Electrical Supplementary Information

**Glycerol oxidation assisted electrocatalytic nitrogen reduction: ammonia and glyceraldehyde co-production on bimetallic RhCu ultrathin nanoflakes nanoaggregates**

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Scheme S1. The molecular structure of (A) glycerol and (B) glyceraldehyde.

Scheme S2. The molecular structure of polyallylamine hydrochloride.

Fig. S1 Absolute calibration of the phenate method using ammonium solutions of known concentration as standards. (A) UV-Vis curves of phenate assays after in darkness for 3 hours at room temperature, (B) calibration curve used for estimation of NH$_3$ by NH$_4^+$ ion concentration. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH$_4^+$ ion concentration ($y = 0.214x + 0.005$) of three times independent calibration curves.
**Fig. S2** Absolute calibration of the phenate method using ammonium solutions of known concentration as standards. (A) UV-Vis curves of phenate assays after in darkness for 3 hours at room temperature, (B) calibration curve used for estimation of NH$_3$ by NH$_4^+$ ion concentration. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH$_4^+$ ion concentration ($y = 0.778x + 0.042$) of three times independent calibration curves.

**Fig. S3** Absolute calibration of the Watt and Chrisp (para-dimethylamino-benzaldehyde) method for estimating N$_2$H$_4$·H$_2$O concentration, using N$_2$H$_4$·H$_2$O solutions of known concentration as standards. (A) UV-Vis curves of various N$_2$H$_4$·H$_2$O concentration after incubated for 10 min at room temperature, (B) calibration curve used for estimation of N$_2$H$_4$·H$_2$O concentration. The absorbance at 455 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows
good linear relation of absorbance with N$_2$H$_4$·H$_2$O concentration ($y = 0.589x+0.055$) of three times independent calibration curves.

Fig. S4 Absolute calibration of the Watt and Chrisp (para-dimethylamino-benzaldehyde) method for estimating N$_2$H$_4$·H$_2$O concentration, using N$_2$H$_4$·H$_2$O solutions of known concentration as standards. (A) UV-Vis curves of various N$_2$H$_4$·H$_2$O concentration after incubated for 10 min at room temperature, (B) calibration curve used for estimation of N$_2$H$_4$·H$_2$O concentration. The absorbance at 455 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with N$_2$H$_4$·H$_2$O concentration ($y = 1.383x+0.023$) of three times independent calibration curves.

Fig. S5 EDX spectrum of RhCu-BUNNs.
Fig. S6 XPS survey spectrum of RhCu-BUNNs.

Fig. S7 Rh 3d XPS spectra of (A) RhCu-BUNNs and (B) Rh-UNNs.

Fig. S8 (A) XRD spectrum of RhCu-BUNNs after the calcination at 600 °C, (B) Enlarged XRD pattern.
**Fig. S9** Photographs of mixture of CuCl₂ + polyallylamine hydrochloride + HCHO (A) before and (B) after heating for 6 h at 140 °C.

**Fig. S10** (A) TEM image, (B) EDX mapping of the obtained products after increasing the amount of Cu⁺ precursor to Rh³⁺/Cu⁺=2:1. As observed, TEM image show an obvious phase separation, in which a large number of tiny nanocrystals are observed (Figure S6 A). Further EDX mapping analysis confirm that these tiny nanocrystals are Cu nanocrystals (Figure S6 B).

**Fig. S11** CV curve of RhCu-BUNNs in Ar-saturated 0.5 M H₂SO₄ solution at 50 mV s⁻¹.
**Fig. S12** UV-Vis absorption spectra of the electrolytes after electrolysis stained with indophenol indicator.

**Fig. S13** N₂H₄·H₂O yield rate at each given potentials.

**Fig. S14** Chronoamperometric curve of RhCu-BUNNs in 0.1 M KOH solution at -0.2 V potential for 25 h.
Fig. S15 Recycling test of RhCu-BUNNs at the potential of −0.2 V.

Fig. S16 SEM image of RhCu-BUNNs after the long-term chronoamperometry.

Fig. S17 The continuous CV curves of RhCu-BUNNs in Ar-saturated 0.1 M KOH solution at 50 mV s⁻¹.
**Fig. S18** EDX spectrum of RhCu-BUNNs after GOR.

**Fig. S19** HPLC chromatogram of the product obtained from the GOR cell in three-electrode system.

**Fig. S20** The HPLC chromatogram of the product obtained from the GOR cell in two-electrode system.