Electronic Supplementary Information

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

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Experimental section

Reagents and chemicals
Carboxyl-modified carbon nanotubes (MWCNTs) was used as-received from XFNANO Materials Technology Company (Nanjing, China). Anhydrous ruthenium trichloride (RuCl₃), PEI (Scheme S1, † MW 10 000) and Nafion solution (5%), Ammonium sulphate ((NH₄)₂SO₄), Hydrazine (N₂H₄), Phenol, Ethanol (95%), Sodium nitroprusside, Trisodium citrate, Sodium hydroxide, Para-(dimethylamino) Benzaldehyde and Concentrated hydrochloric acid (HCl) were purchased from Sigma Aldrich (Shanghai, China). 5-Hydroxymethylfurfural (HMF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) 2,5-furandicarboxylic acid (FDCA), 5-formyl-2-furancarboxylic acid (FFCA) and diformylfuran (DFF) were purchased from Aladdin Reagent Database Inc. (Shanghai, China). Acetonitrile (High Performance Liquid Chromatography (HPLC), ≥99.9%) and acetic acid (HPLC, ≥99.8%) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Potassium hydroxide (KOH) was of analytical reagent grade and purchased from Adamas Reagent Co. Ltd. Nitrogen (N₂) and argon (Ar) were purchased from Xi'an Tenglong Chemical Reagent Co., Ltd. And carbon cloth was from Tsukuba Materials Information Laboratory. Deionized water (18 MΩ·cm) from a Barnstead E-Pure system was used in all experiments.

Instruments
The morphology and crystal structures of Ru(III)-PEI@MWCNTs were investigated using a field-effect scanning electron microscopy (FE-SEM, SU8020), transmission electron microscope (TEM, Tecnai G2 F20) and energy dispersive X-ray spectrometry (EDX). The composition of the catalysis was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, X Series 2, Thermo Scientific USA). X-ray photoelectron spectroscopy (XPS, AXIS ULTRA) was conducted using a Kratos Axis Ultra instrument to explore the surface composition and surface charging of the sample. XPS specific binding energies were calibrated to the C 1s peak of adventitious carbon at 284.6 eV. A Malvern Zetasizer Nano ZS90 system and X-ray diffraction (XRD, DX-2700) spectrometers were also used to analyse the samples used in this work. The reduction process of the Ru(III)-PEI complex was monitored using a UV-Vis absorption spectroscopy (UV-vis, Shimadzu UV2600U) and high-performance
liquid chromatography (HPLC, Shimadzu Prominence LC-20AD).

Scheme S1. Molecular structure of PEI.

Figure S1. Determination of the produced NH$_3$ in 0.1 M KOH. (A) UV-Vis absorption spectra and (B) the corresponding calibration curves for the colorimetric NH$_3$ assay using the indophenol blue method in 0.1 M KOH. The absorbance at 650 nm was used for the calibration, and the fitting curve shows good linear relation of absorbance with NH$_4^+$ ion concentration ($y = 0.2154x - 6 	imes 10^{-4}$, $R^2 = 0.999$) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of phenate indicator with NH$_4^+$ ions.
Figure S2. Determination of the produced NH$_3$ in 5 mM H$_2$SO$_4$ gas absorption liquid. (A) UV-Vis absorption spectra and (B) the corresponding calibration curves for the colorimetric NH$_3$ assay using the indophenol blue method in 5 mM H$_2$SO$_4$ gas absorption liquid. The absorbance at 650 nm was used for calibration, and the fitting curve shows good linear relation of absorbance with NH$_4^+$ ion concentration ($y=0.7920x-3\times10^{-4}$, $R^2=0.998$) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of phenate indicator with NH$_4^+$ ions.
**Figure S3.** Determination of the produced $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in 0.1 M KOH. (A) UV-Vis absorption spectra and (B) the corresponding calibration curves for the colorimetric $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ assay using the Watt and Chrisp method in 0.1 M KOH. The absorbance at 455 nm was used for calibration, and the fitting curve shows good linear relation of absorbance with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ concentration ($y=0.7110x-0.1042$, $R^2=0.998$) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of phenate indicator with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. 
Figure S4. Determination of the produced $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in 5 mM $\text{H}_2\text{SO}_4$ gas absorption liquid. (A) UV-Vis absorption spectra and (B) the corresponding calibration curves for the colorimetric $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ assay using the Watt and Chrisp method in 5 mM $\text{H}_2\text{SO}_4$ gas absorption liquid. The absorbance at 455 nm was used for calibration, and the fitting curve shows good linear relation of absorbance with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ concentration ($y=0.2220x-0.0367$, $R^2=0.998$) of three times independent calibration curves. The inset in (B) shows the chromogenic reaction of phenate indicator with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. 
Figure S5. The standard curves of FDCA, HMFCA, FFCA, HMF, DFF and levulinic acid (LeA). HMF will have a different level of hydrolysis in 0.1 M KOH and resulting in a by-product of LeA. The retention time for LeA is 10.2 s.
Figure S6. The distribution of C, N and Ru elements in the Ru(III)-PEI@MWCNTs. For clarity, some Ru(III) species are highlighted by yellow circles, which confirming Ru(III)-PEI species successfully loaded onto MWCNTs.

Figure S7. Digital photo of Ru(III)-PEI and PEI species after freeze-drying. The Ru(III)-PEI species was further confirmed by adding enough ethanol into Ru(III)-PEI complex solution in acid.
Figure S8. Digital photo of (a) Ru(III)-PEI species solution and (b) RuCl₃ solution in strong alkaline. Ruthenium hydroxide precipitation was generated when RuCl₃ solution was in strong alkaline, while Ru(III)-PEI species can still be stable in strong alkaline due to the robust Ru(III)-N bonds.

Figure S9. (A) UV-vis absorption spectra of Ru(III)-PEI species solution as a function of PEI concentration in the sample. (B) The absorbance changes with the ratio of PEI: Ru(III).
Figure S10. The yield rate of N$_2$H$_4$·H$_2$O at different potentials.

Figure S11. NH$_3$ yield rate and Faradaic efficiency of Ru(III)-PEI@MWCNTs in Ar-saturated at -0.1 V for 2 h. When the reaction proceeded in an Ar-saturated electrolyte at -0.1 V vs. RHE for 2 h, the NH$_3$ yield rate and FE for Ru(III)-PEI@MWCNTs are 8 μg$_{\text{NH}_3}$ mg$_{\text{cat.}}^{-1}$ and 0.3% respectively, which are negligible compared with that of Ru(III)-PEI@MWCNTs under N$_2$-saturated.
Figure S12. NH$_3$ yield rate and FE of Ru(III)-PEI@MWCNTs in Ar-saturated at -0.1 V for 18 h. The NH$_3$ yield rate and FE for Ru(III)-PEI@MWCNTs are 9.3 μg$_{NH_3}$ mg$_{cat.}^{-1}$ and 0.0003% respectively. There is no obvious change in the NH$_3$ yields during 18 h durability test in Ar-saturated as compared to 2 h test, indicating that the NH$_3$ produced in this system is mainly from electrochemical NRR process in N$_2$-saturated electrolyte.

Figure S13. LSV polarization curves for the Ru(III)-PEI@MWCNTs at initial and after 18 h durability test.
**Figure S14.** HPLC results for electrochemical HMF oxidation by Ru(III)-PEI@MWCNTs at 1.34 V in 0.1 M KOH solution containing 1 mM HMF at (a) 0 C, (b) 13 C, (c) 26 C and (d) 39 C.

**Figure S15.** Ru 3P XPS spectra of Ru(III)-PEI@MWCNTs after chronoamperometry test.
Figure S16. N 1s XPS spectra of Ru(III)-PEI@MWCNTs after chronoamperometry test.