A novel 3D-CB/HEC-CH@Cu hybrid electrode for sensitive and rapid ammonia nitrogen detection in environmental water.

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Figure S1. Effect of the square wave amplitude on the voltametric profiles. (a) Response obtained at an amplitude of 75 mV, showing signal distortion and peak splitting. (b) Response obtained at the optimized amplitude of 50 mV, exhibiting a well-defined and symmetric peak suitable for analytical measurements. Signal identification: copper background (▬); 0.7 mg/L AN (▬), 3.5 mg/L AN (▬), 7 mg/L AN (▬), lines correspond to the increasing additions of the standard solution.

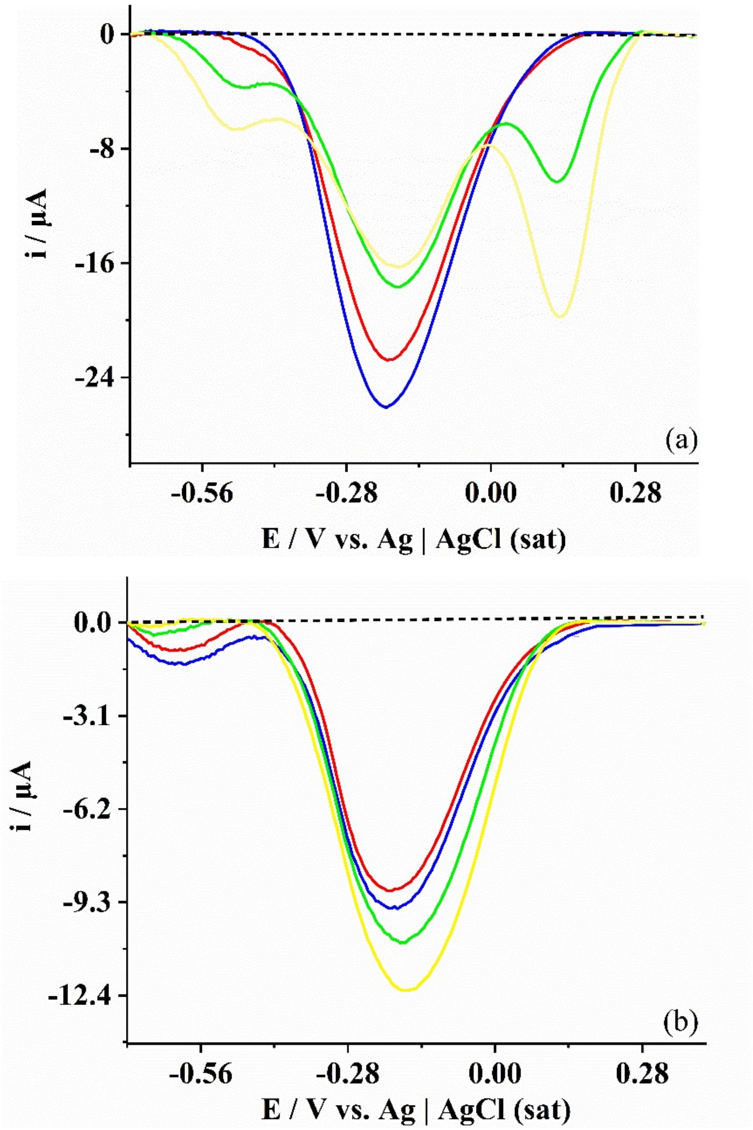

Figure S2. (a) Baseline-corrected SWV responses (n = 3) obtained after injections of standard solutions containing increasing concentrations of AN (0.014 to 0.07 mg/L) at 3D-CB/HEC–CH@Cu electrode, using 0.10 M borate buffer (pH 9) as the supporting electrolyte (- - -). (b) Calibration curve of AN (r = 0.997), obtained from the integration of the net peak areas, calculated by subtracting the copper background (▬) contribution from each signal. SWV conditions: see Fig. 4.

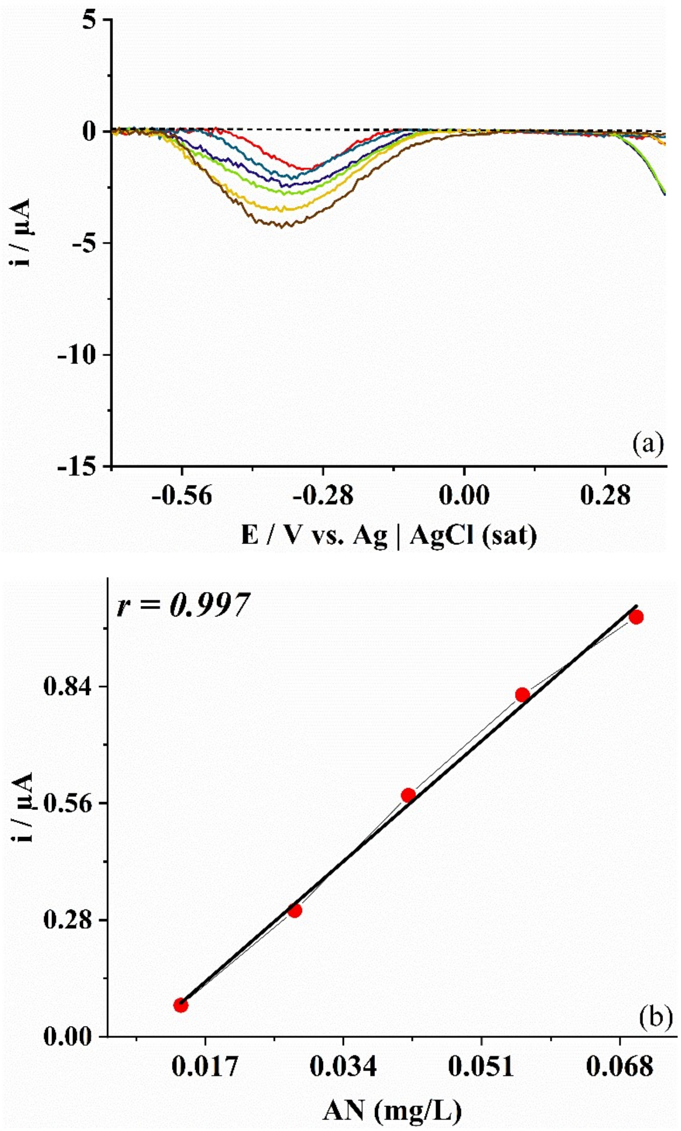

Table S1: Triplicate net peak areas for AN standards (0.7–20.4 mg/L) measured by SWV in 0.10 M borate buffer (pH 9). obtained by integrating signals after subtraction of the copper background; data used to construct the calibration curve in Fig. 5b.

Repetition	Peak area (µA) - R1	Peak area (µA) – R2	Peak area (µA) – R3	Mean area (µA)	Net Signal (µA)
Cu^{2+} electrodeposited	2.39	2.42	2.45	2.42	-
0.7 mg/L	2.72	2.75	2.78	2.75	0.34
3.5 mg/L	3.08	3.12	3.16	3.12	0.70
7 mg/L	3.68	3.73	3.78	3.73	1.31
10.3 mg/L	4.25	4.29	4.33	4.29	1.88
13.7 mg/L	4.80	4.85	4.90	4.85	2.43
17 mg/L	5.30	5.36	5.42	5.36	2.94
20.4 mg/L	5.88	5.95	6.02	5.95	3.53

Table S2: Raw data (n = 10 successive runs per level) for intra- and inter-day precision and response stability of the 3D-CB/HEC–CH@Cu SWV method at 0.7 and 20.4 mg/L AN; used to derive the summary statistics (mean. SD. RSD%) in Table 1.

Series	Concentration (mg/L)	Peak area (µA) - R1	Peak area (µA) - R2	Peak area (µA) - R3	Peak area (µA) - R4	Peak area (µA) - R5	Peak area (µA) - R6	Peak area (µA) - R7	Peak area (µA) - R8	Peak area (µA) - R9	Peak area (µA) - R10

Intra-day	0.7	2.98	3.19	3.18	3.25	3.18	3.23	3.21	3.11	3.14	3.12
Intra-day	20.4	4.67	4.66	4.68	4.46	4.38	4.32	4.32	4.32	4.35	4.27
Inter-day	0.7	3.26	3.16	2.97	3.12	3.18	3.27	3.13	3.18	3.16	2.95
Inter-day	20.4	4.95	4.49	4.42	4.50	4.35	4.34	4.42	4.32	4.32	4.33

Table S3: Raw data for the selectivity study. Measurements (n=3) of the sensor response (µA) in the presence of the target analyte AN) and various potential interfering species (NO_3^-. NO_2^-. NO_3^-+ NO_2^-. Cl^- and SO_4^{2-}).

Peak area (µA)	AN	NO_3^-	NO_2^-	NO_3^-+ NO_2^-	Cl^-	SO_4^{2-}
R1	4.32	4.33	4.48	4.38	4.33	4.35
R2	4.35	4.20	4.47	4.41	4.38	4.32
R3	4.27	4.50	4.49	4.35	4.32	4.33
Mean	4.32	4.34	4.48	4.38	4.34	4.33

Table S4: Triplicate measurements used to assess robustness by perturbing the nominal condition (28 °C. Analyst 1. 0.10 M) to 30 °C. Analyst 2. and 0.12/0.09 M electrolyte. One-way ANOVA (α = 0.05) indicated no statistically significant differences in sensor response.

Parameter	Condition	R1	R2	R3	Mean
Nominal	Control	4.32	4.35	4.27	4.32
Temperature	28°C (Nominal)	4.32	4.35	4.27	4.32
	30°C	4.38	4.41	4.35	4.38
Analyst	Analyst 1 (Nominal)	4.32	4.35	4.27	4.32
	Analyst 2	4.38	4.39	4.35	4.37
Electrolyte Concentration	0.1 M (Nominal)	4.32	4.35	4.27	4.32
	0.12 M	4.33	4.20	4.50	4.34
	0.9 M	4.32	4.20	4.32	4.28

Table S5: Raw data (net peak areas. n = 3) for the standard-addition calibration in Fig. 7b—fish-farming water at 0 µM plus AN spikes of 2.5–20 mg/L—measured by SWV in 0.1 M borate (pH 9) after Cu-background subtraction and signal integration.

Repetition	Peak area (µA) - R1	Peak area (µA) – R2	Peak area (µA) – R3	Mean area (µA)	Net Signal (µA)
Cu^{2+} electrodeposited	1.53	1.54	1.49	1.52	-
Real sample	2.99	2.72	3.25	2.99	1.45
2.5 mg/L	3.34	3.32	3.26	3.30	1.77
5 mg/L	3.49	3.49	3.55	3.51	1.97
7.5 mg/L	3.68	3.70	3.69	3.69	2.16
10 mg/L	3.91	3.91	3.83	3.89	2.35
12.5 mg/L	4.08	4.09	4.08	4.08	2.55
15 mg/L	4.28	4.27	4.31	4.29	2.76
17.5 mg/L	4.42	4.49	4.48	4.46	2.93
20 mg/L	4.68	4.69	4.69	4.69	3.16

Table S6: Concentrations (n=3) found from the standard addition fortification study used for recovery calculations. These data were used to calculate the final Recovery (%) values presented in the main manuscript (Table 3). The recovery was calculated based on the ratio between the experimentally found concentration and the theoretical concentration for each spike level.

Concentration (µM)	Net Signal (µA) - R1	Net Signal (µA) – R2	Net Signal (µA) – R3	Mean area (µA)
Real sample	1.47	1.41	1.49	1.46

2.5	1.67	1.60	1.68	1.65
10	2.26	2.19	2.27	2.24
20	3.06	3.01	3.08	3.05