Braided Copper Cobaltite/MWCNT Composites Enable Acetylcholine Detection at Sub-Nanomolar Levels *In Vitro*

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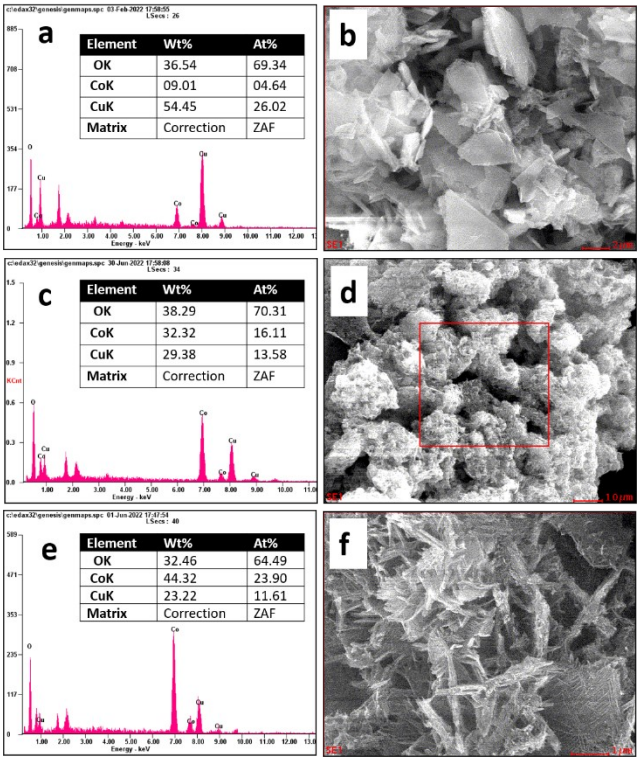
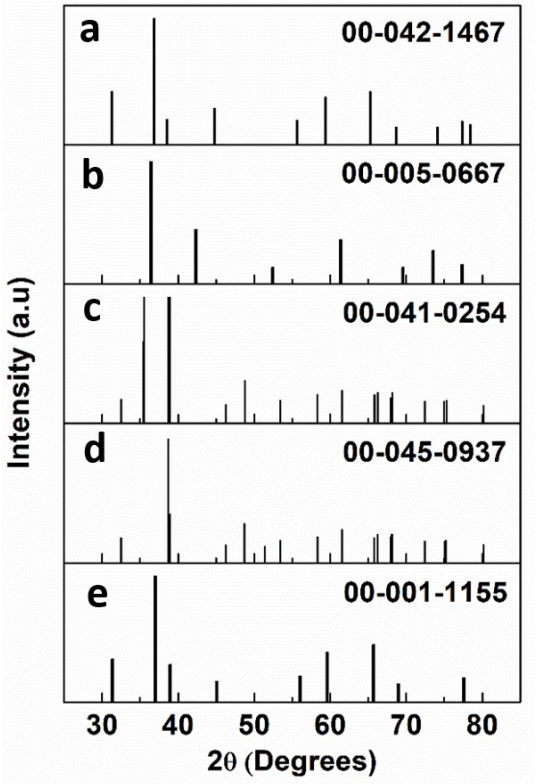
Chemicals and reagents

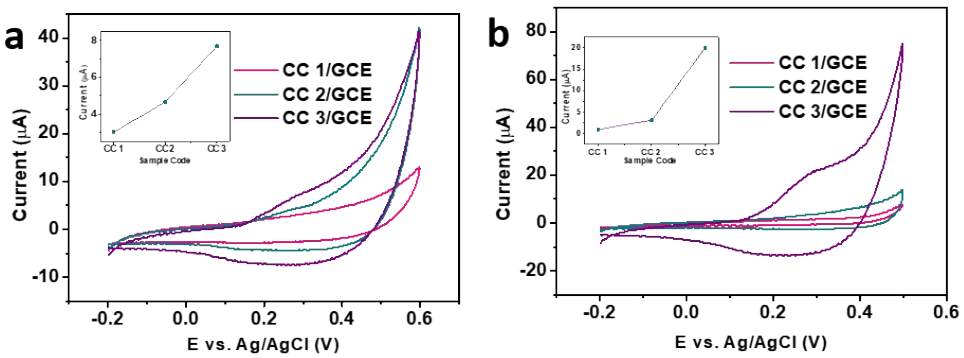
Copper (II) nitrate trihydrate (Fisher Scientific, 22764, 97%), cobalt (II) nitrate hexahydrate (Alfa Aesar, 11341, 98%), urea (Fisher Scientific, 20885, 99%), n-butanol (Fisher Scientific, 71-36-3), multiwalled carbon nanotube (4-6 nm diameter and 5-20 μm length, TMC 220-05), hydroxypropyl methyl cellulose (Himedia, 9004-65-3), ethanol (Changshu Hongsheng Fine Chemical Co. Ltd., Analytical reagent grade), acetylcholine chloride (Sigma-Aldrich, 60-31-1, 99%), sodium hydroxide pellets (Qualigens, Q27815), choline chloride (Sigma-Aldrich, C7017, 99%), potassium chloride (Fisher Scientific, 13305). Transparent polyester films (75 μm thickness, Ganapathi Industries), polyimide adhesive tape (Kapton 50mm), conductive silver paste (Techinstro, Silverpaste-001), pyrolytic graphite sheet (Intelligent materials Pvt. Ltd., 7440-44-0), copper foil tape (Electomania). SH-SY5Y cells were procured from National Centre for Cell Science, Pune) and were maintained in DMEM/F12 (Thermo Fisher Scientific, MA, USA) containing 10% fetal bovine serum (FBS; Thermo Fisher Scientific, MA, USA) and 1% penicillin-streptomycin (Thermo Fisher Scientific, MA, USA. Deionized (DI) water (> 18 MΩ) was used all throughout the synthesis.



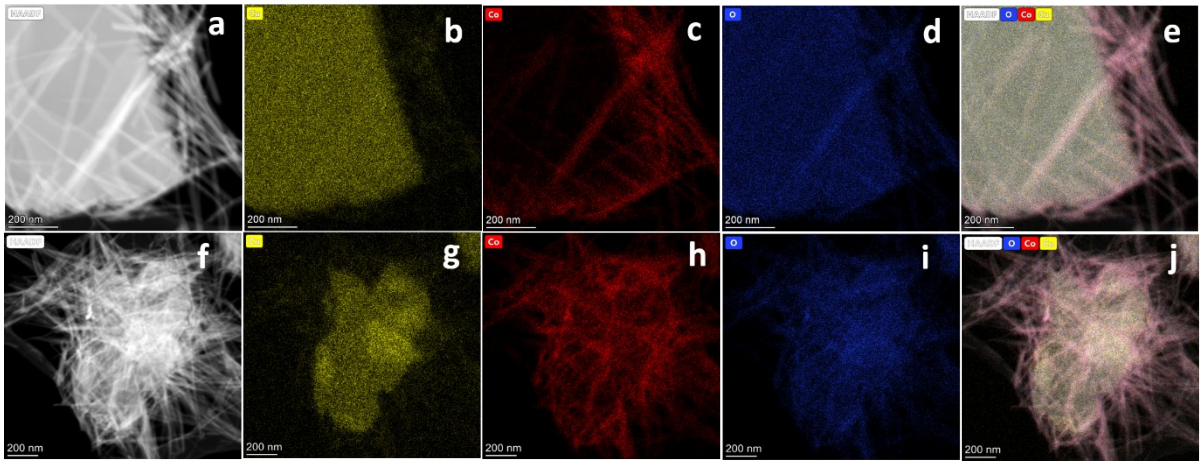
Supporting Fig. S1. EDS spectra and the corresponding HRSEM images of (a,b) CC 1, (c,d) CC 2, and (d,e) CC 3, respectively. The elemental compositions are tabulated in the insets of the spectra.



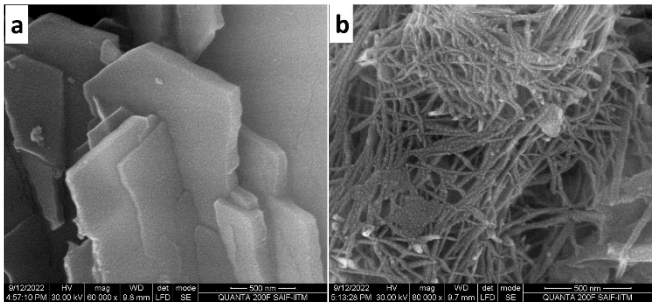
Supporting Fig. S2. Standard JCPDS cards corresponding to the XRD patterns (a) Co_3O_4, (b) Cu_2O, (c,d) CuO, and (e) $CuCo_2O_4$.



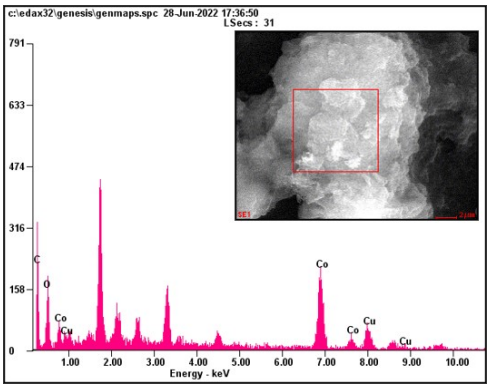
Supporting Fig. S3. Cyclic voltammograms of CC nanostructures in the presence of (a) 0.1M NaOH, and (b) 500 nM ACh at a scan rate of 50mV/s. The corresponding anodic peak currents are given in the insets. The anodic peak current of CC 3 is higher towards both 0.1 M NaOH and 500 nM ACh.



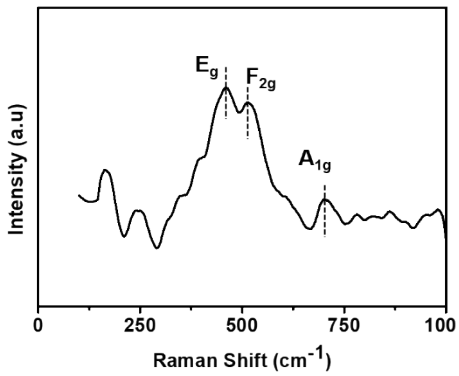
Supporting Fig. S4. (a,f) High-angle annular dark-field image and the corresponding elemental mapping images of (b,g) copper, (c,h) cobalt, (d.i) oxygen, and (e,j) mix present in CC 1 and CC 2, respectively.



Supporting Fig. S5. HRSEM images of (a) copper oxide and (b) cobalt oxide synthesized using bisolvent interface-assisted technique.



Supporting Fig. S6. EDS spectrum and the corresponding HRSEM image (inset) of CC/MWCNT composite. The major elements present in the sample (Cu, Co, and O) are marked in the spectra. The less prominent peaks obtained at 1.7 eV, 2.2 eV, and 3.5 eV corresponds to Si, Nb or K, which might have originated from the cover slip on which the material was coated and the stub used for the analysis.

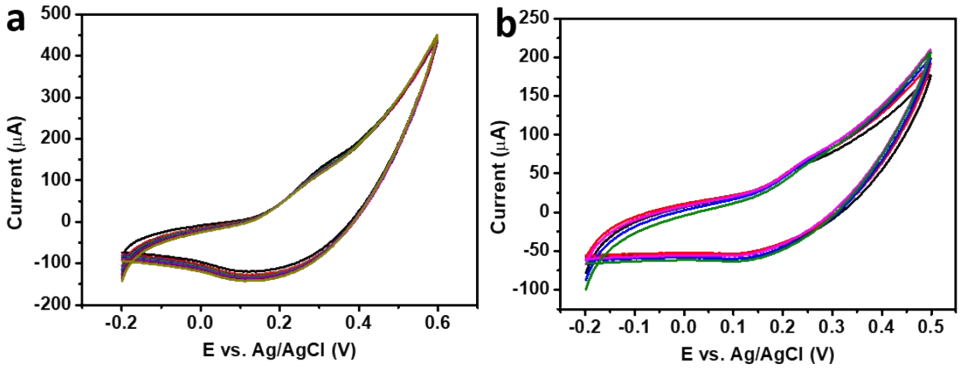


Supporting Fig. S7. Raman Spectra of CC 3. The peaks observed in the range of 220-690 cm^{-1} arise from CC, mainly from its E_g, F_{2g}, and A_{1g} modes, resulting from Cu-O and Co-O vibrations.[1,2]

Sl No	Electrode	Detection method used	Linear range	LOD	Real Sample	Reference
1	ACC-rGO@Cu(BTC)@MnO2	Amperometry	0.1 µM – 3 mM	5 nM	Cell lines, serum, urine	S3
2	$CuCo_2O_4$	Amperometry	0.2 – 3500 µM	30 nM	Serum	S4
3	Cu NP	Amperometry	120 – 2680 µM	39 µM	Serum	S5
4	Ns-Ni-CC/Nf	Amperometry	0.24 – 828 µM	49.3 nM	_	S6
5	Ni-Al LDHs/OMC	Amperometry	2 – 4922 µM	42 nM	_	S7
6	NiO	Amperometry	250 – 5880 µM	26.7 µM	Serum	S8
7	NiAl-LDH/CD	Amperometry	5 – 6885 µM	1.7 µM	_	S8
8	MCSNP/SPE	DPV	1.0×10−7 – 5.0×10−4 M	2.0×10−8 M	Serum, urine	S9
9	Zn-doped TiO_2	DPV	0.05 – 0.1 µM 1 – 10 µM	_	_	S10
10	Nitrogen ion implanted WO_3/ITO	Amperometry	0.1 – 8000 µM	28 nM	Serum	S11
11	GQD/SPE	DPV	1 – 800 µM	0.3 µM	Injection,	S12

					urine	
12	CuMS@C	Amperometry	0.01 – 0.8 mM	0.1 µM	Serum	S13
13	CC/MWCNT	CV	10 – 500 nM	0.8 nM	Serum, neural cell	This work

Supporting Table S1. Comparison of the detection method, linear range, LOD, and the real sample analysis of the proposed sensor with the reported non-enzymatic sensors.



Supporting Fig. S8. (a) Cyclic voltammograms of (a) ten successive scans (b) five different CC/MWCNT-modified electrodes in the presence of 500 nM ACh solution.

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