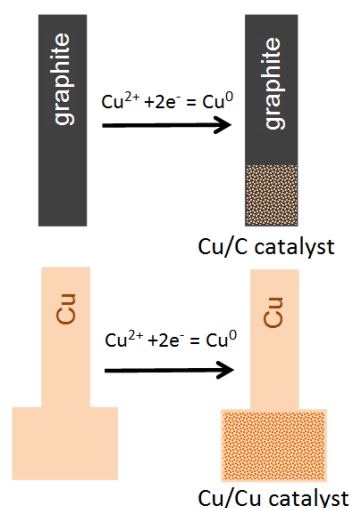


## Electrodeposited copper catalysts for the sustainable electrochemical reduction of nitrate to ammonia

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### The electrode preparation

All reagents: sodium nitrate ( $\text{NaNO}_3$ , reagent grade), sodium sulfate ( $\text{Na}_2\text{SO}_4$ , reagent grade) and copper(II) sulfate ( $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ , reagent grade), were used without further purification. Distilled water was used for all experiments. Graphite plates measuring  $50 \times 7 \times 1$  mm ( $S = 1 \text{ cm}^2$ ) or copper foil measuring  $10 \times 20 \times 0.1$  mm were used as a base for preparing electrocatalysts. The conditions for carrying out the electrochemical deposition are presented in the main article, and the scheme for the fabrication of the two main electrocatalysts is shown in Figure S1.



**Figure S1.** The scheme for the fabrication of the two main electrocatalysts by electrochemical deposition of copper on graphite plate (Cu/C) and copper foil (Cu/Cu) substrates.

Before copper deposition, the substrates were prepared and cleaned.

#### *Graphite substrate preparation.*

The graphite sample surface was cleaned by mechanical grinding, rinsed with distilled water, then rinsed with acetone and air-dried. The electrode working area was  $1 \text{ cm}^2$ .

#### *Copper foil preparation.*

The copper foil surface was pre-etched in a mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (1 : 1, v/v) for 1 min, and then for 10 s in a mixture of concentrated  $\text{H}_2\text{SO}_4$  and 10 wt%  $\text{HCl}$  to remove the natural oxide. The electrode working area was  $1 \text{ cm}^2$ .

After copper deposition, the electrodes were rinsed in distilled water and dried to constant weight.

### The electrochemical studies

An Autolab 302N potentiostat-galvanostat with Nova 2.1.7 software (Metrohm, Netherlands–Switzerland) was used for all electrochemical measurements and electrochemical synthesis under ambient conditions. A silver chloride electrode ( $\text{Ag}/\text{AgCl}$ ) served as the reference electrode, and a platinum plate as the auxiliary electrode. A PS-20 potentiostat-galvanostat (SmartStat, Chernogolovka, Russia) was additionally used as an auxiliary device. A three-electrode standard electrochemical cell was filled with 60 ml of 0.05 M  $\text{Na}_2\text{SO}_4$  + 1.2 mM  $\text{NaNO}_3$  electrolyte and degassed with Ar (99.999%)

for 30 min. Polarization curves were recorded by linear voltammetry with a scan rate of 50 mV s<sup>-1</sup>. To study the Faradaic efficiency, chronoamperometry (*j-t*) was performed at different potential values for 1 h. The current density was obtained by normalization taking into account the geometric area of the working electrode.

Below are the formulas for calculating the Faradaic efficiency (FE), ammonia yield rate (yield) and selectivity applicable to the NO<sub>3</sub>RR process.

$$FE(NH_3) = \frac{8 \cdot F \cdot n(NH_3)}{Q}, \quad (S1)$$

where:

- 8 is the number of electron transfers required to form 1 mol of NH<sub>3</sub>;
- F* is the Faraday constant (96 485 C mol<sup>-1</sup>);
- n(NH<sub>3</sub>)* is the amount (mol) of NH<sub>3</sub>;
- Q* is the total charge passed through the working electrode.

$$yield(NH_3) = \frac{C(NH_3) \times V}{17 \times t \times S}, \quad (S2)$$

where:

- C(NH<sub>3</sub>)* is the mass concentration (mg dm<sup>-3</sup>) of ammonia (calculated using UV-VIS spectra);
- V* is the volume of electrolyte;
- t* is the NO<sub>3</sub>RR electrolysis time (h);
- S* is the geometric area of the working electrode (1 cm<sup>2</sup>).

$$selectivity = \frac{C(NH_3)}{C_0 - C(NO_3^-)_t}, \quad (S3)$$

where:

- C(NH<sub>3</sub>)* is the mass concentration (mg dm<sup>-3</sup>) of ammonia (calculated using UV-VIS spectra);
- C<sub>0</sub>* is the nitrate concentration (mg dm<sup>-3</sup>) at the beginning of the NO<sub>3</sub>RR process;
- C(NO<sub>3</sub><sup>-</sup>)<sub>t</sub>* is the nitrate concentration (mg dm<sup>-3</sup>) at time *t*.

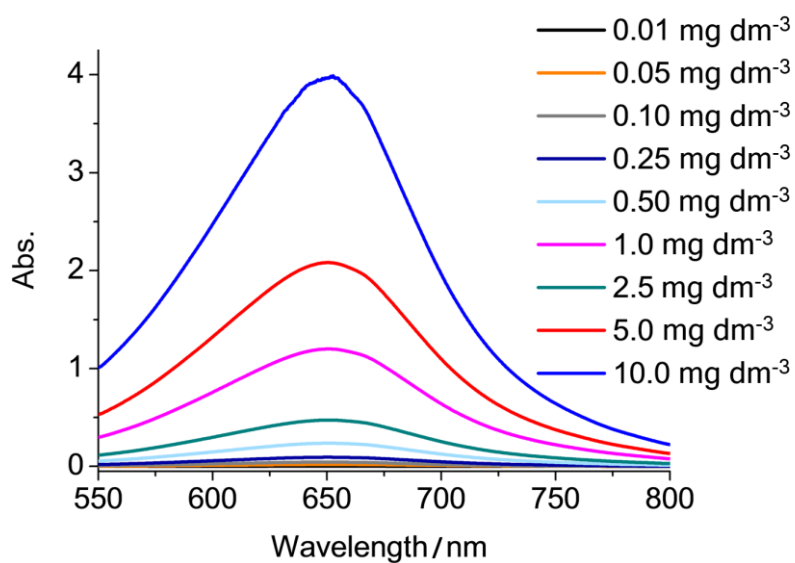
### The detection of ammonia

NH<sub>3</sub> content was determined using the indophenol method, as described previously.<sup>S1</sup> To quantify ammonia content, a calibration curve was constructed using different NH<sub>3</sub> concentrations of in the electrolyte. The determination was based on the difference in absorption intensity of the peak at 652 nm using a Shimadzu UV-3600 Plus spectrophotometer (Shimadzu, Japan). Full details are provided below, as well as in the previous recent work by the present authors.<sup>S1</sup> The detailed method described in that study is cited below:

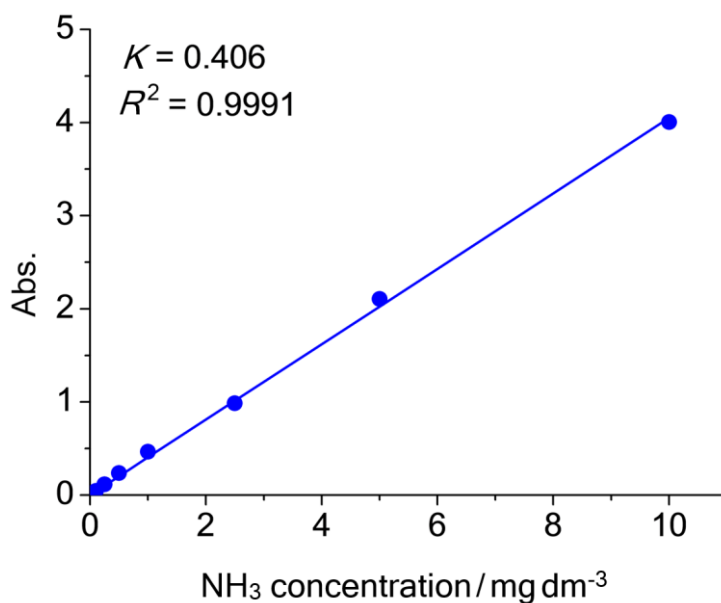
The detection of the ammonia content after NO<sub>3</sub>RR was carried out using the indophenol method, according to the methodology<sup>5</sup>. UV-vis absorption spectra (**Figure S2**) were recorded using a Shimadzu 3600 Plus spectrophotometer (Shimadzu, Japan) in a standard 1 cm quartz cuvette. Two milliliters of 5 wt% sodium salicylate in 1.0 M NaOH was added to 2 ml of the tested solution, then 1 ml of 0.05 M NaClO and Na<sub>2</sub>[Fe(NO)(CN)<sub>5</sub>] (0.2 ml, 1 wt%) was added. The solutions were kept at 40 °C for 1 h. The absorption maximum is observed at λ = 652 nm, for which a calibration graph was plotted. The resulting calibration graph is described by the equation:

$$y = 0.4217x + 0.0641 (R^2 = 0.9993),$$

and shows a good linear relationship between the absorbance value and  $\text{NH}_3$  concentration in the range from 0.25 to  $10 \text{ mg dm}^{-3}$  (**Figure S2**).



**Figure S2.** The detection of ammonia: UV-VIS absorption spectra for standard  $\text{NH}_3$  concentrations.



**Figure S3.** The detection of ammonia: calibration line for  $\text{NH}_3$  testing.

## Reference

S1 I. Kuznetsova, O. Lebedeva, D. Kultin, M. Mashkin, K. Kalmykov and L. Kustov, *Int. J. Mol. Sci.*, 2024, **25**, 7089; <https://doi.org/10.3390/ijms25137089>.