

Supporting Information

Co-reduction coupling of bicarbonate and nitrate toward efficient urea synthesis

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Determination of urea

Based on the diacetyl monoxime method, the production and FE of urea are calculated using a UV-vis spectrophotometer. For the diacetyl monoxime method, two chromogenic solutions A and B are prepared separately. For solution A, 10 mg of ferric chloride, 10 mL of phosphoric acid, and 30 mL of concentrated sulfuric acid are sequentially added to 60 mL of deionized water and mixed until homogeneous. For solution B, 0.5 g of diacetyl monoxime and 10 mg of thiocarbazon are dissolved in 100 mL of deionized water. 2 mL aliquot of the post-test electrolyte is mixed with 2 mL of solution A and 1 mL of solution B. This mixture is placed in an air blast drying oven at 100 °C for 15 minutes. After cooling, the absorbance of the solution at 519 nm is measured using a UV-vis spectrophotometer. Typically, a series of standard urea solutions with known concentrations of 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ppm (where 1 ppm = 1 µg ml⁻¹) are prepared in a 0.1 M KNO₃ and 0.1 M KHCO₃ aqueous solution. These standards are used to establish a calibration curve for determining the urea concentration in the samples. The resulting absorbance-concentration relationship, for instance, in the context of 0.1 M KNO₃ and 0.1 M KHCO₃ as the electrolyte, can be expressed as $y = 0.0573x + 0.01131$, where y represents absorbance and x denotes the concentration of urea. This equation allows for the quantitative determination of urea in the sample based on the absorbance at 519 nm.

Determination of NH₃

Conventionally, the quantification of byproduct NH₃ is accomplished via the indophenol blue method. In this process, 2 mL of the electrolyte after undergoing a 1-hour reaction period, is combined with a mixture containing 2 mL of 1 M NaOH solution, which has been supplemented with 5 wt.% by salicylic acid and 5 wt.% potassium sodium tartrate tetrahydrate (C₄H₄O₆KNa·4H₂O) solution. Subsequently, 1 mL of 0.05 M sodium hypochlorite (NaClO) solution is added to the blend, followed by 0.2 mL of 1 wt.% sodium nitroprusside dihydrate (C₅FeN₆Na₂O) solution. After allowing the resulting solution to stand in darkness for two hours, its UV-visible absorption spectra are analyzed. To establish the calibration curves, the absorbance at 654 nm of standard solutions containing varying concentrations of ammonia (in the form of NH₄Cl) is measured.

Determination of NO₂⁻

The concentration of NO₂⁻ is quantified employing the Griess assay in conjunction with UV spectrophotometry. The Griess reagent is prepared by dissolving 0.1 g of N-(1-naphthyl) ethylenediamine dihydrochloride, 1.0 g of sulfanilamide, and 5 mL of H₃PO₄ in 50 mL of deionized water. In a typical procedure, 5 mL of this prepared Griess reagent is mixed with 1 mL of electrolyte, which has been diluted at a suitable multiple to account for various potential concentrations. After allowing the mixture to stand for 10 minutes, the UV spectroscopy technique is utilized to measure the concentration of NO₂⁻ at the wavelength of 540 nm.

Calculation of urea yield rate and Faradic efficiency

The average yield of urea, NH₃ and NO₂⁻ are calculated from the absorbance measured in the ultraviolet spectrum by the following formula.

$$R_{urea} = \frac{c_{urea} \times V}{t \times m} \#(1)$$

$$R_{NH_3} = \frac{c_{NH_3} \times V}{t \times m} \#(2)$$

$$R_{NO_2^-} = \frac{c_{NO_2^-} \times V}{t \times m} \#(1)$$

In this equation, the average yield rates of urea, NH₃, and NO₂⁻ (µg/mL) are calculated based on their respective measured concentrations; V (mL) is the total volume of the electrolyte, t is the time (h) for electrocatalysis and m is the catalyst loading (mg).

The Faradaic Efficiency (FE) represents the proportion of electrons transferred specifically for the formation of products compared to the total current passing through the circuit. Given that the production of one urea molecule necessitates 16 electrons, one NH_3 molecule requires 8 electrons, and one NO_2^- molecule demands 2 electrons, the FE for urea, NH_3 , and NO_2^- can be individually computed as follows:

$$FE_{\text{urea}}(\%) = \frac{(16 \times F \times c_{\text{urea}} \times V)}{60.06(\text{g/mol}) \times Q} \times 100\% \quad (4)$$

$$FE_{\text{NH}_3}(\%) = \frac{(8 \times F \times c_{\text{NH}_3} \times V)}{17(\text{g/mol}) \times Q} \times 100\% \quad (5)$$

$$FE_{\text{NO}_2^-}(\%) = \frac{(2 \times F \times c_{\text{NO}_2^-} \times V)}{46(\text{g/mol}) \times Q} \times 100\% \quad (6)$$

Here, F signifies the Faraday constant, which has a value of $96485.3 \text{ C mol}^{-1}$, and Q represents the cumulative charge that has traversed the working electrode, measured in Coulomb (C).

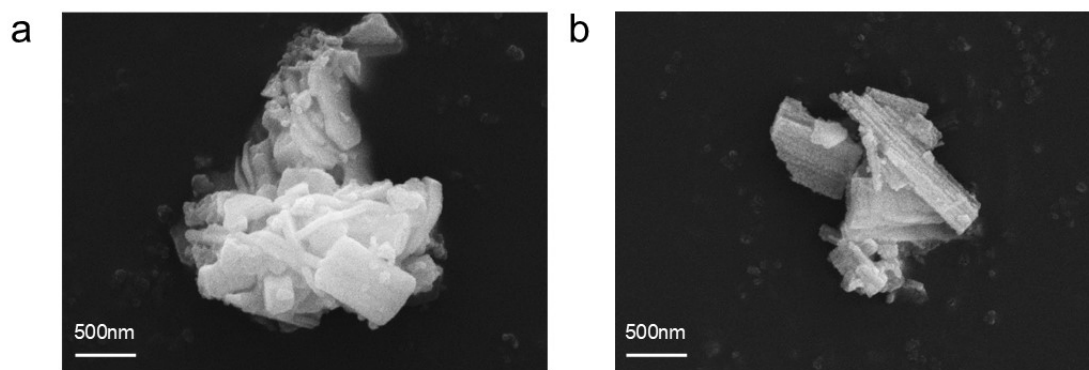


Figure S1 SEM image of (a) Cu-WN; (b) WN.

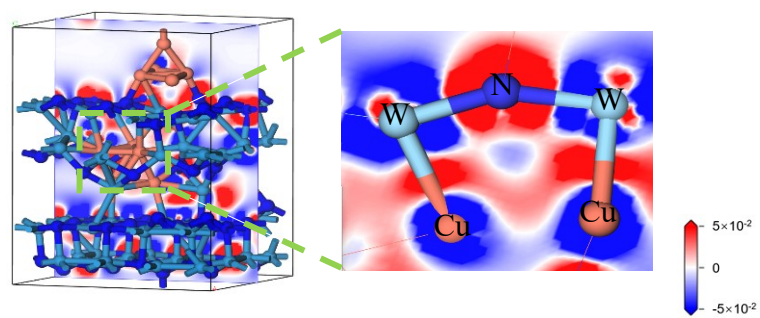


Figure S2 Charge density difference analysis for Cu-WN.

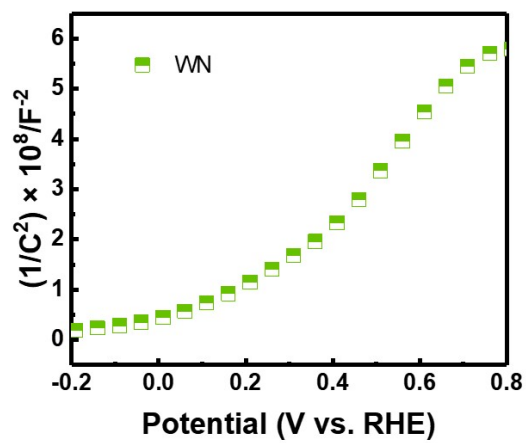


Figure S3 Mott-Schottky plots of WN.

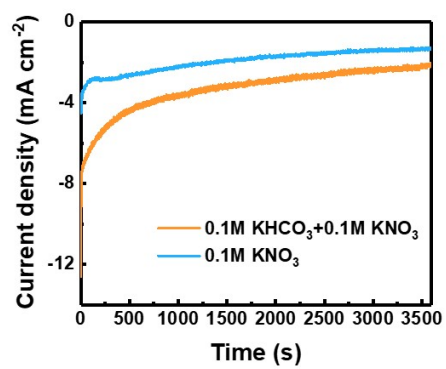


Figure S4 Chronoamperometry curves of Cu-WN samples under different electrolytes conditions.

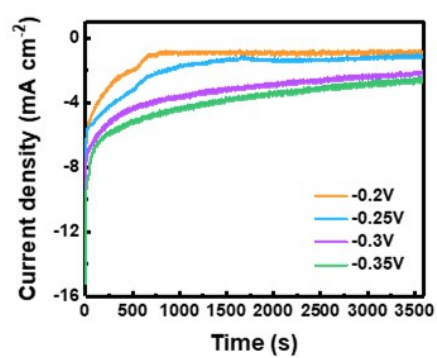


Figure S5 Chronoamperometry curves of Cu-WN samples under different potentials conditions.

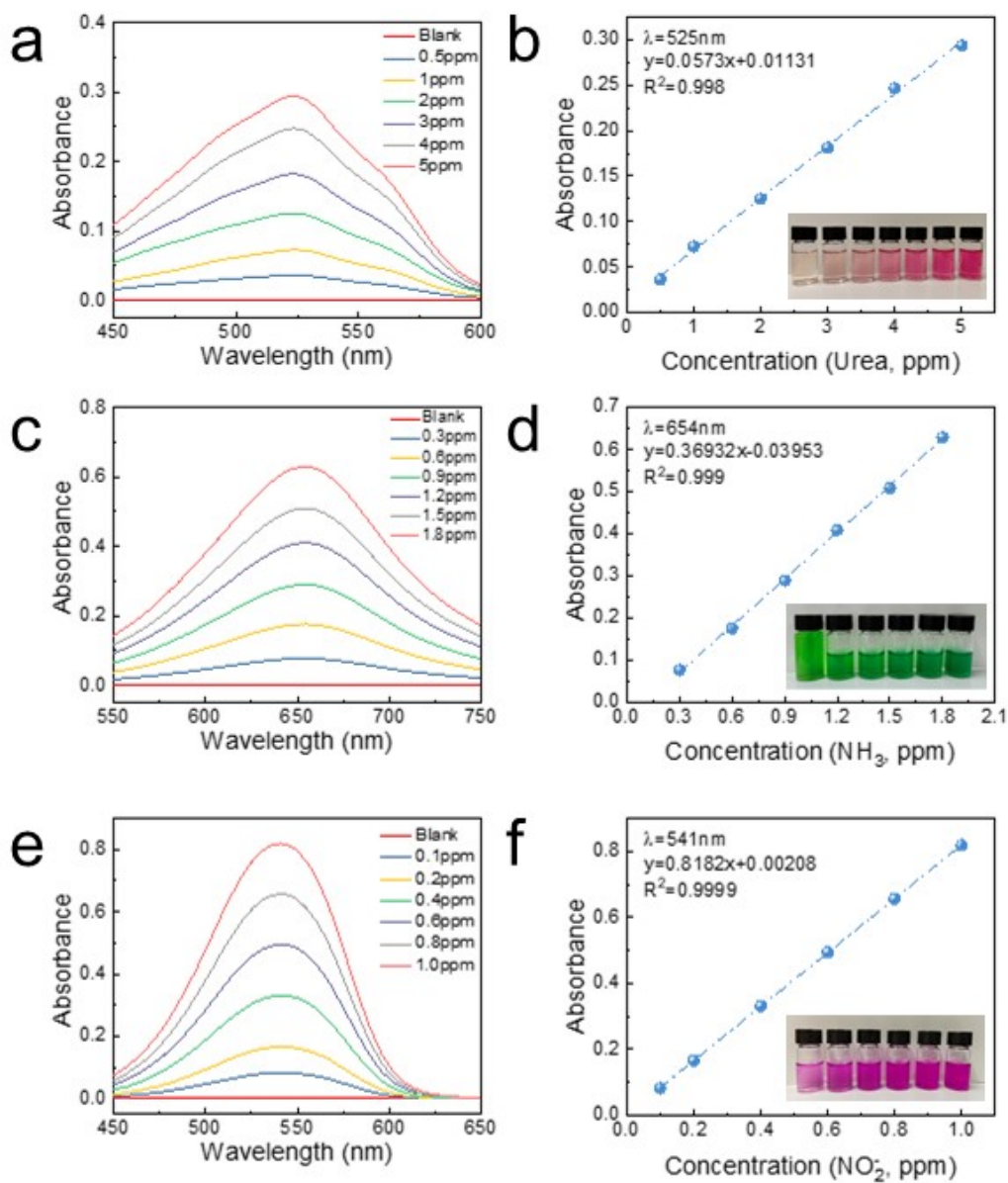


Figure S6 UV-spectrum curves and linear standard curves corresponding to different concentrations of (a,b) urea, (c,d) NH_3 , (e,f) NO_2^- .

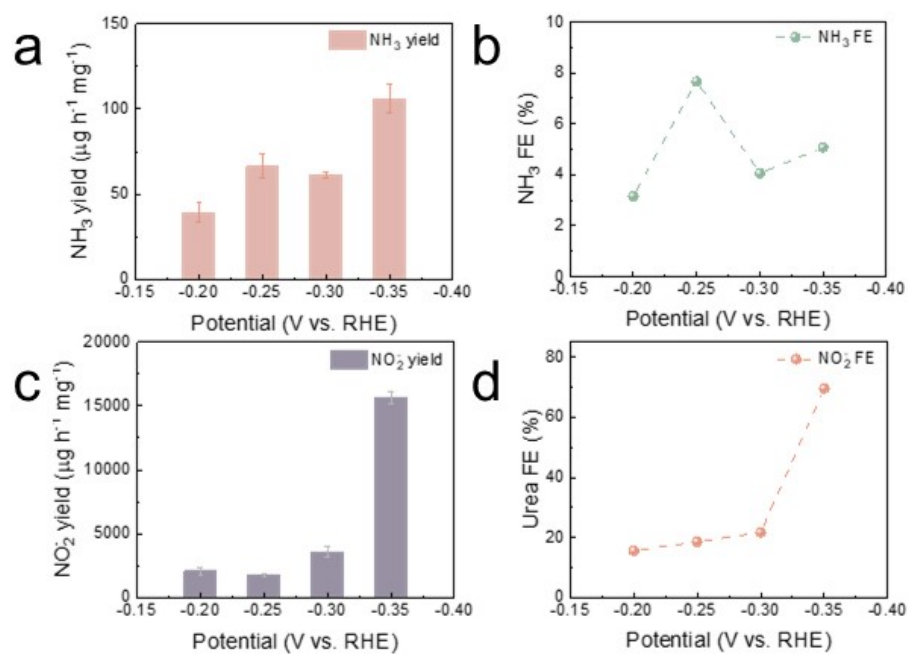


Figure S7 By-product yield and FE of (a,b) NH_3 and (c,d) NO_2^- .

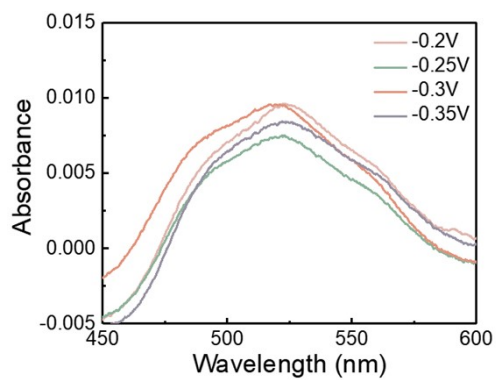


Figure S8 The absorbance of urea in the electrolytic solution of WN samples after electrolysis is measured by ultraviolet spectrophotometer.

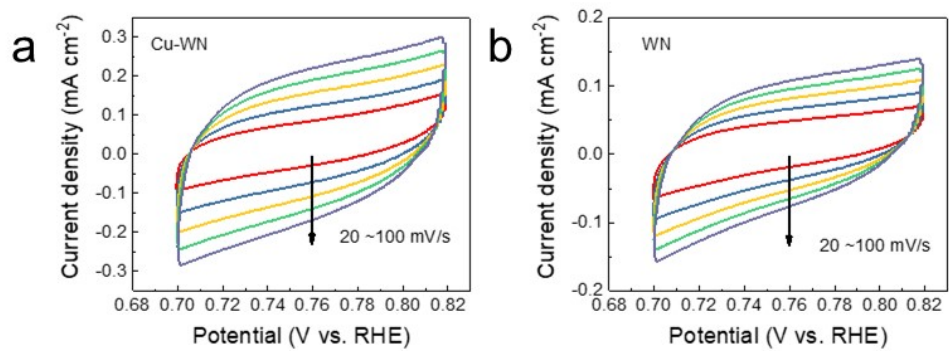


Figure S9 Electrochemically active specific surface (ECSA) of (a) Cu-WN and (b) WN.