

Supplementary Information

Ultrasonic-assisted hydrothermal synthesis of RhCu alloy nanospheres for electrocatalytic urea production

Siyu Fu^{a#}, Kaibin Chu^{a,b#}, Minhao Guo^a, Zhenzhong Wu^a, Yang Wang^a, Jieru Yang^a, Feili Lai^{b*} and Tianxi Liu^{a*}

^a *The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, International Joint Research Laboratory for Nano Energy Composites, Jiangnan University, Wuxi 214122, P. R. China*

^b *Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Leuven 3001, Belgium*

* Corresponding authors (emails: feili.lai@kuleuven.be; txliu@jiangnan.edu.cn)

S. F. and K. C. contributed equally to this work.

1. Experimental procedure

1.1 Chemicals and Materials

Pluronic F-127 was purchased from Sigma-Aldrich. *N,N*-dimethylformamide (DMF) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). 5% Nafion solution was purchased from Sigma-Aldrich. Sodium hexachlororhodate (Na_3RhCl_6 , $\geq 17.1\%$) was purchased from Alfa Aesar. Copper chloride (CuCl_2 , 98%) and ascorbic acid (AA, 99%) were purchased from Adamas Reagent, Ltd. Deionized water was used as the solvent. CO_2 gas (99.999%) was purchased from Wuxi Xinxiyi Technology Co., Ltd. All chemical reagents were used as received without further purification.

1.2 Material synthesis

In a typical synthesis, 20 mg of polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO, F127) block copolymer was completely dissolved in 3.2 mL of *N,N*-dimethylformamide (DMF). The following reagents were added to the above solution in this order: 0.8 mL of hydrochloric acid (HCl, 1 M), 4 mL of sodium hexachlororhodate solution (Na_3RhCl_6 , 40 mM), 4 mL of copper chloride solution (CuCl_2 , 40 mM), and 8 mL of ascorbic acid solution (AA, 100 mM), resulting in a transparent light-brown solution. The solution was kept in a hydrothermal kettle at 100 °C for 4 h with ultrasonic treatment. Then, the sample was collected by centrifugation at 14000 rpm for 20 min, and the residual polymer was removed by five consecutive washing/centrifugation cycles with acetone and water. The procedure for the synthesis of RhCu-none nanospheres was similar to that of RhCu-uls nanospheres except for ultrasonic treatment.

Firstly, the polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO, F127) copolymer self-assembled into spherical micelles with PPO cores and PEO shells in DMF solvent. Secondly, Na_3RhCl_6 , CuCl_2 , HCl, and AA solutions were dissolved into the above solution, which was kept in a hydrothermal kettle at 100 °C for 4 h with ultrasonic treatment. Due to the different dissolution abilities of PEO and PPO segments in DMF solvent, uniform micelles can be generated for the accumulation and co-reduction of Rh^{3+} and Cu^{2+} ions, resulting in the formation of RhCu nanoclusters on the spherical micelles with the assistance of ascorbic acid as a reducing agent. Finally, the samples were collected after removing the residual polymer by consecutive washing/centrifugation cycles with acetone and water.

2. Characterizations

X-ray diffraction (XRD) patterns of samples were collected from a MiniFlex600 X-ray diffractometer with Cu K α radiation ($\lambda = 0.1542 \text{ \AA}$) under a voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectroscopy (XPS) measurements and the valence band were performed on an Axis Supra by Kratos Analytical Inc. The carbon peak at 284.8 eV was used as a reference. Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope. Energy-dispersive X-ray spectroscopies (SEM-EDS) were taken with a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected from a JEM-2100plus transmission electron microscope by applying an acceleration voltage of 200 kV. CO₂ temperature programmed desorption (CO₂-TPD) was collected from MicrotracBEL (BELCAT- II).

3. Electrochemical measurement

Electrochemical experiments in an H-type electrolytic cell were carried out by using a CHI 660E electrochemical station with three electrodes. The pretreated Nafion 117 membrane (Dupont) was used as the separator, and 0.1 M KNO₃ electrolyte was used in the experiment. Before the tests, the Nafion 117 membrane was pretreated by boiling in H₂O₂ (5%) aqueous solution at 80 °C for 1 h and ultrapure water at 80 °C for another 1 h, respectively, followed by treatment in 0.05 M H₂SO₄ for 1 h and ultrapure water for another 3 h. The catalyst (2 mg) was dispersed in 950 μ L ethanol and 50 μ L Nafion (5 wt% aqueous solutions) for 30 min under ultrasonic treatment to form uniform ink. Then, 10 μ L of catalyst ink was loaded onto a piece of carbon paper and dried naturally to obtain the working electrode. The geometric area of the working electrode was $1 \times 1 \text{ cm}^2$, and the loading amount of the catalyst was $\sim 0.02 \text{ mg cm}^{-2}$. The reference electrode was Ag/AgCl electrode containing saturated KCl solution, and the counter electrode was a carbon rod. Prior to the electrochemical testing, the electrolyte was pre-saturated by the corresponding gas. The flow rate was maintained at 15 mL min^{-1} during the catalytic process. The provided potential in this work was converted to the RHE reference scale using the equation of $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.197$.

For electrochemical urea synthesis, potentiostatic tests were carried out in CO₂-saturated 0.1 M KNO₃ (the volume of the electrolyte in the anode and cathode chamber is 30 mL for each), which was bubbled with CO₂ for 30 min before the measurement. Controlled potential electrolysis was then performed at each potential for 3 h.

4. Detection of urea production

The quantification of urea concentration is by the diacetyl monoxime method.¹ A series of standard urea solutions (0, 0.2, 0.4, 0.6, 0.8, and 1 ppm) was prepared. The color reagents are prepared as follows. Solution A: 100 mL of concentrated phosphoric acid was mixed with 300 mL of concentrated sulfuric acid and 600 mL of distilled water. Then, 100 mg of ferric chloride was dissolved in the above solution to obtain solution A. Solution B: 100 mg of thiosemicarbazide (TSC) and 5 g of diacetylmonoxime (DAMO) were dissolved in 1000 mL of distilled water to obtain solution B. For the color generation, 2 mL of solution A and 1 mL of solution B were added to 1 mL of urea-contained solution and mixed vigorously. Then, the solution was heated to 100 °C and maintained for 15 min. After cooling to 25 °C, the absorbance was acquired at 525 nm.

5. Detection of ammonia production

The quantification of ammonia concentration is by the indophenol blue method.² A series of standard solutions with ammonia concentrations of 0, 1, 2, 3, 4, and 5 ppm, and the color reagents (Color reagent A: 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate; Color reagent B: 0.05 M NaClO; Color reagent C: 1 g of sodium nitroferricyanide was dissolved in 100 g of water) were prepared. Then, 2 mL of standard solution was transferred to a glass bottle. And 2 mL of color reagent A, 1 mL of color reagent B, and 0.2 mL of color reagent C were added in turn to the above glass bottle. The absorbance was measured in the range from 500 to 800 nm after the solution was reserved in dark for 2 h, the absorbance was acquired at 661.5 nm.

6. Detection of nitrite production

The quantitative determination of nitrite is by spectrophotometric method.³ A series of

standard solutions with nitrite concentrations of 0.25, 0.50, 1, 1.5, and 2.0 ppm. The color reagent was prepared as follows: 20 g of p-aminobenzene sulfonamide was added to a mixed solution (250 mL of deionized water and 50 mL of phosphoric acid), and then 1 g of N-(1-naphthyl)-ethylenediamine dihydrochloride was dissolved in the above solution, which was transferred to a 500 mL volumetric flask and diluted to the mark. After diluting 1.0 mL of standard solution to 5 mL, 0.1 mL of color reagent was added into it, shaken, and stood for 15 min at room temperature. The absorbance of the reagent was tested through UV-vis spectrophotometry at a wavelength of 540 nm.

7. Detection of N₂H₄ production

The quantification of N₂H₄ concentration is by Watt and Chrisp method.⁴ A series of standard solutions with N₂H₄ concentrations of 0.2, 0.4, 0.6, 0.8, and 1.4 ppm, as well as the color reagent, were prepared. In detail, a mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL), and ethanol (300 mL) was used as a color reagent. The absorbance of the resulting solution was measured at 457 nm.

8. Detection of residual nitrate

The quantitative determination of nitrate is by spectrophotometric method.⁵ A series of standard solutions with nitrate concentrations of 0, 0.02, 0.05, and 1.00 mol L⁻¹ were prepared. Then, 0.1 mL of 1 M HCl and 0.01 mL of 0.8 wt% sulfamic acid solution were added into the aforementioned solutions, respectively. After holding for 15 minutes, the absorbance was detected by UV-Vis spectrophotometry at a wavelength of 220 nm and 275 nm. The final absorbance of nitrate-N is calculated based on the following equation: $A = A_{220 \text{ nm}} - 2A_{275 \text{ nm}}$.

Supplemental figures

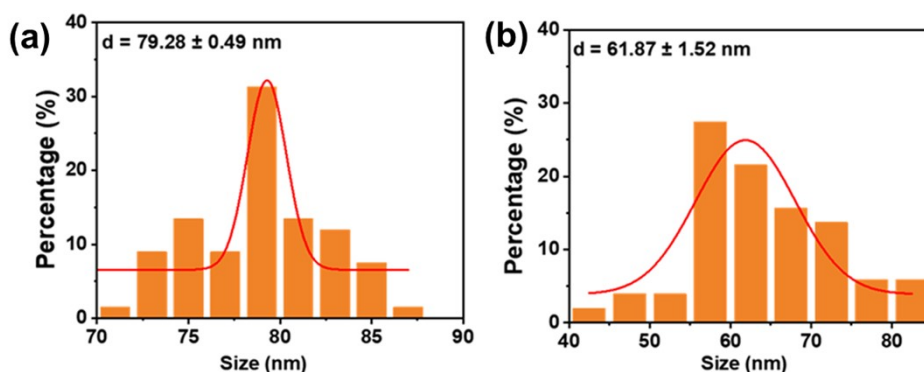


Fig. S1 Particle size distributions for (a) RhCu-none and (b) RhCu-uls nanospheres.

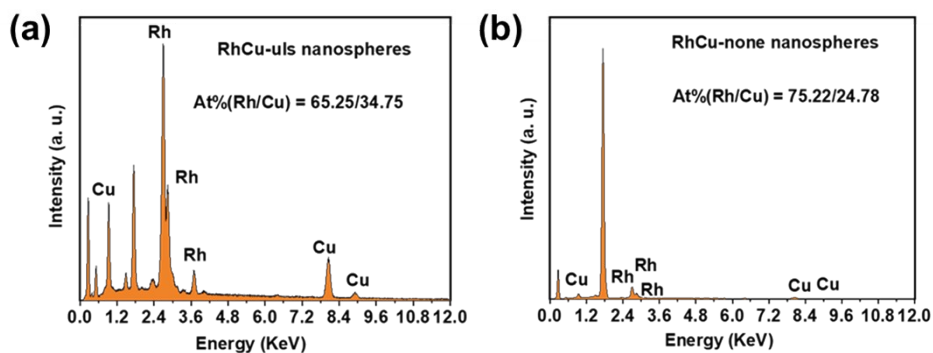


Fig. S2 Energy-dispersive X-ray spectroscopies of (a) RhCu-uls and (b) RhCu-none nanospheres.

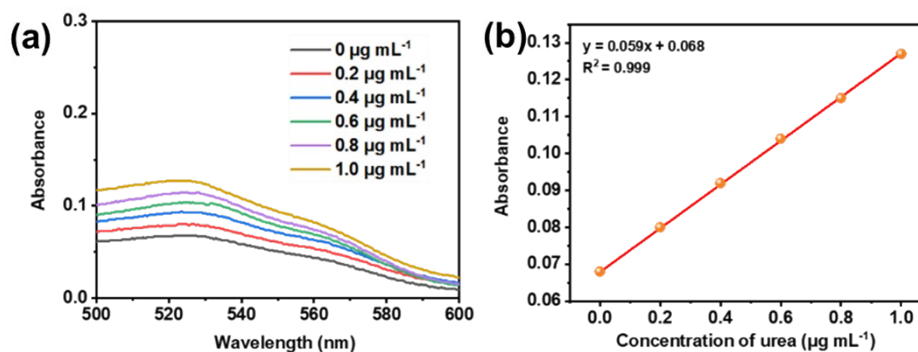


Fig. S3 (a) UV-Vis curves of diacetyl monoxime assays with different urea concentrations after heating at 100 °C for 15 min. (b) The calibration curve for urea quantification with a good linear relation ($y = 0.059x + 0.068$, $R^2 = 0.999$).

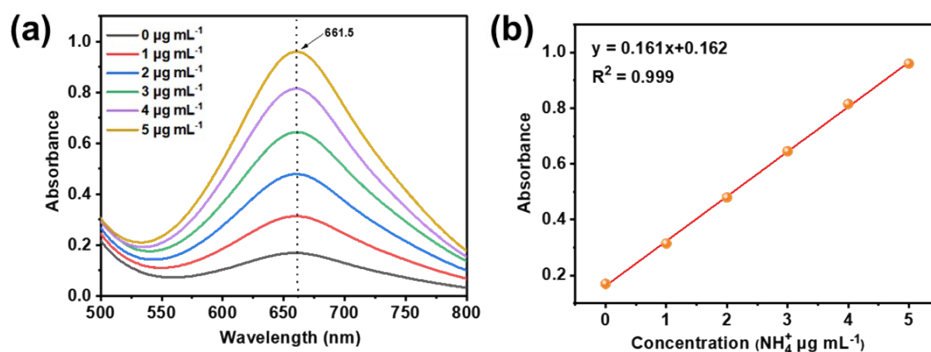


Fig. S4 (a) UV-vis curves of indophenol blue method with different NH_4^+ concentrations after standing at dark for 2 h. (b) The calibration curve for NH_4^+ quantification with a good linear relation ($y = 0.161x + 0.162$, $R^2 = 0.999$).

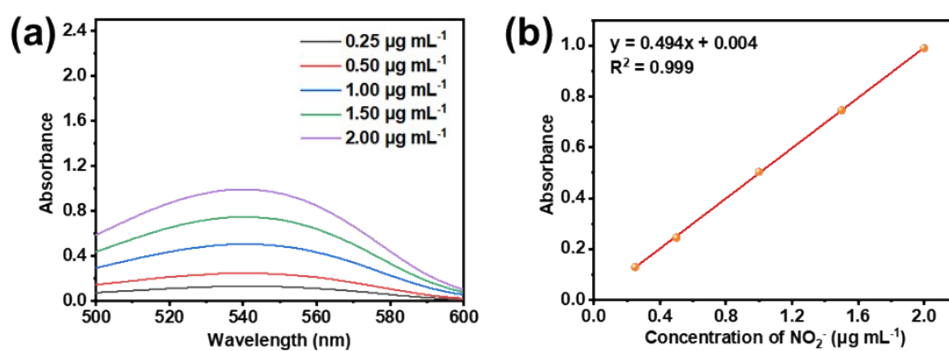


Fig. S5 (a) UV-vis curves with different NO_2^- concentrations after incubating for 15 min via spectrophotometric method. (b) The calibration curve for NO_2^- quantification with a good linear relation ($y = 0.494x + 0.004$, $R^2 = 0.999$).

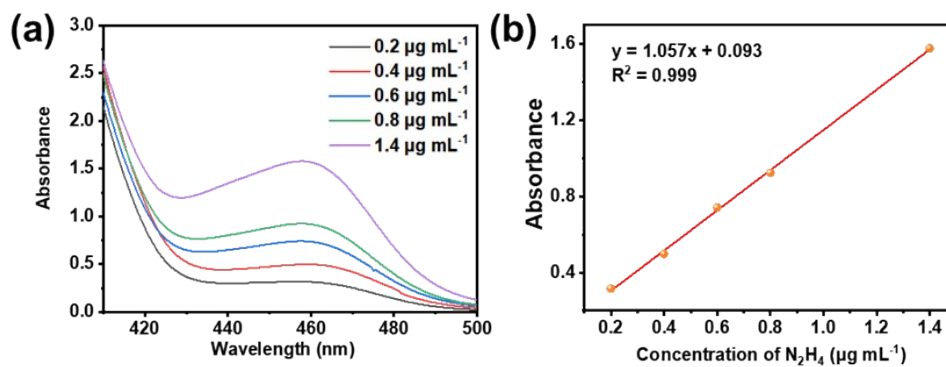


Fig. S6 (a) UV-vis curves with different N_2H_4 concentrations after addition of color reagent for 10 min via Watt and Chrisp method. (b) The calibration curve for N_2H_4 quantification with a good linear relation ($y = 1.057x + 0.093$, $R^2 = 0.999$).

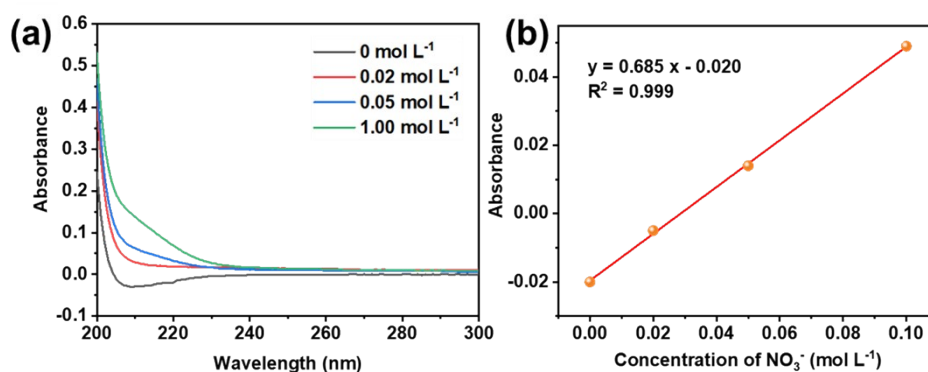


Fig. S7 (a) UV-vis curves with different NO_3^- concentrations after incubating for 15 min via spectrophotometric method. (b) The calibration curve for NO_3^- quantification with a good linear relation ($y = 0.685x - 0.020$, $R^2 = 0.999$).

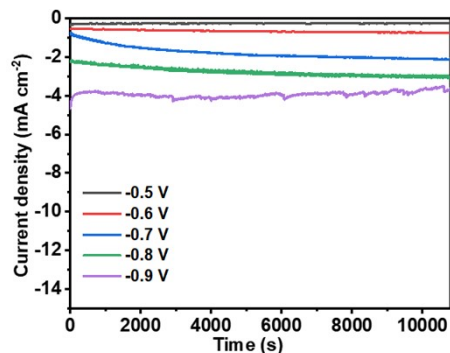


Fig. S8 Chrono-amperometry curves of RhCu-uls nanospheres at different potentials in 0.1 M KNO₃ electrolyte with CO₂ feeding gas.

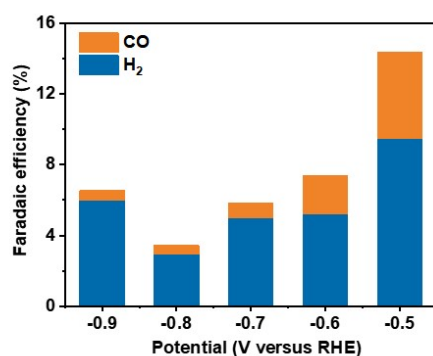


Fig. S9 The Faradaic efficiencies of CO and H₂ gases for RhCu-uls nanospheres under different potentials in 0.1 M KNO₃ electrolyte with CO₂ feeding gas.

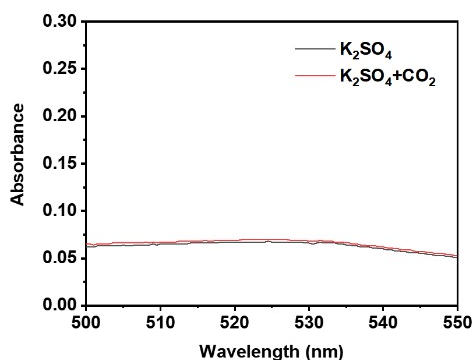


Fig. S10 UV-Vis spectra of the electrolyte (0.1 M K₂SO₄) with and without CO₂ feeding gas for RhCu-uls nanospheres after charging for 3 h by using diacetyl monoxime method.

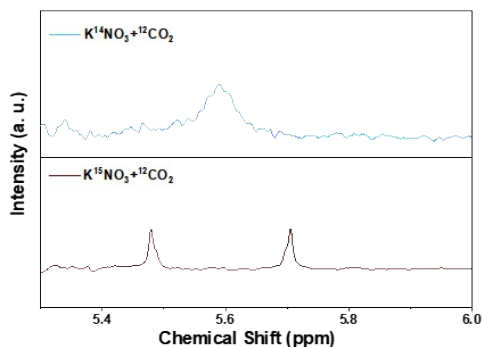


Fig. S11 ^1H NMR spectra obtained by using K^{15}NO_3 and K^{14}NO_3 as the reactants with CO_2 .

Isotope experiments were conducted to further verify the source of $\text{CO}(\text{NH}_2)_2$ production. When the reactants are K^{14}NO_3 and $^{12}\text{CO}_2$, the signature singlet peak formed by $\text{CO}(\text{NH}_2)_2$ in ^1H NMR spectrum is about 5.6 ppm. When the reactants are K^{14}NO_3 and $^{12}\text{CO}_2$, a doublet peak formed by $\text{CO}(\text{NH}_2)_2$ in ^1H NMR spectrum (ESI, Fig. S11).

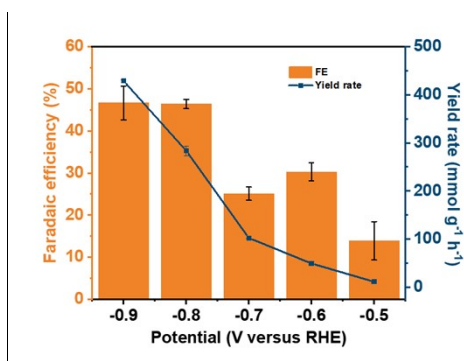


Fig. S12 Electrocatalytic performance of NH_3 synthesis for RhCu-uls nanospheres in 0.1 M KNO_3 electrolyte with CO_2 feeding gas.

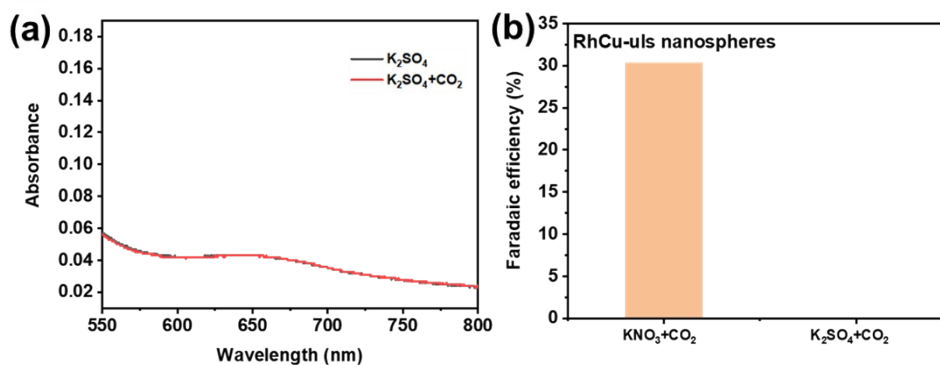


Fig. S13 (a) UV-Vis spectra of the electrolytes (0.1 M K_2SO_4) with and without CO_2 feeding gas for RhCu-uls nanospheres after charging for 3 h by using indophenol blue method. (b) Electrocatalytic performance of NH_3 synthesis for RhCu-uls nanospheres in 0.1 M KNO_3 electrolyte with CO_2 feeding gas and 0.1 M K_2SO_4 electrolyte with CO_2 feeding gas.

To exclude the interference from the external environment, a control experiment was conducted without any nitrogen source and results in no NH_3 production (ESI, Fig. S13), which indicates that the N element in NH_3 comes from the nitrate in the KNO_3 electrolyte.

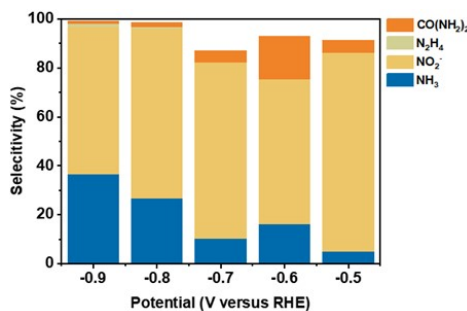


Fig. S14 N-selectivity at different potentials for RhCu-uls nanospheres in 0.1 M KNO_3 electrolyte with CO_2 feeding gas.

By calculating the product yields, the N-selectivity has been obtained as shown in ESI, Fig. S14, where the $\text{CO}(\text{NH}_2)_2$ selectivity reaches to 17.63% at -0.6 V versus RHE.

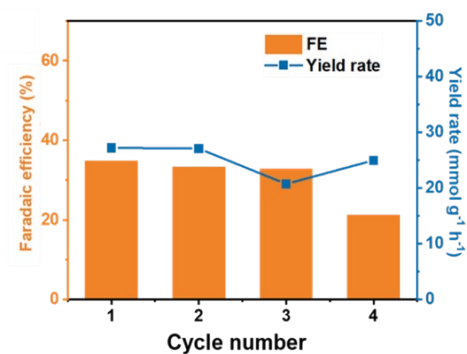


Fig. S15 Cycling electrocatalytic performance for urea synthesis of RhCu-uls nanospheres at -0.6 V versus RHE in 0.1 M KNO₃ electrolyte with CO₂ feeding gas.

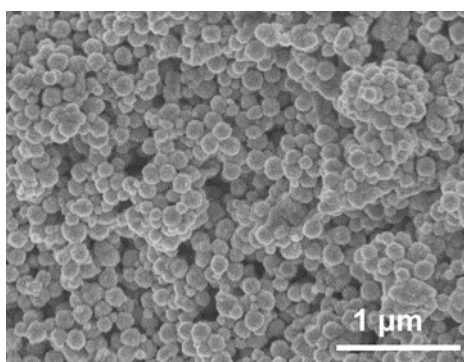


Fig. S16 SEM image of RhCu-uls nanospheres after electrocatalytic test.

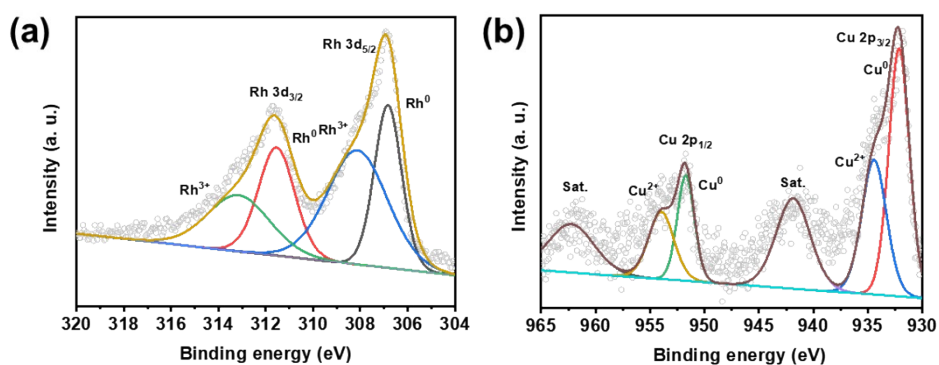


Fig. S17 High-resolution XPS spectra of RhCu-uls nanospheres after electrocatalytic test: (a) Rh 3d and (b) Cu 2p.

The RhCu-uls nanospheres after catalysis were characterized by SEM and XPS techniques. The SEM image shows that the RhCu-uls nanospheres can still maintain the morphology of nanospheres after electrocatalytic test (ESI, Fig. S16). The XPS spectra show that the contents of Rh^0 and Cu^0 in RhCu-uls nanospheres increase slightly, but their binding energy positions maintain unchanged (ESI, Fig. S17), thus indicating its well-maintained electronic structure. Overall, the RhCu-uls nanospheres exhibits superior stability for catalytic process.

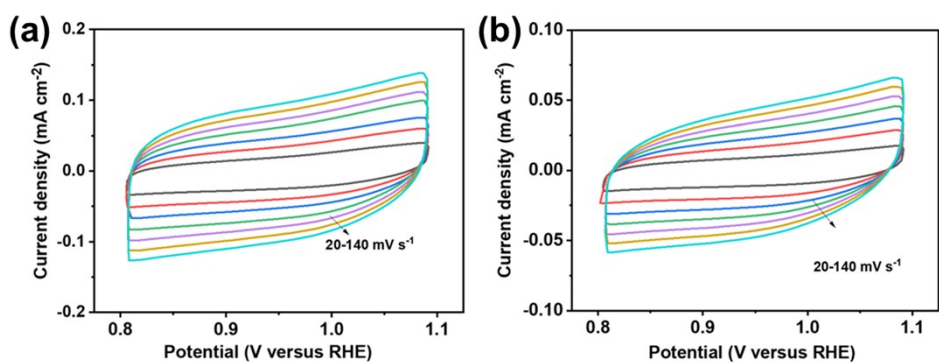


Fig. S18 Cyclic voltammogram curves of (a) RhCu-uls and (b) RhCu-none nanospheres at different scan rates from 20 to 140 mV s^{-1} .

Table S1. Summary of recent reports of electrocatalysts for urea synthesis.

Catalyst	N-source	FE _{urea} (%)	Yield (mmol h ⁻¹ g ⁻¹)	Potential (V vs. RHE)	Ref.
PdCu/TiO ₂	N ₂	8.92	3.36	-0.4	<i>Nat. Chem.</i> 2020, 12, 717-724.
Bi-BiVO ₄	N ₂	12.55	5.91	-0.4	<i>Angew. Chem. Int. Ed.</i> 2021, 60, 10910-10918.
BiFeO ₃ / BiVO ₄	N ₂	17.18	4.94	-0.4	<i>Chem. Sci.</i> 2021, 12, 6048-6058.
Te-Pd	NO ₂ ⁻	12.2	--	-1.1	<i>Nano Lett.</i> 2020, 20, 8282-8289.
Pd	NO ₂ ⁻	4.2	--	-1.2	<i>Nano Lett.</i> 2020, 20, 8282-8289.
V _o -InOOH	NO ₃ ⁻	51.0	9.87	-0.5	<i>ACS Nano</i> 2022, 16, 8213-8222.
In(OH) ₃ -S	NO ₃ ⁻	53.4	8.88	-0.6	<i>Nat. Sustain.</i> 2021, 4, 868-876.
F-CNT	NO ₃ ⁻	18	6.36	-0.65	<i>Appl. Catal. B: Environ.</i> 2022, 316, 121618.
Cu ₁ -CeO ₂	NO ₃ ⁻	N.M	52.84	-1.6	<i>Adv. Mater.</i> 2023, 2300020.
RhCu-uls	NO ₃ ⁻	34.82	26.81	-0.6	This work
RhCu-none	NO ₃ ⁻	13.27	18.53	-0.6	This work

References

1. M. Rahmatullah and T. R. C. Boyde, *Clin. Chim. Acta*, 1980, **107**, 3-9.
2. F. L. Lai, J. J. Huang, X. F. Liao, W. Zong, L. F. Ge, F. Gan, Y. T. Fang, Y. E. Miao, J. Hofkens, T. X. Liu and L. M. Dai, *Adv. Mater.*, 2022, **34**, 2201853.
3. S. Murmu, S. Paul, S. Kapse, R. Thapa, S. Chattopadhyay, N. Abharana, S. N. Jha, D. Bhattacharyya and U. K. Ghorai, *J. Mater. Chem. A*, 2021, **9**, 14477-14484.
4. U. K. Ghorai, S. Paul, B. Ghorai, A. Adalder, S. Kapse, R. Thapa, A. Nagendra and A. Gain, *ACS Nano*, 2021, **15**, 5230-5239.
5. R. Jia, Y. Wang, C. Wang, Y. Ling, Y. Yu and B. Zhang, *ACS Catal.*, 2020, **10**, 3533-3540.