

Supporting Information

Ultra-small dispersed Cu_xO nanoparticles on graphene fiber for miniaturized electrochemical sensor applications

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Experimental Section

Preparation of 0.1 M phosphate buffer (PBS, pH=7.0)

In a typical synthesis, 2.26816 g of KH_2PO_4 was added to a beaker (250 mL), followed by 11.9380 g of Na_2HPO_4 . The mixture was dissolved in about 200 mL of ultrapure water. Finally, the mixed solution was transferred to a volumetric flask (500 mL), diluted with ultrapure water to volume and mixed. The obtained PBS was stored at room temperature.

Preparation of 5 mM potassium ferricyanide solution ($\text{K}_3\text{Fe}[(\text{CN})_6]$)

Typically, 1.86375 g of KCl powder (0.1 M) and 0.411560 g of $\text{K}_3\text{Fe}[(\text{CN})_6]$ were dissolved in ultrapure water. The mixed solution was transferred to a 250 mL volumetric flask, diluted with ultrapure water to volume, and mixed. The obtained 5 mM $\text{K}_3\text{Fe}[(\text{CN})_6]$ was stored at 4 °C.

Measurement

The cyclic voltammetry (CV), differential pulse voltammetry (DPV) and amperometry were operated on a CHI 760E electrochemical workstation (CH Instruments, China) with a three-electrode system at room temperature, where $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$ acted as the working electrode, Pt plate as the counter electrode, and saturated calomel electrode as the reference electrode. 0.1 M PBS (pH 7.0) as electrolyte in the electrochemical experiments. All of the solutions were deoxygenated by bubbling N_2 for 30 min before electrochemical measurements. CVs and DPVs were recorded in the potential range from -0.6 to 0.6 V at the scan rate of 50 mV s^{-1} . Amperometry was recorded in 10 mL N_2 saturated PBS under magnetic stirring at -0.15 V. Oxygen dissolved in human serum and milk were removed with N_2 for 30 min and 100 μL of the human serum or milk was injected into 10 mL N_2 saturated PBS by micro syringe. Appropriate H_2O_2 (0.47, 0.60, 5.30, and 94.10 μM H_2O_2) were then injected into the solution.

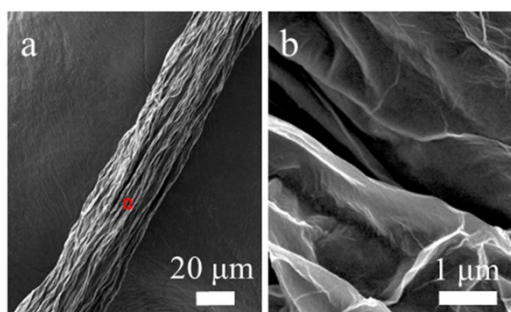


Figure S1. (a) SEM image of bare GF, (b) the enlarge view of the rectangle area in (a).

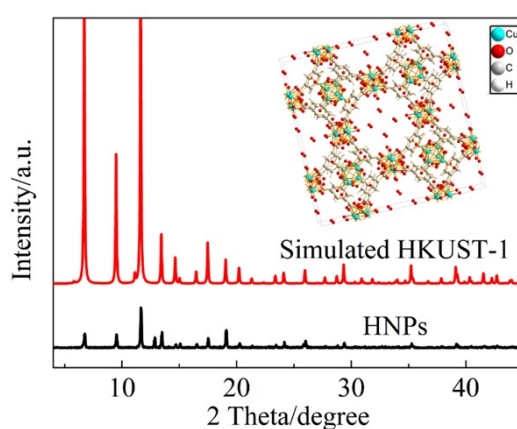


Figure S2. XRD patterns of HNPs and the simulated HKUST-1.

The XRD pattern of HNPs shows similar peaks to that of the simulated HKUST-1, suggesting the copper MOF of HKUST-1 with fourfold symmetry about 1 nm channels was prepared.¹

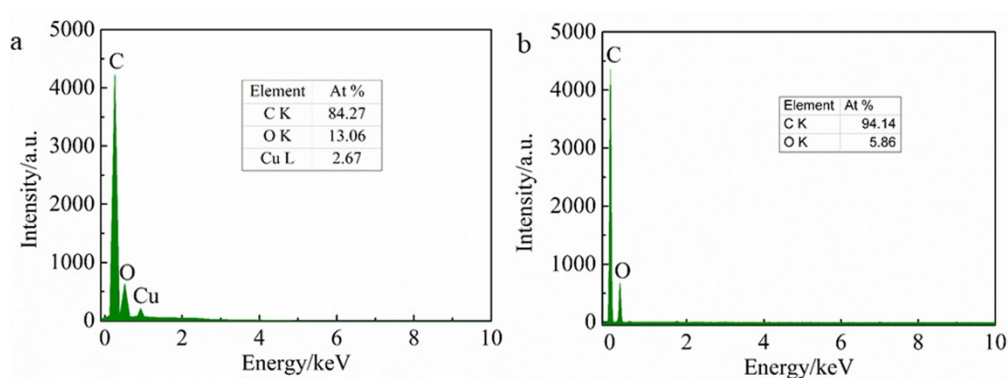


Figure S3. EDS spectrums of (a) $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$ and (b) bare GF.

Table S1. The element content (at %) of $\text{Cu}_x\text{ONPs}_{30}/\text{GF}_{400}$, $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$, $\text{Cu}_x\text{ONPs}_{90}/\text{GF}_{400}$ and $\text{Cu}_x\text{ONPs}_{120}/\text{GF}_{400}$ determined by energy-dispersive X-ray spectroscopy (EDS).

Sample	C	O	Cu
$\text{Cu}_x\text{ONPs}_{30}/\text{GF}_{400}$	92.92	6.84	0.24
$\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$	86.99	12.27	0.74
$\text{Cu}_x\text{ONPs}_{90}/\text{GF}_{400}$	85.50	12.48	2.03
$\text{Cu}_x\text{ONPs}_{120}/\text{GF}_{400}$	84.27	13.06	2.67

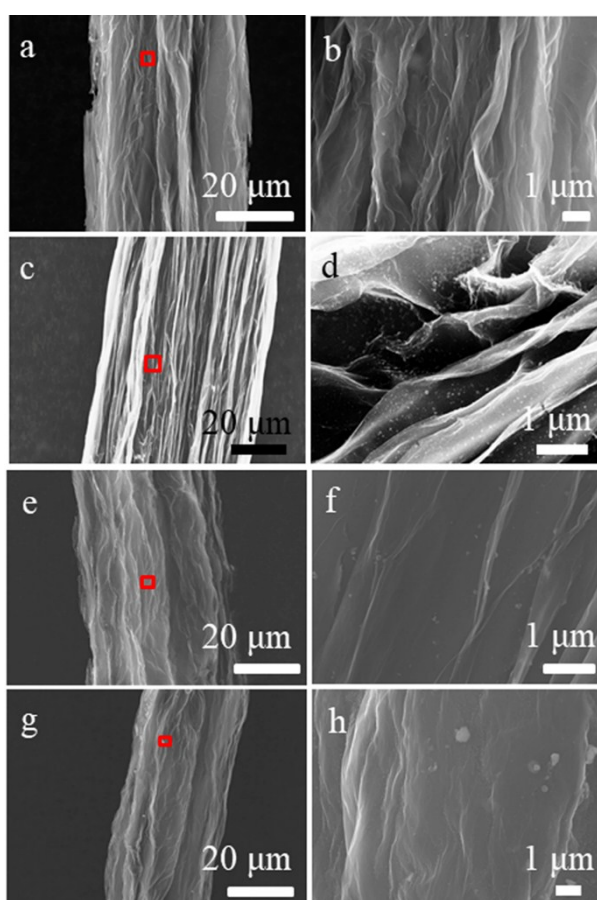


Figure S4. (a) SEM image of $\text{HNP}_{30}/\text{GF}_{400}$. (b) The enlarged view of the rectangle area in (a). (c) SEM image of $\text{HNP}_{60}/\text{GF}_{400}$. (d) The enlarged view of the rectangle area in (c). (e) SEM image of $\text{Cu}_x\text{ONPs}_{90}/\text{GF}_{400}$. (f) The enlarged view of the rectangle area in (e). (g) SEM image of $\text{Cu}_x\text{ONPs}_{120}/\text{GF}_{400}$. (h) The enlarged view of the rectangle area in (g).

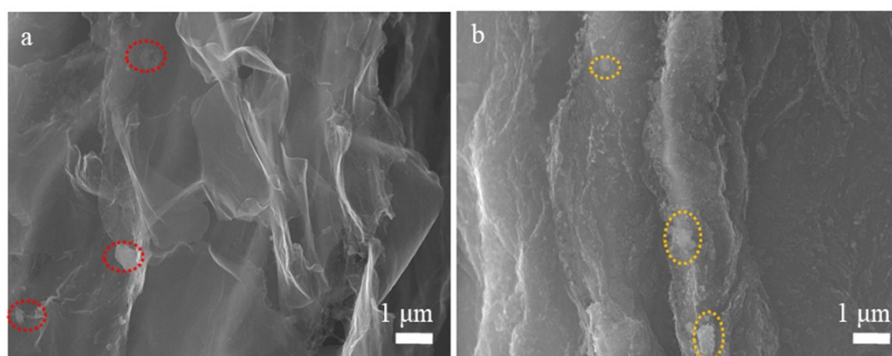


Figure S5. (a) SEM image of $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{300}$, the incomplete decomposition of HNP_{s60} precursors are in red circles, (b) SEM image of $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{500}$, agglomerations of Cu_xONPs are in the yellow circles.

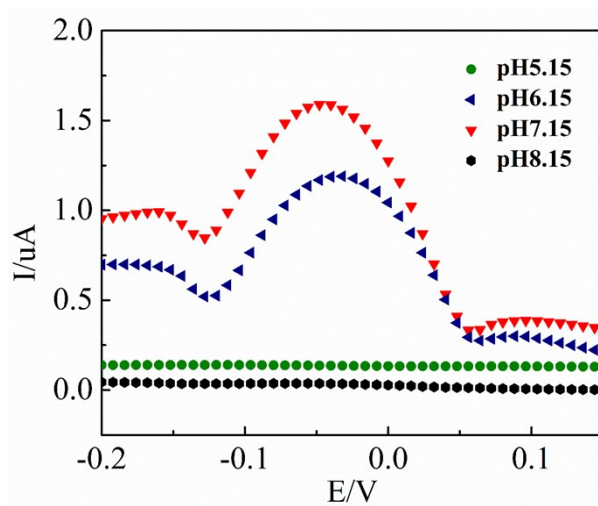


Figure S6. DPVs of the $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$ in 0.1 M PBS with 0.2 mM H_2O_2 under pH values of 5.15, 6.15, 7.15 and 8.15.

Table S2. Comparison of various copper-based electrode sensors for H₂O₂ detection

Active material	Linear range (μM)	Limit of detection (μM)	Sensitivity (mAmm ⁻¹ cm ⁻²)	Electrode	Method	Reference
{[Cu ₂ (bep)(ada) ₂ •H ₂ O]}	0.05-3	0.014	5.56	GCE	I-t	2
Cu@CuO	3-800	210	~	GCE	DPV	3
Cu ₂ ONPs/N-GN	5-3750	0.8	26.67	GCE	I-t	4
Cu ₂ O/GNs	300-7800	20.8	~	GCE	I-t	5
Cu-MOF	0.1-2.75	0.068	78220	GCE	CV	6
Cu ₂ O/rGO	30-12800	21.7	20.7	GCE	I-t	7
CuO-SiNWs	10-13180	1.6	22.27	GCE	I-t	8
Cu ₂ O	~	0.0039	52.3	GCE	I-t	9
CuO Nanosheet	10-20000	10	0.0255	Cu foil	I-t	10
Cu-Ni(OH) ₂	5-145	1.5	0.4081	GCE	I-t	11
Cu _x ONPs/GF	0.07-133	0.023	3437.5	graphene fiber	DPV	This work

Abbreviation: GCE: glass carbon electrode, I-t: amperometric, DPV: differential pulse voltammogram, CV: cyclic voltammograms.

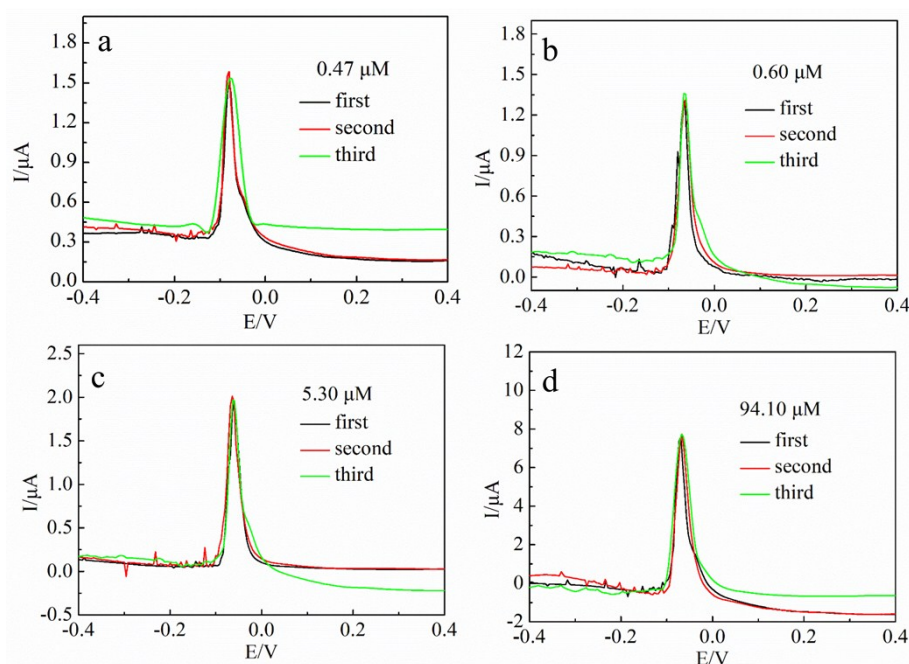


Figure S7. DPVs response of Cu_xONPs₆₀/GF₄₀₀ electrode in diluted milk with 0.47, 0.60, 5.30, 94.10 μM H₂O₂, n=3. All potential values are -0.15 V and the pH value of PBS is 7.15. The real samples were diluted to 100 times with 0.1 M PBS solution, pH=7.15.

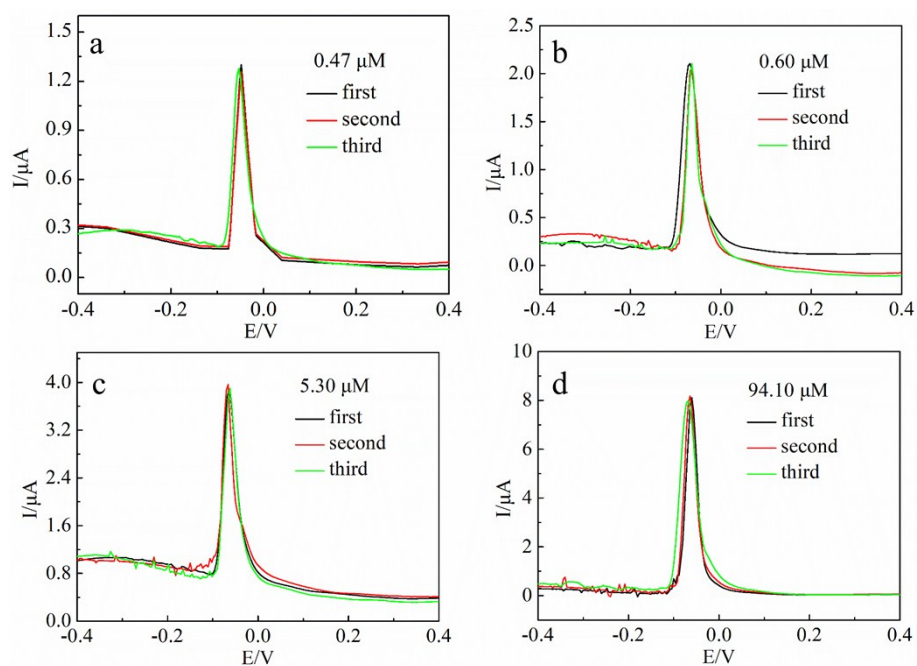


Figure S8. DPVs response of $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$ electrode in diluted human serum with 0.47, 0.60, 5.30, 94.10 μM H_2O_2 , $n=3$. All potential values are -0.15 V and the pH value of PBS is 7.15. The real samples were diluted to 100 times with 0.1 M PBS solution, $\text{pH}=7.15$.

References

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