure that exhibited apparent HER activity arising from electronic coupling between C₃N₄ and NG. However, the η₁₀ value remained quite high at −240 mV. The HER performance may be enhanced by morphological engineering of C₃N₄ and graphene, but it is difficult to reduce η₁₀ to below −200 mV.[21–23] In a more recent study,[24] we showed that when ruthenium metal ions were embedded into C₃N₄ nanosheets, the resulting Ru–C₃N₄ complex exhibited much-enhanced HER activity. This was accounted for by the formation of Ru–N coordination bonds, owing to the strong affinity of ruthenium(II) ions to pyridinic nitrogen of the tri-s-triazine units of C₃N₄ that facilitated the adsorption and reduction of hydrogen with an η₁₀ of −140 mV and Tafel slope of 57 mV dec⁻¹, whereas only minimal activity was observed with other metal ions, such as Fe³⁺, Co³⁺, Ni²⁺, and Cu²⁺.[24]

In the present study, the HER performance was further improved by incorporating graphene into the Ru–C₃N₄ complex. Experimentally, C₃N₄ nanosheets were mixed with reduced graphene oxide (rGO) and then embedded with ruthenium metal ions by thermal refluxing of RuCl₃ in water (Scheme 1). Despite a low Ru loading of only 1.93 at.%, the resulting Ru–C₃N₄/rGO nanocomposite exhibited markedly enhanced electrocatalytic activity towards HER over those of the individual components
and their binary composites, with a low \( \eta_{10} \) of only \(-80\) mV, a Tafel slope of 55 mV dec\(^{-1}\), and an exchange current density of 0.462 mA cm\(^{-2}\). Notably, this performance is comparable to that of Pt/C.

Results and Discussion

The synthesis of the Ru–C\(_3\)N\(_4\)/rGO hybrid is shown in Scheme 1. Briefly, GO was prepared by a modified Hummers method by using graphite flakes as precursors,\(^{[25, 26]}\) and C\(_3\)N\(_4\) nanosheets were synthesized by sonication of graphitic C\(_3\)N\(_4\) obtained by thermal treatment of melamine in air.\(^{[27, 28]}\) Refluxing of the mixture of C\(_3\)N\(_4\) and GO in water with the addition of ascorbic acid led to the production of C\(_3\)N\(_4\)/rGO composites, likely in the form of a sandwich structure.\(^{[29, 21, 20]}\) With the addition of a calculated amount of RuCl\(_3\) into the solution, ruthenium metal ions were incorporated into the nanocomposites by complexation with the pyridinic nitrogen of the tri-s-triazine units of the C\(_3\)N\(_4\) scaffolds, forming Ru–C\(_3\)N\(_4\)/rGO hybrid materials.

The formation of the composites was first confirmed by atomic force microscopy (AFM) topographic measurements, from which one can see that C\(_3\)N\(_4\) nanosheets are well-dispersed without apparent aggregation (Figure 1a). Line scans show that the nanosheets are about 2 nm in thickness (Figure 1a). Statistical analysis based on more than 100 nanosheets shows that the average thickness is 2.0 ± 0.4 nm (see the histogram in Figure 1a), corresponding to roughly 6 layers in C\(_3\)N\(_4\) (interlayer spacing of C\(_3\)N\(_4\) is about 0.33 nm).\(^{[24]}\) With
the addition of rGO, substantial aggregation occurred with the resulting C₃N₄/rGO composites (Figure 1b), and the thickness increased markedly up to 10 nm (Figure 1b), with an average of 6.3 ± 3.7 nm (Figure 1b). This is likely due to the formation of C₃N₄/rGO sandwich-like ensembles as a result of strong π–π interactions between the C₃N₄ and rGO nanosheets (Figure S1 in the Supporting Information). Additionally, no apparent variation was observed with the morphology or thickness of the nanocomposites after the embedment of ruthenium ions into the C₃N₄ scaffold (Figure 1c). From the TEM images of the C₃N₄/rGO and Ru–C₃N₄/rGO nanocomposites and the corresponding elemental maps (Figure 1d, e), one can see that no particulate materials were produced, that both C₃N₄/rGO and Ru–C₃N₄/rGO exhibited similar agglomeration, and that all elements were distributed evenly across the respective samples. Note that although Ru was not detected in C₃N₄/rGO, the signals were quite visible for Ru–C₃N₄/rGO.

Further structural insights were obtained by X-ray photoelectron spectroscopy (XPS). Figure 2a depicts the survey spectra of (i) C₃N₄, (ii) C₃N₄/rGO, and (iii) Ru–C₃N₄/rGO, where the peaks at 284, 399, and 531 eV may be assigned to the C 1s, N 1s, and O 1s electrons, respectively. In addition, the peak at 464 eV in curve (iii) for Ru–C₃N₄/rGO, which is absent in those for the other two samples, can be ascribed to Ru 3p electrons (Ru 3d overlaps with C 1s), suggesting that indeed ruthenium metal ions were successfully incorporated into the nanocomposites. Furthermore, based on the integrated peak areas, the elemental composition in Ru–C₃N₄/rGO can be estimated to be 67.88 at.% for C, 7.48 at.% for N, 22.75 at.% for O and 1.93 at.% for Ru (see the Supporting Information, Table S1). From the high-resolution spectra (Figure 2b), deconvolution yields a major peak at 287.40 eV for C₃N₄ (curve i) that may be assigned to the sp²-hybridized carbon in C–C=C and a minor one at 284.20 eV from defective carbon.[34] For C₃N₄/rGO (curve ii) and Ru–C₃N₄/rGO (curve iii), the C–C=N peak shifted positively to 287.85 and 288.02 eV, respectively, indicating reduced electron density of the sp² C in C₃N₄, likely due to charge transfer from C₃N₄ to rGO and/or Ru centers.[35] Two additional peaks can be identified at 284.31 and 286.16 eV, which may be ascribed to carbon in C–C and C–O of rGO, respectively. The peaks are somewhat lower than those observed with rGO alone (C–C at 284.60 eV and C–O at 286.50 eV), suggesting enhanced electron density of these carbon moieties.[36] For the Ru–C₃N₄/rGO sample (Figure 2b, curve iii), deconvolution also yields a doublet at 281.96 and 286.16 eV that is very consistent with the 3dₓ₂ and 3d₃/2 electrons of Ru⁺ ions in Ru–N moieties, indicating that Ru⁺ was reduced to Ru²⁺ during the refluxing process, most probably by hydroxy species,[37] and incorporated into the C₃N₄ matrix by Ru–N coordination bonds.[24, 39] Figure 2c shows the N 1s spectra, where two subpeaks can be resolved in all three samples. For C₃N₄ (curve i), the peak at 397.86 eV may be assigned to sp²-hybridized pyridinic nitrogen (C–N=C) and that at 399.62 eV to sp²-hybridized tertiary nitrogen (NC₃).[39] For C₃N₄/rGO (curve ii) and Ru–C₃N₄/rGO (curve iii), the C–N=C peak had undergone an apparent blueshift to 398.47 eV and 398.65 eV, respectively. Taken together, these results suggest efficient charge transfer from C₃N₄ to rGO and Ru centers.[24,29,40,41] Furthermore, based on the integrated peak areas, the atomic ratio of N (C–N=C) to Ru was estimated to be approximately 2.3 for the Ru–C₃N₄/rGO sample, similar to that observed previously with Ru–C₃N₄, where the ruthenium ions were coordinated to two N sites in C–C=N.[24] Overall, results from the XPS measurements suggested strong electronic interactions among the three structural components of Ru–C₃N₄/rGO, which may have significant impacts on the electrocatalytic activity towards HER (see below).

Significantly, the resulting Ru–C₃N₄/rGO nanocomposites exhibited high HER activity, which was markedly better than those of C₃N₄, C₃N₄/rGO, and Ru–C₃N₄ and comparable to that of Pt/C. Figure 3a depicts the polarization curves in N₂-saturated 0.5 m H₂SO₄ of the various samples loaded onto a glassy carbon electrode, from which η₁₀ can be estimated to be –416, –206, and –80 mV for C₃N₄, C₃N₄/rGO, and Ru–C₃N₄/rGO, respectively. Note that η₁₀ for Ru–C₃N₄ was –140 mV.[24] Taken together, these results indicate that the embedding of ruthenium metal ions into the C₃N₄ matrix significantly increased the HER activity, and the performance may be further enhanced by the incorporation of rGO nanosheets. Significantly, the η₅₀ for Ru–C₃N₄/rGO was also comparable to that of Pt/C (–41 mV). Consistent results can be obtained from analysis of the Tafel plots, which included the linear segments of the polarization curves (Figure 3b). From the y axis intercept by linear regression, the exchange current density (i₀, Figure S2) for 2018 ChemSusChem 11, 130 –136 www.chemsuschem.org 132 © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
The HER performance of Ru was estimated to be 1,366 W/C0, which was 125 mV dec⁻¹ at an overpotential of −100 mV. Insert is the equivalent circuit of the electrocatalyst-coated electrode, where $R_\text{ct}$ is uncompensated resistance, $R_\alpha$ is charge transfer resistance, and CPE is constant-phase element (equivalent to electrode double-layer capacitance, $C_\text{dl}$).

Electrochemical impedance measurements were then carried out to evaluate the corresponding charge-transfer resistance ($R_\alpha$). Figure S5 shows the Nyquist plots of Ru–C3N4/rGO at various overpotentials, from which $R_\alpha$ was quantified by fitting the data to the Randle’s equivalent circuit (inset to Figure 3d) and found to decrease significantly with increasing overpotentials: 46.4 Ω at −50 mV, 19.7 Ω at −100 mV, 9.1 Ω at −150 mV, and 5.0 Ω at −200 mV. Figure 3d compares the Nyquist plots of the various samples at the same overpotential of −100 mV, where $R_\alpha$ was estimated to be 1,366 Ω for C3N4, 157 Ω for C3N4/rGO, 88 Ω for Ru–C3N4 [24] and 20 Ω for Ru–C3N4/rGO. Therefore, the poor HER performance of C3N4 may be ascribed to its semiconducting nature and sluggish electron-transfer kinetics. However, the incorporation with rGO greatly facilitates the electron-transfer reaction with $R_\alpha$ markedly reduced by over an order of magnitude. Further enhancement can be observed when ruthenium metal ions were embedded into the nanocomposites where $R_\alpha$ was approximately 70 times smaller.

In the previous study with Ru–C3N4 [24] we observed that the incorporation of ruthenium metal ions into the C3N4 scaffold by Ru–N coordination bonds led to electron redistribution within the composites, which facilitated the adsorption of hydrogen and proton reduction to hydrogen. This formation of an increasing number of HER active sites can be evidenced in the corresponding effective electrochemical surface area, as reflected by the electrode double-layer capacitance ($C_\text{dl}$). Figure 4a shows the voltammograms of Ru–C3N4/rGO (data for C3N4 and C3N4/rGO are included in Figure S6, and those for Ru–C3N4 in our previous study [24]) at scan rates of 10–60 mVs⁻¹ within a potential range of +0.1 to +0.2 V where no faradaic reaction occurred. As shown in Figure 4b, $C_\text{dl}$ was estimated to be 0.036 mA cm⁻² for C3N4 and 0.462 mA cm⁻² for Ru–C3N4/rGO, and 103 times that of C3N4/rGO nanocomposite exhibited excellent durability. There was almost no change in the voltammetric profiles after 5000 cycles of potential scanning and chronoamperometric measurements for up to 9 h (Figure S4). Furthermore, the corresponding Tafel slope can be estimated to be 125 mV dec⁻¹ for C3N4, 82 mV dec⁻¹ for C3N4/rGO, 57 mV dec⁻¹ for Ru–C3N4 [24] and 55 mV dec⁻¹ for Ru–C3N4/rGO—the latter is, again, very comparable to that (32 mV dec⁻¹) of Pt/C. This suggests that hydrogen evolution catalyzed by Ru–C3N4/rGO likely followed a mechanism similar to that by Pt/C with the Volmer–Heyrovsky reaction being the rate-determining step [22]. The HER performance of Ru–C3N4/rGO is also drastically better than many other recently reported carbon-based catalysts listed in Figure 3c and Tables S2 and S3 (see the References therein).
be 27.8 mF cm$^{-2}$ for Ru–C$_3$N$_4$/rGO, over 7 times that of C$_3$N$_4$ (3.9 mF cm$^{-2}$), 3 times that of C$_3$N$_4$/rGO (8.4 mF cm$^{-2}$), and 1.5 times that of Ru–C$_3$N$_4$ (18.4 mF cm$^{-2}$).\cite{44} This dramatic enhancement of the effective electrochemical surface area might be ascribed to the enhanced electrical conductivity of the composite with the incorporation of rGO and Ru centers into C$_3$N$_4$. Indeed, from the Nyquist plots (Figure 4c), the uncompensated resistance $R_0$ was estimated to be 35.4 Ω for C$_3$N$_4$, and markedly reduced to 10.0 Ω when rGO was incorporated to form C$_3$N$_4$/rGO, and further to 7.9 Ω in Ru–C$_3$N$_4$/rGO where ruthenium metal ions were embedded.

To unravel further insights into the HER performance, a Mott–Schottky analysis was performed. From Figure 4d, it can be clearly seen that all samples exhibited a positive slope, indicating n-type semiconducting nature of the C$_3$N$_4$-based materials.\cite{19} Additionally, the flat-band potential ($E_{fb}$) of C$_3$N$_4$ was estimated to be $-1.35$ V (vs. Ag/AgCl), but shifted anodically to around $-0.95$ V for the other two. Thermodynamically, $E_{fb}$ of an n-type semiconductor determines the conduction band position, and the positive shift of the conduction band suggests lowering of the energy barrier of hydrogen evolution (H$^+$/H$_2$; $-0.59$ V vs. Ag/AgCl in 0.1 M Na$_2$SO$_4$), leading to enhanced electrocatalytic performance of the material.\cite{43} Furthermore, the charge-carrier densities ($N_d$) of the catalysts can be calculated by Equation (1):

$$N_d = \frac{2}{\varepsilon \varepsilon_0 m}$$

where $\varepsilon$ is the elementary charge of an electron, $\varepsilon$ is the dielectric constant (ca. 10 in the present study),\cite{44} $\varepsilon_0$ is permittivity in a vacuum ($8.85 \times 10^{-12}$ F m$^{-1}$), and $m$ is the slope of the Mott–Schottky plot. From Figure 4d, the charge-carrier densities were estimated to be $3.67 \times 10^{15}$ cm$^{-3}$ for C$_3$N$_4$, $1.42 \times 10^{17}$ cm$^{-3}$ for C$_3$N$_4$/rGO, and $9.05 \times 10^{17}$ cm$^{-3}$ for Ru–C$_3$N$_4$/rGO. That is, the charge-carrier density of Ru–C$_3$N$_4$/rGO is about 250 times of that of C$_3$N$_4$ and 6 times of that of C$_3$N$_4$/rGO. This observation is consistent with results from impedance and voltammetric measurements.

**Conclusion**

In summary, a new functional nanocomposite was prepared by embedding ruthenium metal ions into C$_3$N$_4$/rGO composites where the ruthenium centers were bonded to the pyridinic nitrogen of the carbon nitride scaffold. The resulting Ru–C$_3$N$_4$/rGO nanocomposites exhibited markedly enhanced electrocatalytic activity towards HER, with a low $\eta_{10}$ of only $-80$ mV, a Tafel slope of $55$ mV dec$^{-1}$, and an exchange current density of $0.462$ mA cm$^{-2}$. This performance is markedly better than those of C$_3$N$_4$/C$_3$N$_4$/rGO, and Ru–C$_3$N$_4$ and is even comparable to that of commercial Pt/C. The impressive performance was accounted for by electron redistribution upon the incorporation of ruthenium ions into the C$_3$N$_4$/rGO composites, which led to efficient narrowing of the material band gap, enhanced electric conductivity and charge-carrier density, increased number of active sites, and reduced charge-transfer resistance. Such inter-
actions between the structural components (C₃N₄, rGO, and Ru ions) facilitate an effective strategy in the rational design and engineering of functional composites in the development of high-performance HER electrocatalysts.

**Experimental Section**

**Chemicals**

Melamine (99%, Acros), ruthenium chloride (RuCl₃, 35–40%, Ru, Acros), sulfuric acid (H₂SO₄, 98%, Fisher Chemicals), sodium chloride (NaCl, 99%, Acros), sodium nitrate (NaNO₃, 99%, Acros), potassium permanganate (KMnO₄, 99%, Fisher Chemicals), and ascorbic acid (99%, 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 MΩ cm).

**Synthesis of graphitic carbon nitride**

C₃N₄ was synthesized by direct pyrolysis of melamine in air. Briefly, melamine (10 g) was placed in a crucible with a cover and then heated at 600 °C for 3 h. After being cooled down to room temperature, the yellow product was collected and ground to fine powder. 50 mg of the obtained C₃N₄ powder was then mixed with Nanopure H₂O (50 mL) under sonication overnight to produce well-dispersed thin-layer C₃N₄.

**Synthesis of graphene oxide**

GO was synthesized by a modified Hummers method. Initially, graphite flakes (1 g) were ground with NaCl (20 g) for 15 min, and NaCl was washed away by rinsing with water in a vacuum filtration apparatus. The remaining graphite was dried in an oven at 70 °C, and then transferred to a 250 mL round-bottom flask. Concentrated H₂SO₄ (23 mL) was added into the flask and the mixture was stirred at room temperature for 24 h before being heated in an oil bath at 40 °C. NaNO₃ (100 mg) was added to the suspension and allowed to dissolve in 5 min. This step was followed by the slow addition of KMnO₄ (3 g), with the solution temperature kept below 45 °C, under magnetic stirring for 30 min. The flask was removed from the oil bath and Nanopure water (140 mL) and 30% H₂O₂ (10 mL) were added to the reaction. The mixture was under magnetic stirring at room temperature for 5 min. It was then repeatedly centrifuged and washed with 5% HCl solution twice, followed by rinsing with copious amounts of water. The final precipitate was dispersed in water (100 mL) and sonicated for 30 min. Insoluble solids were removed by centrifugation at 3000 rpm for 5 min, and the brown supernatant was collected and dried in an oven at 70 °C.

**Synthesis of C₃N₄/rGO composites**

C₃N₄/rGO composites were synthesized by following a reported protocol. In brief, GO (50 mg) was added into a 1 mg/mL thin-layer C₃N₄ solution (50 mL; see above for preparation). The mixture was sonicated for 1 h before being heated at reflux with ascorbic acid (176 mg) for 2 h. The products were collected by centrifugation.

**Synthesis of Ru–C₃N₄/rGO complexes**

To synthesize Ru–C₃N₄/rGO hybrids, the C₃N₄/rGO composites obtained above were dispersed in Nanopure H₂O (50 mL) into which was then added RuCl₃ (28 mg). The mixture was heated at reflux for 2 h. The product was collected by centrifugation at 4500 rpm for 10 min and washed with H₂O and ethanol (2 × 20 mL). At this feed ratio, the supernatant showed a light brown color, indicating that there was a small excess of ruthenium ions in the solution and C₃N₄ was saturated with ruthenium complexation.

**Characterization**

The morphology of the samples was characterized by transmission electron microscopy (TEM; Philips CM300 at 300 kV) and atomic force microscopy (AFM; Molecular Imaging PicoLE SPM). The samples were prepared by dropcasting a dilute dispersion of the nanocomposites in ethanol onto a TEM grid or clean mica surface, and dried in a vacuum oven. X-ray photoelectron spectroscopic (XPS) measurements were carried out with a PHI 5400XPS instrument equipped with an AlKα source operated at 350 W and 10⁻⁷ torr.

**Electrochemistry**

Electrochemical tests were performed using a CHI710 workstation and electrochemical impedance and Mott–Schottky measurements were carried out with a Gamry Reference 600 instrument. A Ag/AgCl electrode (1 M KCl) and Pt wire were used as the reference electrode and counter electrode, respectively, and a glassy carbon electrode (5 mm in diameter, 0.196 cm²) was used as the working electrode. The Ag/AgCl electrode was calibrated against a reversible hydrogen electrode (RHE), and all potentials were referred to this RHE except for the Mott–Schottky analysis, where the potential was referenced to Ag/AgCl. To prepare catalyst inks, 2 mg of the catalysts (obtained as described 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⁻² for the catalysts. All measurements were carried out in 0.5 M H₂SO₄ except for Mott–Schottky analysis, which was performed in 0.1 M Na₂SO₄.

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**Conflict of interest**

The authors declare no conflict of interest.


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