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Ruthenium(III) polyethyleneimine complexes for bifunctional ammonia production and biomass upgrading†

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As an effective strategic approach to produce ammonia (NH₃), electrocatalytic nitrogen reduction reaction (NRR) at ambient conditions through renewable energy sources (e.g. solar) has attracted significant attention, but designing an efficient electrocatalyst has been of central research interest. Herein we report the synthesis of ruthenium(III) polyethyleneimine (Ru(III)-PEI) catalysts supported on carboxyl-modified carbon nanotubes (Ru(III)-PEI@MWCNTs) through a self-assembly process driven by electrostatic forces at room temperature. Our newly designed Ru(III)-PEI@MWCNTs are employed as bifunctional catalysts for NRR and 5-hydroxymethylfurfural (HMF) oxidation. At −0.10 V vs. reversible hydrogen electrode (RHE), our Ru(III)-PEI@MWCNTs exhibited a high NH₃ yield rate of 188.90 μg_{NH₃} mg_{cat}^{−1} h^{−1} and faradaic efficiency (FE) of 30.93% at room temperature. Furthermore, owing to its favorable thermodynamics of HMF oxidation, Ru(III)-PEI@MWCNTs electrode demonstrated an impressive electrocatalytic HMF oxidation at 1.24 V, 220 mV lower than that of oxygen evolution. The two-electrode electrolyzer employing Ru(III)-PEI@MWCNTs as the bifunctional catalyst for both cathode and anode showed a current density of 0.50 mA cm^{−2} with a cell voltage of only 1.34 V over 27 hours of stable electrolysis with 94% FE for 2,5-furandicarboxylic acid (FDCA) production, suggesting an outstanding performance for NRR coupling with HMF oxidation. This work represents the first attempt at a ground demonstration of combining NH₃ production and biomass upgrading.

Introduction

Ammonia (NH₃) is widely recognized as not only an important source for industrial utilization, but also a key renewable (hydrogen) energy carrier.¹ Currently, the industrial method of NH₃ manufacture is Haber–Bosch process, which relies significantly on harsh conditions, i.e. 350–550 °C and 150–300 atm;² while the input of energy consumption is mainly from fossil fuels. In addition to the ever-increasing fuel price, significant damage to the environment, caused by the fuel-burning process, must be taken into account. Therefore, developing an efficient strategy for ammonia synthesis is of great importance. Owing to its high energy density and low liquefying pressure, nitrogen (N₂) holds specific promise for the NH₃ production. The synthesis of NH₃ via electrocatalytic nitrogen reduction reaction (NRR) under ambient conditions is sustainable and economically viable process.³ Although N₂ is the main component of the earth's

atmosphere, nitrogen reduction reaction (NRR) is difficult to occur due to the high energy required to break the N≡N triple bond and the sluggish kinetics of N₂ adsorption.^{2,4,5}

Electrocatalyst materials play a central role in the NH₃ production and excellent progress has been made in designing a wide range of efficient catalysts over the past few years.^{2,6,7} The ruthenium (Ru) based catalysts were found to be one of the most effective candidates for NRR.^{6,8} For instance, Zeng's group reported Ru single atoms distributed on nitrogen-doped carbon, which exhibited high activity for NRR due to the promoted N₂ dissociation by the atomically dispersed Ru species.⁹ Similarly, Sun's group prepared single Ru sites supported on N-doped porous C achieved an outstanding NRR activity owing to the small size of Ru and the significant role of ZrO₂ to suppress hydrogen evolution reaction (HER) process.⁶ On the other hand, as a class of interstitial compounds, metal nitrides have attracted much attention owing to their high chemical stability, unique electronic properties and outstanding electrochemical properties.^{10,11} Sun and coworkers successfully synthesized Mo₂N nanorods showing an FE of 4.5% to convert N₂ to NH₃ under ambient conditions.¹² A theoretical study on metal-nitride complex suggested that using metal complex with suitable ancillary ligands, atmospheric N₂ can directly be cleaved to yield metal-nitride which subsequently reacted with protons and electrons to yield ammonia.¹³ However, the metal center coordinated by the multidentate N ligands (MeNx) forming electroactive clusters, and further investigation is still needed to clarify its critical role in the electrochemical process.

Conventional electrocatalytic synthesis of NH₃ in alkaline media can be divided into the cathodic NRR: N₂ + 8H₂O + 6e[−] = 2NH₃H₂O + 6OH[−] and the anodic OER: 4OH[−] = O₂ + 2H₂O + 4e[−] (oxygen evolution reaction). However, the OER usually requires a high overpotential to

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achieve relatively high catalytic current density due to the sluggish kinetics.^{14, 15} Efficient electrocatalysts for both NRR and OER are necessary to reduce the overall voltage during electrolysis. Recently, many catalysts have been reported to improve NRR and OER activities; but the OER is still remained to be the bottleneck in the whole process.¹⁴⁻¹⁷ At present, IrO₂ and RuO₂ are considered as the state-of-the-art electrocatalysts for OER although they suffer from element scarcity and high cost. Inspiringly, a new strategy has been developed in the overall water splitting process by replacing OER with thermodynamically favorable biomass (such as benzylamine oxidation,¹⁶ benzyl alcohol, furfuryl alcohol, furfural, 5-hydroxymethylfurfural (HMF)¹⁵) oxidation reactions.^{14-16, 18, 19} However, till now, there has been no effort in coupling biomass upgrading with electrocatalytic NRR.

It is known that many raw biomass materials can be converted to high-value chemicals upon oxidative biomass upgrading.²⁰⁻²³ The as-produced high-value chemicals are widely used in pharmaceuticals, organic chemical synthesis, chemical industry and commodities. One typical example is the oxidation of HMF needs much lower oxidation overpotential as compared to the OER and can be transformed to a large variety of high-value products including 2,5-furandicarboxylic acid (FDCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFA), 5-formyl-2-furancarboxylic acid (FFCA), and diformylfuran (DFF), all of which are the key intermediates to synthesize bio-based polymers.^{23, 24} The main challenge is the selective oxidation of biomass-derived intermediates to their corresponding aldehydes in alkaline media. Electrocatalytic HMF oxidation is a promising strategy to gain the main product of FDCA, as it can be driven by electricity while no chemical oxidants are involved. Additionally, the thermodynamic oxidation potential of HMF is lower than that of OER, thus avoiding the production of oxygen at the anode.¹⁸ Recently, a few research attempts on electrocatalytic HMF oxidation using noble-metal-based catalysts (Pt, Au, Ru and Pd) have been published,^{20, 26-29} clearly demonstrating that the electrochemical HMF oxidation has the great potential to replace OER to match with other cathodic reactions like NRR.

Herein, we report for the first time a facile electrochemical strategy to couple NRR with HMF oxidation in alkaline condition using a novel bifunctional electrocatalyst based on ruthenium(III) polyethyleneimine (Ru(III)-PEI) supported carboxyl-modified carbon nanotubes (Ru(III)-PEI@MWCNTs). Due to the excellent catalytic performance of the Ru(III)-PEI@MWCNTs, the cell voltage of the electrocatalytic NRR coupling with HMF oxidation is 220 mV lower than that of the electrocatalytic NRR coupling with OER. In addition, Ru(III)-PEI@MWCNTs endowed the electrocatalytic NRR with a high NH₃ yield rate (188.90 μg_{NH3} mg_{cat}⁻¹ h⁻¹) and an outstanding faradaic efficiency (FE: 30.93%) at -0.10 V vs reversible hydrogen electrode (RHE). After long-time controlled potential electrolysis, we achieved remarkable FE of 94% for the production of FDCA with robust stability. Also, this work opens a new research avenue in combining biomass upgrading with NRR to achieve a high energy conversion efficiency.

Experimental section

Preparation of Ru(III)-PEI@MWCNTs

In a typical synthesis, 0.02 g RuCl₃ was added into 50 mL 0.1 M PEI solution with vigorous stirring, followed by adding 0.18 g carboxyl-modified carbon nanotubes (MWCNTs) in the mixture. After vigorously stirring for 1 h, the sample was vacuum filtered and

washed with deionized (DI) water for three times. Finally, the black product was dried at 60 °C for 12 h in the vacuum drying oven.

Electrochemical measurements

All electrochemical measurements were conducted on CHI 660D electrochemical workstation with three-electrode or two-electrode system using a saturated calomel electrode and a carbon rod as the reference electrode and counter electrode, respectively. Nitrogen reduction experiments were performed in a two-compartment cell with an N₂-saturated 0.1 M KOH solution (80 mL in each cell compartment) under ambient conditions. The H-type cell was separated by a Nafion 117 membrane. Before nitrogen reduction test, the Nafion membrane was protonated by boiling subsequently in DI water, in H₂O₂, in DI water for 1 h, in 0.5 M H₂SO₄ for 3 h, and finally in DI water for 6 h. Carbon clothes were used as the working electrode after distilling in the mixture solution of 75% H₂SO₄ and 25% HNO₃ for 10 h at 120 °C and washing several times with DI water. The electrocatalyst ink was prepared by dispersing 40 mg sample and 20 μL Nafion in 10 mL DI water. Then 20 μL black ink was dropped on the carbon cloth electrode with an area of 1×1 cm². The linear sweep voltammetry (LSV) was scanned at a rate of 10 mV s⁻¹ with or without HMF in an N₂-saturated or Ar-saturated 0.1 M KOH solution. Chronoamperometry was used to generate NH₃ during the NRR at different potentials ranging from 0 to -0.50 V with an interval of 0.10 V vs RHE. The electrolyte was purged with N₂ for 0.5 h before measurement. Pure N₂ was continuously fed into the cathodic compartment using a properly positioned sparger during the experiments. As a gas absorption liquid, 5 mM H₂SO₄ (20 mL) in another glass beaker was set at the end of the cell. The Ru(III)-PEI@MWCNTs catalyst was used as bifunctional catalyst electrodes for both anode electrocatalytic ammonia synthesis and cathode HMF oxidation for two-electrode electrolysis at 1.34 V. All electrochemical analyses were performed without iR correction.

Product analysis

Determination of the produced NH₃

After the electrocatalytic NRR, both the electrolyte and gas absorption liquid were collected and analyzed using the indophenol blue method and spectrophotometric analysis to determine the NH₃ yield.^{23, 28} For the electrolyte or gas absorption liquid, 10 mL of the above solution after the electrolysis was added into a test tube, and 400 μL of solution containing 10 g phenol in 100 mL ethanol (95%), and 400 μL of 0.5 wt% C₅FeN₆Na₂O (sodium nitroferricyanide) were successively added. Then, 1000 μL oxidizing reagent containing 800 μL of 50 g trisodium citrate and 2.5 g sodium hydroxide dissolved in 250 mL DI water and 200 μL sodium hypochlorite was also added into the above solution. The UV-Vis absorption of the electrolytes and gas absorption liquid was measured at a wavelength of 650 nm after storing in a no-light environment for 3 h. Standard NH₄Cl solutions at a series of concentrations in 0.1 M KOH and 5 mM H₂SO₄ were prepared to build the calibration curves and quantify the produced NH₃ (Fig. S1† and Fig. S2†).

The equation of the equilibrium potential:

$$E = E^{\ominus} - RT/6F \times \ln([\text{NH}_4\text{OH}]^2/[\text{H}^+]^6) + 0.059 \text{ V} \times \text{pH} \quad (1)$$

The equation of mass-normalized yield rate of NH₃:

$$\text{NH}_3 \text{ yield rate} = (C_{\text{NH}_3} \times V) / (m \times t) \quad (2)$$

The equation of FE of NH₃ production:

$$\text{FE} = 3F \times C_{\text{NH}_3} \times V / (17 \times Q) \times 100\% \quad (3)$$

where $E^{\ominus}$ is 0.092 V, the universal gas constant R is 8.314 J K⁻¹ mol⁻¹, T is the temperature in Kelvins, F is the Faraday constant (96485 C

mol^{-1}), c_{NH_3} is the sum of the NH_3 concentration in 0.1 M KOH solution and 5 mM H_2SO_4 , V is the volume of electrolyte, t is the reduction reaction time, A is the surface area of the working electrode, and Q is the total charge passed through the electrodes during the reaction duration according to total current density.

Determination of the produced hydrazine

The concentration of hydrazine in the electrolyte and gas absorption liquid was determined by the Watt and Chrisp method.^{23, 29} In both cases, 10 mL of the solution after electrolysis was taken, followed by adding 5 mL colour reagent which was prepared by mixing ethanol (300 mL), HCl (concentrated, 30 mL), and p-dimethylaminobenzaldehyde (5.99 g). After stirring for 15 min at room temperature, UV-vis absorption was carried out at a wavelength of 455 nm. Standard hydrazine monohydrate solutions at a series of concentrations in 0.1 M KOH and 5 mM H_2SO_4 were prepared to plot the calibration curves and to quantify the produced hydrazine (Fig. S3† and Fig. S4†).

Determination of the product in the anode

The HMF conversion and oxidation product during the electrochemical reactions were calculated from the anode compartment and monitored by high-performance liquid chromatography (HPLC, Shimadzu Prominence LC-20AD) containing an UV-vis detector at 262 nm wavelength.^{15, 28} 1.5 mL of the electrolyte solution was taken from the cell during chronoamperometry testing and diluted with 0.5 mL eluting solvents. Then to obtain pH below 7.0, the solution was diluted with sulfuric acid, and then 10 μL of the sample aliquots was injected directly into a 4.6 mm $\times$ 150 mm Shim-pack GWS 5 μm C 18 column.¹⁵ A mixture of eluting solvents (acetonitrile: 5 wt% acetic acid = 30%:70%, v/v) was

used as the mobile phase in the isocratic mode with a constant flow rate of 0.6 mL/min at 30 °C. The identification and quantification of the HMF and its oxidation products were determined from the calibration curves by applying standard solutions with known concentrations (Fig. S5†). The retention times were 7.1, 7.3, 7.6, 8.6, and 11.2 min for FDCA, HMFA, FFCA, HMF and DFF, respectively. The FE of the HMF conversion was calculated using the following equation:^{15, 28}

$$\text{FE} = nF N_{\text{HMF}} / Q \times 100\% \quad (4)$$

where n is the number of electron transfer for each product formation, N_{HMF} is the number of oxidation product, F is the Faraday constant (96485 C mol⁻¹), Q is the total charge passed through the electrodes during the reaction duration according to total current density.

Results and discussion

Materials synthesis and characterization

As illustrated in Scheme 1, Ru(III)-PEI@MWCNTs were obtained through a self-assembly protocol driven by electrostatic forces at room temperature. Firstly, Ru(III)-PEI species were formed by dropwise adding PEI into RuCl₃ solution. The resultant composites were then mixed with carboxylic multi-walled carbon nanotubes (MWCNTs) followed by stirring for another 30 min (see Experimental section for details). The Ru(III) mass loading of the as-prepared Ru(III)-PEI@MWCNTs was determined to be 6.2wt% using inductively coupled plasma atomic emission spectrometer (ICP-AES).

Scheme. 1 The synthetic route of Ru(III)-PEI@MWCNTs.

As shown in scanning electron microscopy (SEM) and transmission electron microscope (TEM) images of Ru(III)-PEI@MWCNTs, no aggregated particles on the MWCNTs surfaces were observed (Fig. 1A, B). The existence of nanotubes in the sample can be highlighted

by the three-dimensional (3D) network which can promote electrolyte infiltration and is potentially favorable for electrocatalysis. In the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, a large number of bright dots can

be observed, demonstrating that the isolated Ru(III)-PEI species coordinated by PEI are uniformly dispersed on the surface of MWCNTs (Fig. 1C). The highly dispersed Ru(III)-PEI species were further confirmed by the high-resolution TEM (HRTEM) (Inset in Fig. 1C). The HAADF-STEM image and the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping also reveal the homogenous distribution of the N and Ru elements on the MWCNT surface (Fig. S6†).

Fig. 1 (A) SEM, (B) TEM, (C) HAADF-STEM images of Ru(III)-PEI@MWCNTs and Inset in panel C: HRTEM image of Ru(III)-PEI@MWCNTs.

PEI can interact with RuCl₃ due to their abundant -NH₂ groups with strong coordination ability.^{29, 30} The RuCl₃ solution has a strong absorption peak at a wavelength of 400 nm (Fig. 2A), which disappears after Ru(III)-PEI complex formation.³¹ Our previous work showed that when ethanol is added into a PEI solution under acidic conditions, the white precipitate is immediately generated due to the decreased PEI solubility in acidic media.^{29, 30} The Ru(III)-PEI species were further confirmed by adding enough ethanol into Ru(III)-PEI complex solution in acid, and the brick red precipitate was obtained after freeze-drying, which is different from the milky white precipitated from PEI (Fig. S7†). We therefore found that the Ru(III)-PEI species can be very stable in strong base condition owing to the robust Ru(III)-N bonds (Fig. S8†). As a type of high molecular weight polymer (see Scheme S1), the strong coordinating capability of PEI originates from the nitrogen sites. The zeta potential of Ru(III)-PEI@MWCNTs was measured to be ca. +72.1 mV at pH 4, while the surface of carboxylated MWCNTs was negatively charged (ca. -20.6 mV at pH 4), indicating that the surface of Ru(III)-PEI@MWCNTs contains an abundant Ru(III)-PEI species. Thus, Ru(III)-PEI@MWCNTs were achieved through self-assembly driven by electrostatic forces of positively charged Ru(III)-PEI species and negatively charged carboxylated CNTs. Due to the robust Ru(III)-N bonds formed by RuCl₃ and PEI, Ru(III) were spread evenly over the skeleton of Ru(III)-PEI complex. Given that the interaction between Ru(III) and PEI, Ru(III)-PEI and carboxyl groups on CNTs, Ru(III)-PEI species were uniformly dispersed on the surface carboxylated CNTs (Fig. 1C and Inset in Fig. 1C).

To investigate the optimal coordination ratio between RuCl₃ and PEI, a series of UV-vis absorption spectra was collected (Fig. S9A†). The result showed that the absorbance decreases with the addition of PEI until the ratio of Ru(III):PEI reaches 1:10 at pH 4. With further increasing the addition of PEI, the absorbance remained to be similar,

indicating that the Ru(III) were completely complexed (Fig. S9B†). Nevertheless, no characteristic peaks for Ru(III) were detected due to the low amount of Ru(III) species in the sample (Fig. 2B), as further confirmed by X-ray diffraction (XRD). The surface compositions of the Ru(III)-PEI@MWCNTs were investigated by X-ray photoelectron spectroscopy (XPS). The N 1s signal of the Ru(III)-PEI@MWCNTs shows up at around 400.08 eV, which was slightly positive in comparison to that of the pure PEI (Fig. 2C). Given that the XPS spectrum of Ru (3d3/2 and 3d5/2) is covered by C 1s peak, the oxidation state of Ru was examined at the binding energies of Ru (3p3/2 and 3p1/2) (see Fig. 2D).³² The binding energies of Ru 3p3/2 and 3p1/2 at 484.3 and 462.0 eV for the Ru(III)-PEI@MWCNTs, respectively, were slightly negative shifted (by 1.3 eV) as compared to that of the RuCl₃ (485.6 and 463.3 eV). These shifts in the binding energies of Ru 3p and N 1s, resulted from the strong interactions between Ru and N, provides excellent evidence for the formation of Ru(III)-PEI complexes.

Fig. 2 (A) UV-vis absorption spectra of single-component RuCl₃ solution, single-component PEI solution and the mixture solution of RuCl₃ and PEI at pH=4. (B) XRD patterns of MWCNTs and Ru(III)-PEI@MWCNTs. (C) N 1s XPS spectra of Ru(III)-PEI@MWCNTs (red line) and PEI (blue-green line). (D) Ru 3P XPS spectra of Ru(III)-PEI@MWCNTs (red line) and RuCl₃ (claybank line).

Electrocatalytic NRR coupled with OER

Nitrogen reduction experiments were carried out in a two-compartment cell with an N₂-saturated 0.1 M KOH solution under ambient conditions. The H-type cell was separated by a Nafion 117 membrane. Nafion membrane can allow the H⁺ protons pass through in the KOH solution to regulate the pH of the solution as well as membrane of OH⁻ group, which were widely used in the field of electrocatalysis NRR.^{3, 5, 12, 28, 33-35} Here, our newly designed Ru(III)-PEI@MWCNTs was used as the cathodic catalyst. According to the calculation results of the Nernst equation, the standard potential for N₂ + 8H₂O + 6e⁻ = 2NH₃H₂O + 6OH⁻ is 0.194 V vs. RHE,³ which is slightly positive as compared to HER, leading to the competition between these two reactions.

The NRR electrocatalytic performance of the Ru(III)-PEI@MWCNTs was studied by LSV measurements in N₂-saturated and Ar-saturated 0.1 M KOH solutions at room temperature and atmospheric pressure (Fig. 3A). The polarization curves obtained by both N₂ and Ar bubbling were the same, but exhibits higher catalytic current, implying N₂ gas is involved in the reduction reaction initiated by Ru(III)-PEI@MWCNTs. Since the NRR and HER are competitive

reactions, it is necessary to select an optimum potential for the NRR. Thus, chronoamperometry measurements of Ru(III)-PEI@MWCNTs in an N₂-saturated 0.1 M KOH solution were conducted at different electrode potentials (Fig. 3B). The current densities increased with decreasing potentials, but when the overpotential exceeds -0.3 V vs. RHE, the current density increased significantly. This is due to the dominating HER at a relatively high potential region. The indophenol blue method was used to detect the generated NH₃ (Fig. S1–S2†),^{36, 37} and the method of Watt and Chrisp was employed to detect the possible by-product hydrazine (N₂H₄) (Fig. S3–S4†).^{37, 38} After charging at different potentials for 2 h, the UV-vis absorption spectra of the electrolytes colored with the indophenol indicator in dark condition for 3 h were recorded (Fig. 3C and 3D). The NH₃ yields and the corresponding FEs at given potentials were calculated and plotted in Fig. 3E, demonstrating a high NH₃ yield and FE at low potentials. Notably, the maximum NH₃ yield of the Ru(III)-PEI@MWCNTs was 188.90 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$ with a high FE of 30.93% at -0.1 V. This catalyst compares favorably to the behaviors of most state-of-the-art reported NRR catalysts, including Ru single-atom catalysts (120.9 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$, 29.60%)⁹, Mo₂N nanorod (78.4 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$, 4.50%)¹², sulfur dots–graphene nanohybrid (28.56 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$, 7.07%),³⁹ and few-layer black phosphorus nanosheets (FL-BP NSs) (31.37 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$, 3.09%).⁴⁰ Both NH₃ yields and FEs decreased when the potential is below -0.1 V is due to the HER process. Moreover, it should be noted that no N₂H₄ was detected in the electrolyte after charging at -0.2 V for 2 h (Fig. S10†), indicating the high selectivity of our Ru(III)-PEI@MWCNTs for N₂ toward NH₃ production.

In order to verify that the NH₃ produced by our Ru(III)-PEI@MWCNTs was generated by the reduction of introduced N₂, a series of control experiments were performed. When the reaction was carried out in an Ar-saturated electrolyte at -0.1 V vs. RHE for 2 h, the NH₃ yield rate and FE for Ru(III)-PEI@MWCNTs were 8.0 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1}$ and 0.3%, respectively, which are negligible as compared to the N₂-saturated electrolyte (Fig. S11†). To further evaluate the stability, the long-time durability of Ru(III)-PEI@MWCNTs toward electrocatalytic NRR and HER was investigated at -0.1 V for 18 h (Fig. 3F). It can be seen that the Ru(III)-PEI@MWCNTs exhibited higher initial and final current densities in the N₂-saturated solution as compared to the Ar-saturated electrolyte, further proving the NRR process. Additionally, even after 18 h test in Ar, no detectable NH₃ was observed (Fig. S12†), indicating the produced NH₃ was produced from the N₂ gas introduced into the system. After long-time durability, a negligible change in the LSV was observed as compared to the initial value, suggesting its excellent stability for NH₃ synthesis (Fig. S13†).

Fig. 3 (A) LSV curves of Ru(III)-PEI@MWCNTs in N₂-saturated and Ar-saturated 0.1 M KOH electrolyte measured at 10 mV s⁻¹. (B) Chronoamperometric curves of Ru(III)-PEI@MWCNTs in N₂-saturated 0.1 M KOH electrolyte at different potentials. (C) UV-visible absorption spectra of Ru(III)-PEI@MWCNTs after electrolysis in 5 mM H₂SO₄ gas absorption liquid at different potentials for 2 h. (D) UV-visible absorption spectra of Ru(III)-PEI@MWCNTs after electrolysis in 0.1 M KOH electrolyte at different potentials for 2 h. (E) NH₃ yields rate and FEs of Ru(III)-PEI@MWCNTs at different potentials. (F) Durability test of Ru(III)-PEI@MWCNTs in N₂-saturated 0.1 M KOH electrolyte and in Ar-saturated 0.1 M KOH electrolyte at -0.1 V.

To shed the light on the advantage of Ru(III)-PEI@MWCNTs, the NRR activities of several control groups were tested under the same conditions. The Ru(III)@MWCNTs were also synthesized in the absence of PEI, and Ru(III) species were attached to MWCNTs through the surface functional groups. PEI@MWCNTs was also prepared in the absence of RuCl₃. The chronoamperometry curves of Ru(III)-PEI@MWCNTs, Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs showed that the current density of the Ru(III)-PEI@MWCNTs is substantially higher than that of the Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs (Fig. 4A). The Ru(III)@MWCNTs showed poor stability due mainly to the weak interaction between the Ru and functional groups and the low Ru mass loading of 0.8 wt% of Ru(III)@MWCNTs. The UV-vis absorption spectra of the four electrolytes coloured with the indophenol indicator in a dark environment for 3 h were measured and plotted in Fig. 4B and 4C, demonstrating that the Ru(III)-PEI@MWCNTs exhibit the highest NH₃ content. The NH₃ yields for Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs were 36.80, 22.48 and 9.40 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$, respectively, all of which are significantly lower than that (188.90 $\mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$) of the Ru(III)-PEI@MWCNTs (Fig. 4D). Meanwhile, FEs of the Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs were 2.64, 1.42 and 0.60%, respectively, while the Ru(III)-PEI@MWCNTs displayed an outstanding FE of 30.93% (Fig. 4D). All of these findings indicate that the presence of Ru(III)-N coordination in the Ru(III)-PEI@MWCNTs plays a significant role in the NRR process. According to Sun and coworkers, the N₂ adsorption was favorable on Ru single atoms to initiate the activation process of NRR.⁶ From the XPS, the binding energies of the Ru and N showed significant shifts after the formation of Ru(III)-PEI species, confirming that the N atom

influenced the electronic structure of the Ru and thereby promoted the catalytic activity. It is worth noting that Nafion membrane may not be optimal membrane for NRR in alkaline solution. The OH⁻ can pass through the alkaline membrane to directly regulate the acid-base balance of the solution, which may be more suitable for NRR. With the development of the technology of membrane, alkaline membrane with specific performance may be extensively used in the future.

Fig. 4 (A) Chronoamperometric curves of Ru(III)-PEI@MWCNTs, Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs in N₂-saturated 0.1 M KOH electrolyte at -0.1 V. (B) UV-visible absorption spectra of Ru(III)-PEI@MWCNTs, Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs after electrolysis in 5 mM H₂SO₄ gas absorption liquid at -0.1 V for 2 h. (C) UV-visible absorption spectra of Ru(III)-PEI@MWCNTs, Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs after electrolysis in 0.1 M KOH electrolyte at -0.1 V for 2 h. (D) NH₃ yields rate and FEs of Ru(III)-PEI@MWCNTs, Ru(III)@MWCNTs, PEI@MWCNTs and MWCNTs at -0.1 V.

Electrocatalytic NRR coupled with HMF oxidation

Due to the sluggish kinetics of OER that largely restricts the overall efficiency of the electrolysis process, HMF oxidation with a thermodynamically favourable reaction was selected in this work to replace the anode OER. The electrocatalytic NRR and HMF oxidation performances of the Ru(III)-PEI@MWCNTs were evaluated in a modified H-type electrochemical cell (Fig. 5A). The results show that there is no obvious variation for the LSV curves of NRR with or without HMF oxidation (1 mM) in 1 M KOH solution (Fig. 5B), indicating that the presence of HMF oxidation does not impair the NRR performance. The simulated LSV curve of the pure NRR was obtained based on the LSV current density and the corresponding FE (obtained by a 2 h chronoamperometry test) and showed that the highest NH₃ yield and FE of NRR is at -0.1 V vs. RHE. This is in excellent agreement with the previous results shown in Fig. 3.

At the anode, the Ru(III)-PEI@MWCNTs electrodes showed an impressive electrocatalytic HMF oxidation at 1.34 V with a current density of 0.50 mA cm⁻², which is 220 mV lower than that of the OER (Fig. 5B), implying more favorable HMF oxidation than OER. For instance, the current density of the HMF oxidation was 0.50 mA cm⁻² at 1.24 V, while the current density was only 0.06 mA cm⁻² at the same potential. In general, there are two pathways for HMF oxidation: the first step is the conversion of HMF into either DFF or HMFCA. Both DFF and HMFCA can be further oxidized into FFCA and then to FDCA. Chronoamperometry was carried out in a two-electrode configuration at a 1.34 V cell voltage in an N₂-saturated 0.1 M KOH in the presence of HMF in the anode (Fig. 5C). The resulting electrolyte was analyzed by HPLC and 94% of FE was obtained for the FDCA production (Fig. S14†). Notably, for the Ru(III)-PEI@MWCNTs catalyst, a long-term controllable potential electrolysis was repeated for three times and no significant decrease in the FE was observed. After long time chronoamperometry test, XPS spectra show that the binding energies of Ru 3p and N 1s have the negligible slight shift (Figure S15 and Figure S16), confirming that Ru(III)-PEI@MWCNTs are highly stable.

Fig. 5 (A) Schematic diagram of the electrochemical system used for electrocatalytic NRR coupled with HMF oxidation and the overall cell reactions. (B) A comparison of LSV polarization curves of Ru(III)-PEI@MWCNTs for electrocatalytic NRR coupled with OER and HMF oxidation at the anode. (C) The stability test for Ru(III)-PEI@MWCNTs toward the electrocatalytic NRR coupled with HMF oxidation at 1.34 V.

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Conclusions

In summary, we have demonstrated a facile and efficient strategy to synthesize Ru(III)-PEI@MWCNTs catalysts for electrocatalytic NRR and HMF oxidation in alkaline media. Our newly designed Ru(III)-PEI@MWCNTs exhibited a high NH_3 yield rate of $188.90 \mu\text{g}_{\text{NH}_3} \text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$ and an outstanding FE of 30.93% at -0.1 V vs. RHE under ambient conditions. Owing to the more favorable thermodynamics of HMF oxidation than OER, the cell voltage reduced from 1.56 V to 1.34 V to match the electrocatalytic NRR at the cathode. The oxidation production of FDCA was found to be much more valuable than the raw HMF or O_2 from pure water splitting, while the yield and FEs for both NH_3 and FDCA were remarkably high. We anticipate that this strategy provides a guideline for promoting not only ammonia industry, but also play an important role in the future development of biomass utilization.

Conflicts of interest

There are no conflicts to declare.

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