Electronic Supplementary Information

Sculpturing Metal Foams toward Bifunctional 3D Copper Oxide Nanowire Arrays for Pseudo-capacitance and Enzyme-free Hydrogen Peroxide Detection

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Preparation of TO-CuO/Cu composite foam

Preparation of the TO-CuO/Cu was accomplished as follows. First, a Cu foam was cleaned in deionized water and ethanol under sonication and dried in N_2 flow. Then it was heated to 300 °C in a furnace for 400 min and naturally cooled to room temperature without opening the furnace. The ramp rate was ~2 °C min^{-1}.

Notes: The XRD pattern of the TO-CuO/Cu can be attributed to Cu_2O and Cu. The moderate intensity of signals from copper oxide and strong diffraction peaks from metallic copper typically suggest the limited oxidation into the Cu bulk. However, the occurrence of nanowire structures also exemplify the phenomenon of well-studied dry oxidation of copper substrate, where similar condition led to formation of CuO nanowires, CuO outer layer, Cu_2O interlayer on the Cu substrate. [1,2] Combined with the SEM image of TO-CuO/Cu in Fig. S1b, the XRD pattern of the TO-CuO/Cu, and the information from previous reports on the thermal oxidation of Cu substrates, it can be concluded that the TO-CuO/Cu prepared in this work possesses very low-density scattered short CuO nanowires on its surface, a CuO surface and a Cu_2O interlayer on the macroscopic Cu foam, which can serve as a control that stands for macroporous CuO/Cu foam with planar surface without high-density CuO nanowire arrays.

Calculations

For CV measurements, the areal specific capacitance of the 3D-CuONA/Cu and the TO-CuO/Cu composites were calculated using the following equation:

$$C_{AS} = 1 / (2v \times \Delta V) \times \int J(V)\mathrm{d}V$$

where C_{AS} is the areal specific capacitance (mF cm^{-2}), v is the scan rate (V s^{-1}), ΔV is the potential window (V), and J is the current density (mA cm^{-2}).

For galvanostatic measurements, the areal specific capacitance of the 3D-CuONA/Cu and the TO-CuO/Cu composites were calculated using the following equation:

$$C_{AS} = J \times \Delta t / \Delta V$$

where C_{AS} is the areal specific capacitance (mF cm^{-2}), Δt is the discharge time (s), ΔV is the potential window (V), and J is the current density (mA cm^{-2}).

For other materials from previous published literatures mentioned in the main text, their areal specific capacitances are either directly given in the corresponding references or calculated from the weight specific capacitance with the loading mass of active materials that can be obtained from the corresponding references. The equation for calculation is as below:

$C_{AS} = C_{WS} \times M_A = C_{WS} \times M / S$

where C_{AS} is the areal specific capacitance (mF cm^{-2}), C_{WS} is the weight specific capacitance (mF mg^{-1}), M_A is the loading mass of active materials per geometric/nominal area of the electrode (mg cm^{-2}), M is the total loading mass of active materials (mg), and S is the geometric/nominal area of the electrode (cm^2). The M is obtained by measuring the weight of the 3D-CuONA/Cu sample before and after treatment in excessive hydrochloride acid using a microbalance (METTLER TOLEDO) with an accuracy of 10 ug. The loading mass of the active materials is 3.58 mg cm^{-2}.

FIGURES

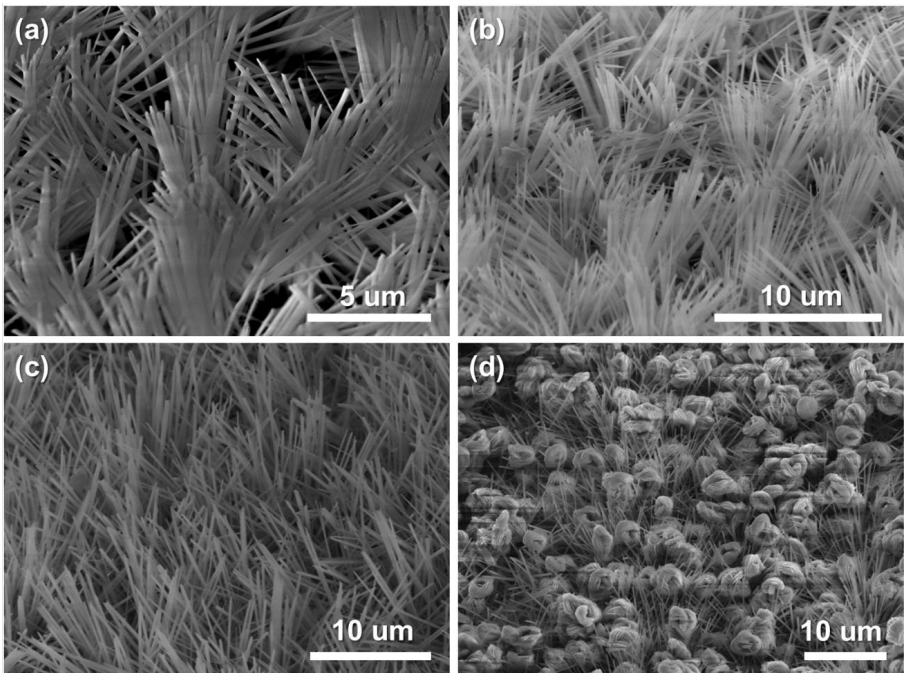

Fig. S1 Microstructure morphologies formed after wet-chemical treatment of Cu substrate at different immersion duration: (a) 10 min, (b) 15 min, (c) 30 min, with respective nanowire length of about 6, 9 and 12 um, and (d) 60 min, with flower-like particles deposited on the nanowire arrays.

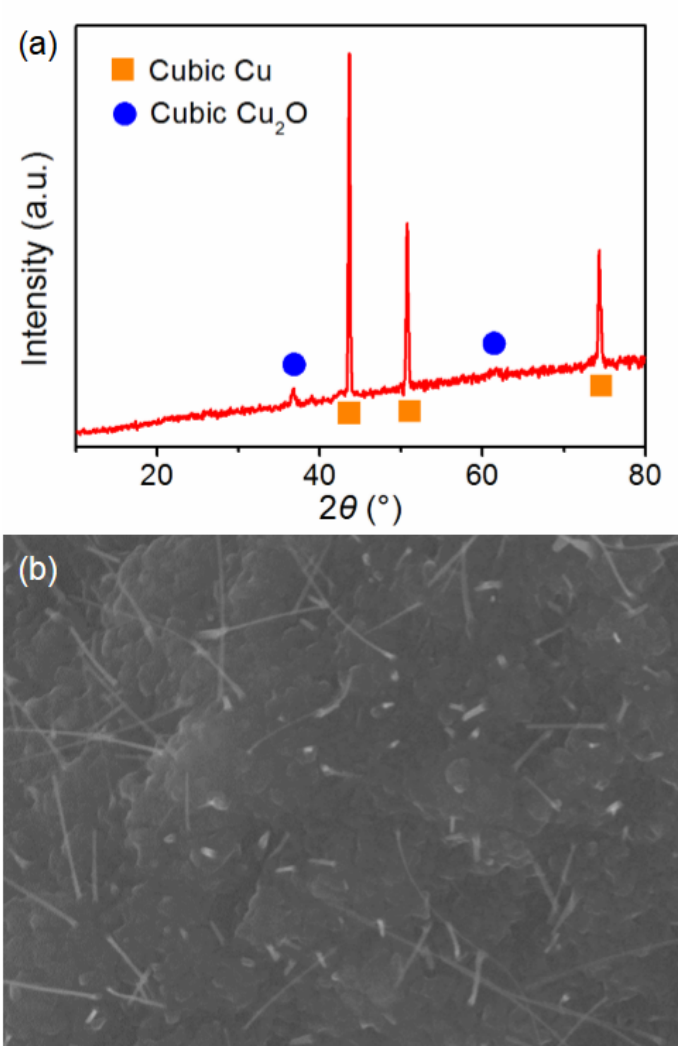

Fig. S2 XRD pattern (a) and SEM image (b) of the TO-CuO/Cu foam.

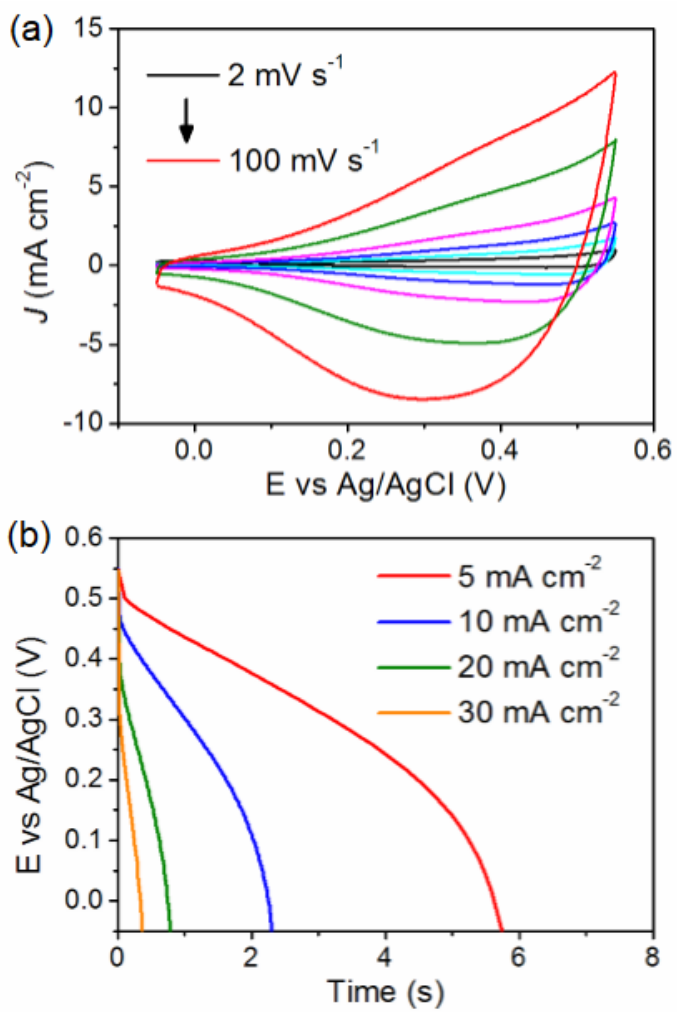

Fig. S3 (a) CV of the TO-CuO/Cu at scan rates from 2 to 100 mV s^{-1}. (b) Galvanostatic discharge curve of the TO-CuO/Cu at current densities from 5 to 30 mA cm^{-2}.

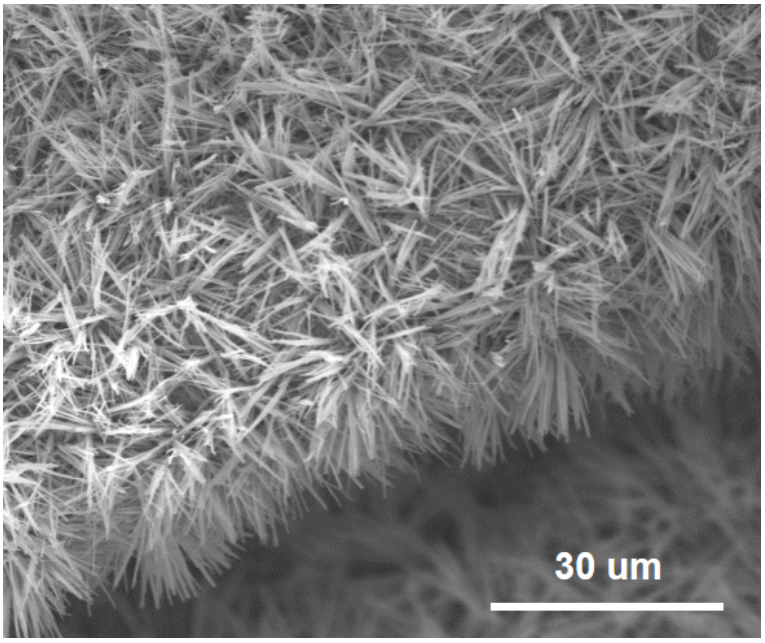

Fig. S4 SEM image of 3D-CuONA/Cu after the cycling tests.

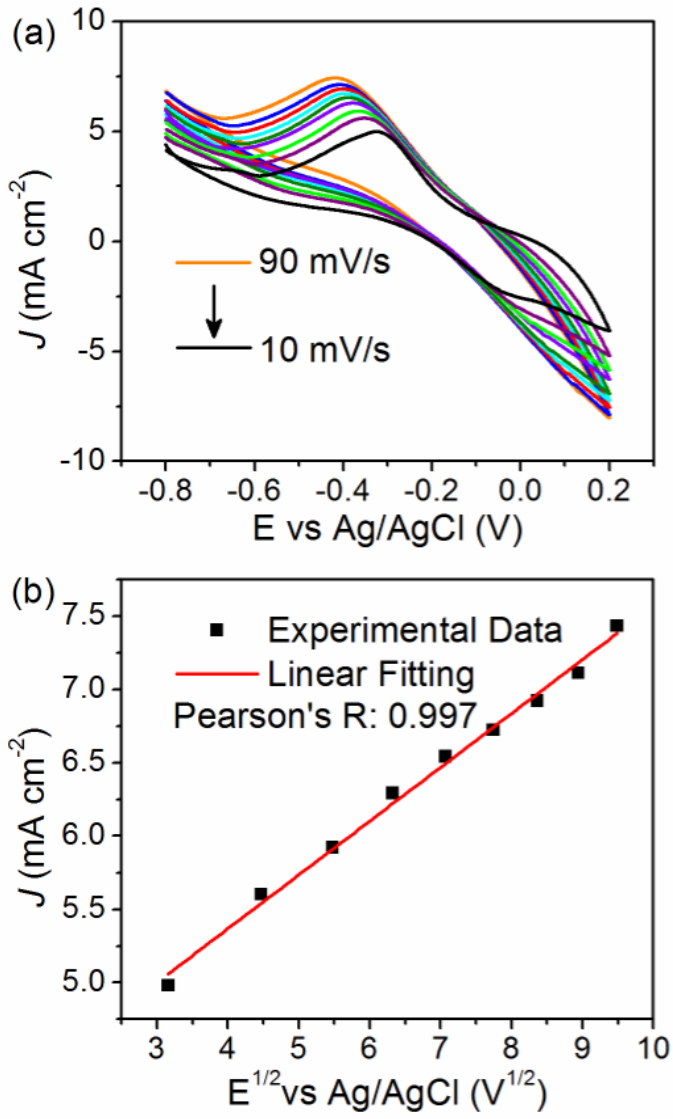

Fig. S5 (a) CV of the 3D-CuONA/Cu foam at scan rates from 10 to 90 mV/s with 2 mM H_2O_2 in presence and (b) its calibration plot.

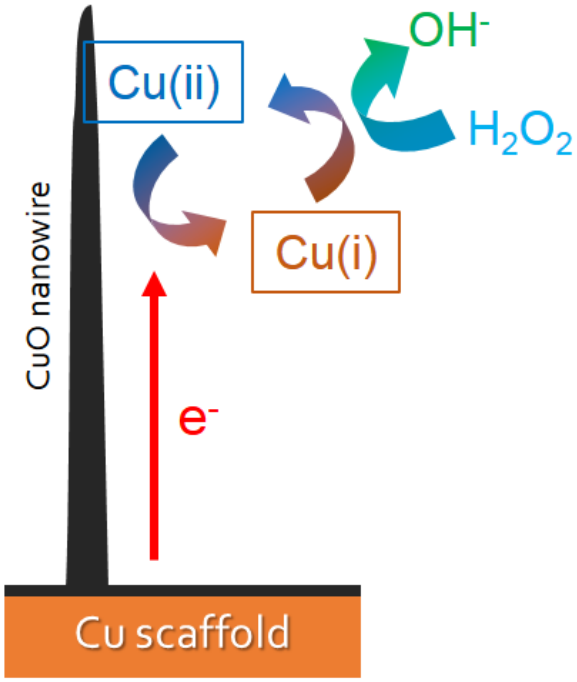

Fig. S6 Schematic illustration of possible H2O2 sensing mechanism for the 3D-CuONA/Cu composite.

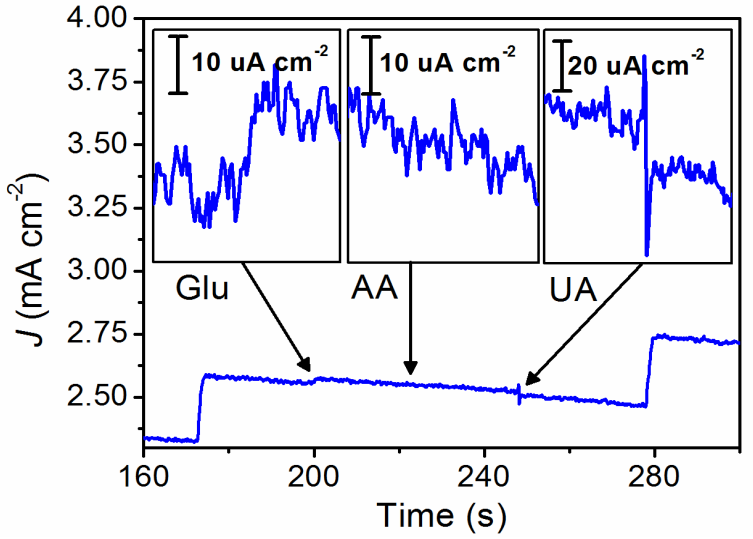

Fig. S7 Amperometric measurement for selectivity of 3D-CuONA/Cu with successive addition of 50 uM target analyte and interfering species. The adding sequence is H_2O_2, D-glucose, ascorbic acid, uric acid and H_2O_2. Insets show magnified current curve where interfering species are introduced.

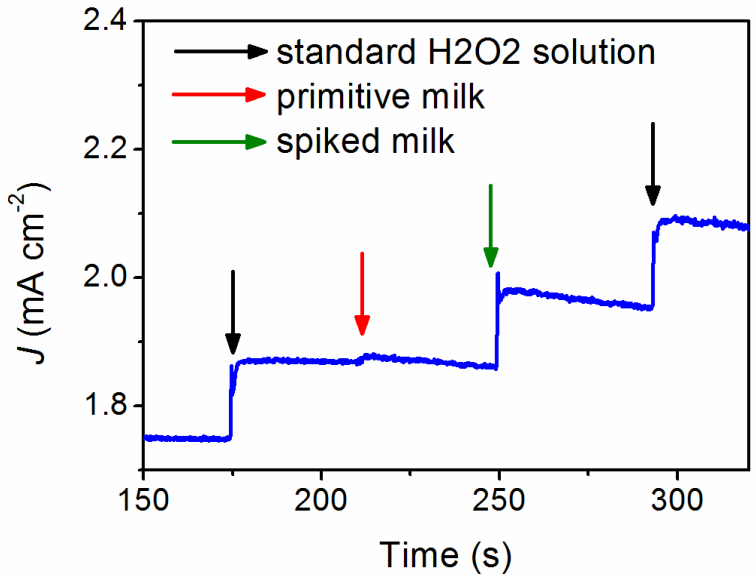

Fig. S8 Amperometric measurement with addition of primitive and spiked milk samples and standard H_2O_2 solution, 20 uM H_2O_2 for all injections.

TABLES

Tab. S1 Capacity of 3D-CuONA/Cu at various scan rates (by cyclic voltammetry) and current densities (by chronopotentiometry)

Scan Rate/Current Densities ($mV\ s^{-1}$/$mA\ cm^{-2}$)		**Areal Specific Capacitance ($mF\ cm^{-2}$)**	**Weight Specific Capacitance ($F\ g^{-1}$)**
Cyclic Voltammetry	2	608	170
	5	536	150
	10	471	132
	20	391	109
	50	268	75
	100	173	48
Chronopotentiometry	5	535	149
	10	453	127
	20	373	104
	30	280	78

Tab. S2 Performance comparison for electrochemical H_2O_2 detection based on enzyme-free materials

Electrode Materials	**Sensitivity (uA mM^{-1} cm^{-2})**	**Detection Limit (uM)**	**Response Time (s)**	**Ref.**
CoOOH nanosheet	99	40	<3	3
Au nanoparticles-graphene-chitosan	Not available	1.6	<5	4
Grass-like CuO	80.4	0.167	<3	5
Ag-MnO_2-Multiwalled Carbon Nanotube	82.5	1.7	2	6
Ag@AgCl Nanoboxes	88.8	1.7	~1	7
Multiwalled carbon nanotube/polyaniline/platinum nanoparticles	748.4	2.0	<5	8
Pt nanoparticles-Ni foam	829	0.3	Not Specified	9
Co_3O_4 nanowires/3D N-doped carbon foam	0.23	1.4	≤3	10
3D GN/ Multiwalled carbon nanotube /Pt Nanoparticle	Not available	0.0086	1.5	11
CuO nanoparticle-Si nanowire	315	1.6	1.5	12
3D-CuONA/Cu foam	5750	0.56	~2	This work

REFERENCES

1 A. Kargar, Y. Jing, S. J. Kim, C. T. Riley, X. Pan and D. Wang, *ACS Nano*, 2013, **7**, 11112-11120.

2 A. T. Garcia-Esparza, K. Limkrailassiri, F. Leroy, S. Rasul, W. Yu, L. Lin and K. Takanabe, *J. Mater. Chem. A*, 2014, **2**, 7389-7401.

3 K. K. Lee, P. Y. Loh, C. H. Sow and W. S. Chin, *Biosens. Bioelectron.*, 2013, **39**, 255-260.

4 N. Jia, B. Huang, L. Chen, L. Tan and S. Yao, *Sens. Actuators, B*, 2014, **195**, 165-170.

5 P. Gao and D. Liu, *Sens. Actuators, B*, 2014, **208**, 346-354.

6 Y. Han, J. Zheng and S. Dong, *Electrochim. Acta*, 2013, **90**, 35-43.

7 Y. Li, J. Zheng, Q. Sheng and B. Wang, *Microchim. Acta*, 2014, **182**, 61-68.

8 H. Zhong, R. Yuan, Y. Chai, Y. Zhang, C. Wang and F. Jia, *Microchim. Acta*, 2012, **176**, 389-395.

9 X. Lu, X. Xiao, Z. Li, F. Xu, H. Tan, L. Sun and L. Wang, *Anal. Methods*, 2014, **6**, 235-241.

10 M. Liu, S. He and W. Chen, *Nanoscale*, 2014, **6**, 11769-11776.

11 X. Cao, Z. Zeng, W. Shi, P. Yep, Q. Yan and H. Zhang, *Small*, 2013, **9**, 1703-1707.

12 J. Huang, Y. Zhu, H. Zhong, X. Yang and C. Li, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7055-7062.