Ultra-small dispersed CuₓO nanoparticles on graphene fibers for miniaturized electrochemical sensor applications†

Jinfeng Zeng,a Xiaoteng Ding,b Liwei Chen,a Le Jiao,a Yuze Wang,a Christopher D. Windle,c Qing Han,x,a and Liangti Qua

A graphene microfiber (GF) modified with ultrafine CuₓO nanoparticles (CuₓONPs/GF) has been fabricated by direct annealing of electrodeposited nano-sized copper-based metal organic frameworks (HKUST-1) and used as an electrode for nonenzymatic H₂O₂ sensing. Benefiting from the unique microfiber architecture and synergistic effects, as well as strong coupling between components with many active sites and boosted electron transport, the CuₓONPs/GF electrode shows prominent sensitivity, selectivity and long-term operational stability for the detection of H₂O₂. Further work successfully applied this CuₓONPs/GF electrode to detection of H₂O₂ in real samples such as milk and human serum. These results indicate that the CuₓONPs/GF is a promising mini-sized sensor in electrochemical analysis.

Introduction

The demand for electrochemical sensors with high sensitivity, low cost, excellent selectivity, and facile miniaturization has stimulated extensive research into developing versatile materials with remarkable electrocatalytic activity. Compared to conventional macro-electrodes, fiber-type electrodes with a one-dimensional microstructure, particularly carbon fiber microelectrodes possessing one dimensional diffusion, have been widely fabricated and used in sensors due to their low cost, small volume, portability and good biocompatibility. However, the poor electrocatalytic activity and low current response of carbon fiber microelectrodes seriously restrict their application in sensing.

Graphene has potential as an electrode for electrochemical analysis owing to its large specific surface area, excellent electron mobility, high mechanical properties and good biocompatibility. Recently, we reported a graphene fiber assembled with chemically reduced graphene sheets, which exhibited promising electrochemical sensing activity, mainly owing to the inherent defects and residual oxygenated functional groups as active sites. However, the weak electrocatalytic properties of graphene restrict its wide application in electrochemical analysis. It is revealed that combining graphene fiber with catalytically active nanomaterials such as metals and metal oxides is an efficient way to enhance the electrocatalytic activity. Copper oxide nanoparticles (CuₓONPs) are an attractive alternative electroactive species due to their abundance, low cost, good chemical stability and unique electronic properties. Hybridizing graphene with CuₓONPs is an effective way, where the composite materials have fully exploited the structural merits of individual components and improved the analytic performance. So far, various strategies, including thermal conversion, ion exchange, wet chemistry, microwave template growth, and anion-assisted approaches have been employed to prepare CuₓONPs/graphene hybrids. Unfortunately, as-prepared CuₓONPs from these approaches suffer from aggregation on graphene-based materials, leading to poor dispersion and a low number of active sites with poor electrocatalytic performance. In addition, although CuₓONPs/graphene composites have been widely investigated and demonstrated with great potential for electrochemical analysis, there is still a lack of exploration for its miniaturized sensors. Thus, it is urgent to design and develop a simple and effective method for the production of CuₓONPs/graphene fiber-based microsensor with a high number of active sites and highly efficient electrocatalytic activity.

Hydrogen peroxide (H₂O₂) is indispensable to ecosystems and is widely used in foodstuffs, the environment, medicine and industry. Excess H₂O₂ can lead to toxicity for humans and to the environment. Although electrochemical enzyme-based sensors have good selectivity and high performance, their applications are limited because of their poor stability and high cost. Therefore, the development of non-enzymatic sensors has drawn tremendous attention. Herein, we report...
a graphene microfiber electrode modified by well-dispersed and ultrafine Cu$_2$O nanoparticles (Cu$_2$ONPs/GF) derived from copper-based metal organic frameworks (HKUST-1) by a direct electrodeposition self-assembly technique for nonenzymatic electrochemical H$_2$O$_2$ detection. The unique nanoarchitecture and synergetic effect as well as strong coupling between components endow them with a high density of active sites and enhanced electron transport leading to improved electrochemical micro-sensing. The resulting hybrid fiber electrode exhibits a very low detection limit of 0.023 μM and a rapid response time of 1 s. Our work provides a straightforward method for synthesizing highly efficient nonenzymatic micro-sensing electrodes for H$_2$O$_2$ detection.

**Experimental**

**Synthesis of graphene fiber (GF)**

Graphene oxide (GO) was synthesized by oxidation of graphite powder according to the modified Hummers’ method. Then, graphene oxide fibers (GOF) were prepared by a wet spinning strategy. Typically, 3 mL GO (20 mg mL$^{-1}$) was spun into a methanol solution saturated by potassium chloride (KCl) with a speed of 0.1 m s$^{-1}$ by an injector (with a diameter of 0.25 mm), followed by drying. To obtain GF, the GOF was heated to 200 °C for 2 h at first and then further heated to 1000 °C for 2 h with a heating rate of 10 °C min$^{-1}$ under N$_2$/H$_2$ (v/v = 4 : 1) atmosphere.

**Synthesis of HKUST-1 nanoparticles decorated GF (HNPs/GF)**

A two-electrode system was used for the preparation of HNPs/GF (HNPs = HKUST-1 nanoparticles). Firstly, 0.2416 g of cupric nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O), 0.2102 g of 1,3,5-benzene tricarboxylic acid (H$_3$BTC), and 0.7748 g of tetrabutylammonium hexafluorophosphate (NBu$_4$PF$_6$) were dispersed in 20 mL of N,N-dimethylformamide (DMF) solution, and the mixture was treated by ultrasound for 30 min to obtain a homogenous solution. Next, the as-synthesized GF (2.0 mm length) and a commercial Pt plate were used as the working electrode and counter electrode, respectively. The HNPs/GF was fabricated by the electrodeposition of HNPs on the GF surface in the above mixed solution (degassed with N$_2$ for 30 min) at −1.5 V for 60 s, the obtained sample is denoted HNPs$_{60}$/GF. For comparison, a series of HNPs/GF samples with different amounts of HNPs were obtained by adjusting the electrodeposition time (30 s, 90 s, and 120 s) in the same mixed solution, which were denoted HNPs$_{30}$/GF, HNPs$_{90}$/GF and HNPs$_{120}$/GF, respectively.

**Synthesis of Cu$_2$ONPs/GF**

The Cu$_2$ONPs/GF was synthesized by direct annealing of HNPs/GF (HNPs$_{30}$/GF, HNPs$_{90}$/GF, HNPs$_{90}$/GF and HNPs$_{120}$/GF) samples from room temperature to 400 °C in N$_2$ with a ramp rate of 10 °C min$^{-1}$ and stabilized for 2 h, then cooled to room temperature naturally, and denoted Cu$_2$ONPs$_{30}$/GF$_{400}$, Cu$_2$ONPs$_{90}$/GF$_{400}$, Cu$_2$ONPs$_{90}$/GF$_{400}$, and Cu$_2$ONPs$_{120}$/GF$_{400}$, respectively.

In order to study the influence of the annealing temperature on the performance of the final samples, a series of Cu$_2$ONPs/GF samples were obtained by annealing the HNPs$_{60}$/GF sample at 300 °C and 500 °C, respectively. The obtained samples were denoted Cu$_2$ONPs$_{60}$/GF$_{500}$ and Cu$_2$ONPs$_{60}$/GF$_{500}$, respectively.

**Synthesis of Cu$_2$ONPs/GF electrode**

The Cu$_2$ONPs/GF was glued with silver conductive adhesive onto stainless steel sheets (2.5 × 0.5 cm). The end of the tip was sealed with molten paraffin. The exposed Cu$_2$ONPs/GF was cut down to 2.0 mm in length and used as the electrode. The exposed stainless steel sheet was then connected with the electrochemical workstation.

**Results and discussion**

The procedure for the fabricated Cu$_2$ONPs/GF is shown in Fig. 1. Firstly, GO suspension (Fig. 1a) was converted into a GO fiber (GOF, Fig. 1b) by a wet spinning strategy. After drying naturally, the GOF was thermally reduced to graphene fiber (GF, Fig. 1c). The obtained GF with a diameter of 44 μm appears as wrinkled sheet-like surface morphologies (Fig. S1†). Then, electrodeposition self-assembly of the copper MOF (HKUST-1 nanoparticles, HNPs) occurred in a mixed solution containing cupric nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O) and 1,3,5-benzene tricarboxylic acid (H$_3$BTC), in which HNPs grew in situ on the surface of GF after 60 s of electrodeposition (HNPs$_{60}$/GF, Fig. 1d), which was confirmed by X-ray diffraction (XRD, Fig. S2†). As shown in Fig. 2a, the obtained HNPs$_{60}$/GF shows fiber features with a diameter of 45 μm, larger than that of the bare GF. Fig. 2b demonstrates that the HNPs$_{60}$/GF with an octahedral structure have a uniform size of 200 nm and are well distributed over the surface of GF. Further annealing at 400 °C led to pyrolysis of HNPs$_{60}$/GF with simultaneous formation of Cu$_2$O.
nanoparticles (CuONPs60, the size is about 10 nm) well distributed on the sheets of GF (CuONPs60/GF400, Fig. 2c–e). High-resolution transmission electron microscopy (HR-TEM) of CuONPs/GF (Fig. 2f) indicates clear lattice fringes with a spacing of 0.24, 0.27 and 0.30 nm, corresponding to the Cu2O(111), CuO(110) and Cu2O(110), respectively. Element mapping reveals the coexistent and uniform distribution of C, O and Cu elements for CuONPs60/GF400 (Fig. 3a). An X-ray photoelectron spectrum (XPS) of the bare GF shows C 1s (284.6 eV) and O 1s (531.2 eV) peaks. Apart from the C 1s and O 1s peaks observed in the GF, the CuONPs60/GF400 shows the two apparent Cu 2p3/2 and Cu 2p1/2 features at 934.2 eV and 944.4 eV with a Cu atomic percentage of 0.76% (Fig. 3b), indicating the presence of CuONPs60, which is consistent with the energy-dispersive X-ray spectroscopy measurement (EDS, Fig. S3 and Table S1†). The ratio of C/O decreases from 11.1 (GF) to 8.4 (CuONPs60/GF400), demonstrating an increase in the oxygen content resulting from the introduction of CuO. In addition, the chemical states of copper in CuONPs60/GF400 are revealed by the high-resolution XPS spectra (Fig. 3c). The signals of Cu 2p3/2 and Cu 2p1/2 can each be deconvoluted into two peaks of Cu2O (933.4 eV and 935.4 eV) and CuO (941.9 eV and 944.2 eV)‡ ascribed to the oxidation products of HNPs after annealing.

**H2O2-sensing properties**

The electrochemical properties of the CuONPs60/GF400 electrode are investigated in 0.1 M PBS saturated with N2 at a scan rate of 50 mV s⁻¹. Considering the electrodeposition self-assembly time has a significant effect on the content and size of CuONPs, as well as the catalytic performance of the CuONPs/GF electrode, various CuONPs/GF electrodes were obtained by adjusting the electrodeposition self-assembly time (30 s, 90 s and 120 s), which were denoted CuONPs30/GF400, CuONPs90/GF400 and CuONPs120/GF400, respectively. The SEM images and EDS analysis of the CuONPs/GF samples (Fig. S4 and Table S1†) imply that with the increasing time of electrodeposition self-assembly, the content and size of the CuONPs increase. As a result, there is almost no reductive peak at the CuONPs30/GF400 electrode (Fig. 4a), which can be attributed to only trace amounts of CuO with inferior electrocatalytic activity (Fig. S4a and b and Table S1†). In comparison, an obviously reductive peak (about –0.05 V) was observed for the CuONPs60/GF400 electrode, which was attributed to the successful electrode surface reaction process.

A further increase of electrodeposition self-assembly time causes severe agglomeration of CuONPs with a reduction in the number of active sites (Fig. S4e–h†) resulting in a decrease in the current response. The annealing temperature also has a significant effect on the size of CuONPs and performance of...
the final CuONPs/GF electrode. For comparison, a series of CuONPs/GF electrodes were prepared by annealing the precursors of HNPs/GF derived from the optimal electrodeposition time at different temperatures (300 °C and 500 °C, which were denoted CuONPs60/GF300 and CuONPs60/GF500, respectively). Apparently, the current response signal of the CuONPs60/GF400 electrode is obviously higher than that of the CuONPs60/GF300 and the CuONPs60/GF500 electrodes (Fig. 4b). This may be attributed to the incomplete decomposition of the HNPs60 precursor for the CuONPs60/GF500 electrode (Fig. S5a†). The residual non-conductive HNPs60 inhibit electron transport on the surface of GF, leading to poor electrocatalytic activity towards H2O2 sensing. For the CuONPs60/GF500 electrode, an increase of CuONPs60 size can be observed as shown in Fig. S5b,† hence reducing the utilization of active sites and leading to a decrease in electrocatalytic performance.32

As a result, compared with the bare GF (no redox peaks, Fig. 4c), the CuONPs60/GF400 electrode displays a couple of sharp redox peaks, indicating an excellent electrocatalytic activity of the CuONPs60/GF400 electrode towards H2O2 detection. Meanwhile, the CuONPs60/GF400 electrode shows an obvious reduction peak at pH = 7.15 (Fig. S6†), which means that the electrode can be applied to a physiological environment. The low detection limit and the linear range of the CuONPs60/GF400 electrode for H2O2 were measured by differential pulse voltammetry (DPV). As shown in Fig. 5a, the CuONPs60/GF400 electrode displays two linear responses for H2O2 detection with a good sensitivity of 56.25 µA mM⁻¹ cm⁻² and a low detection limit of 0.023 µM in the range of 0.07–133 µM (Fig. 5b), whilst displaying an ultrahigh sensitivity of 3437.5 µA mM⁻¹ cm⁻² in the range of 1.20–133 µM (Fig. 5c). The reason for two linear relationships herein was probably caused by the different H2O2 absorption and activation on the CuONPs60/GF400 electrode catalyst under different H2O2 concentrations.32 At extremely low H2O2 concentration, the electrocatalytic process is dominated by H2O2 absorption, but at high H2O2 concentration, the process is dominated by H2O2 activation. Accordingly, the low detection limit obtained at the CuONPs60/GF400 electrode was estimated to be 0.023 µM (S/N = 3). As a contrast, the sensing performances of recently reported H2O2 sensors based on copper-based electrodes are shown in Table S2.†33–41 Detection limit of 0.023 µM and linear range of 0.07–133 µM achieved by using the CuONPs60/GF400. The overall performance of CuONPs60/GF400 exceed the most of copper-based electrodes, which benefitting from the unique

Fig. 4 (a) Differential pulse voltammograms (DPVs) of the CuONPs30/GF400, CuONPs60/GF400, CuONPs90/GF400 and CuONPs120/GF400 in 0.1 M phosphate buffer solution (PBS) with 0.2 mM H2O2 (pH = 7.15). (b) DPVs of the CuONPs30/GF300, CuONPs60/GF400 and CuONPs90/GF500 in 0.1 M PBS with 0.2 mM H2O2 (pH = 7.15). (c) Cyclic voltammograms (CVs) of the bare GF and the CuONPs400/GF400 electrodes in 0.1 mM PBS (pH = 7.15) without and with 0.2 mM H2O2.

Fig. 5 (a) DPVs of the CuONPs50/GF400 electrode in PBS (pH = 7.15) of various H2O2 concentrations. The concentration of H2O2 is from 0.07 µM to 1.13 mM, scan rate: 50 mV s⁻¹. (b) The fitting curves of reductive current vs. concentration of H2O2 (0.07, 0.09, 0.11, 0.13, 0.33, 0.53, 0.73, 0.93, 1.13 µM). (c) The fitting curve of current response vs. H2O2 concentration (1.2, 5.2, 9.2, 13.2, 53.2, 93.2, 133, 733, 1130 µM). (d) Amperometric responses of CuONPs50/GF400 electrode at potential of –0.15 V in the 0.1 M PBS with 0.2 mM H2O2, 0.04 mM glucose, 0.04 mM dopamine, 0.04 mM ascorbic acid, 0.04 mM uric acid and 0.04 mM adrenaline. (e) Amperometric curve of the CuONPs50/GF400 consistently adding 0.2 mM H2O2 under gentle agitation. (f) The amperometric curve of the same CuONPs50/GF400 after 24 h with addition of 0.2 mM H2O2.
microfiber architecture and synergistic effect as well as strong coupling between components with countless active sites and boosted electrons transport. In addition, few group attempt for coupling between components with countless active sites and enhanced electron-transfer ability. It shows highly efficient electro-catalytic activity for nonenzymatic electrochemical \( \text{H}_2\text{O}_2 \) detection, greater than any previously reported CuONPs-based electrodes. This work provides a simple method for the rapid production of a novel fiber electrode for electrochemical sensor applications.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This work was supported by the NSFC (21575014, 21905025), Beijing Natural Science Foundation (2184122), the Fundamental Research Funds for the Central Universities (2018CX01017), Beijing Institute of Technology Research Fund Program for Young Scholars, the project of State Key Laboratory of Explosion Science and Technology (Beijing Institute of Technology, YBKT18-03), and Analysis & Testing Center, Beijing Institute of Technology.

### Table 1

| Sample | Added (\( \mu \text{M} \)) | Founded (\( \mu \text{M} \)) | Recovery (%) | Repeatability (% RSD) |
|--------|------------------------|------------------------|-------------|-----------------|
| Milk   | 0.47                   | 0.49                   | 104.3       | 4.01            |
|        | 0.60                   | 0.58                   | 96.7        | 3.15            |
|        | 5.30                   | 5.39                   | 101.7       | 3.08            |
|        | 94.10                  | 94.83                  | 100.8       | 2.15            |
| Human  | 0.47                   | 0.48                   | 102.1       | 3.34            |
| Serum  | 0.60                   | 0.57                   | 95.0        | 2.08            |
|        | 5.30                   | 6.11                   | 115.3       | 4.10            |
|        | 94.10                  | 95.06                  | 101.0       | 4.05            |

### References

1. J. Zhang, J. Han, Z. Shi, Y. Ju, Z. Zhang and M. Gu, *Appl. Surf. Sci.*, 2019, **465**, 357–361.
2. L. Gao, J. Zhuang, L. Nie, J. Zhang, Y. Zhang, N. Gu, T. Wang, J. Feng, D. Yang, S. Perrett and X. Yan, *Nat. Nanotechnol.*, 2007, 2, 577.
3. Z. Zhang, J. Hao, W. Yang, B. Lu, X. Ke, B. Zhang and J. Tang, *ACS Appl. Mater. Interfaces*, 2013, 5, 3809–3815.
4. F. Natalio, R. André, A. F. Hartog, B. Stoll, K. P. Jochum, R. Wever and W. Tremel, *Nat. Nanotechnol.*, 2012, 7, 530.
5. P. Pengo, S. Polizzi, L. Pasquato and P. Scrimin, *J. Am. Chem. Soc.*, 2005, **127**, 1616–1617.
6. W. Shi, X. Zhang, S. He and Y. Huang, *Chem. Commun.*, 2011, **47**, 10785–10787.
7. W. Chen, J. Chen, A. L. Liu, L. M. Wang, G. W. Li and X. H. Lin, *ChemCatChem*, 2011, 3, 1151–1154.
8. X. X. Wang, Q. Wu, Z. Shan and Q. M. Huang, *Biosens. Bioelectron.*, 2011, **26**, 3614–3619.
9. P. Roy, Z. H. Lin, C. T. Liang and H. T. Chang, *Chem. Commun.*, 2012, **48**, 4079–4081.
10. Z. Chen, J. J. Yin, Y. T. Zhou, Y. Zhang, L. Song, M. Song, S. Hu and N. Gu, *ACS Nano*, 2012, 6, 4001–4012.
11. M. Baghayeri, H. Alinezhad, M. Tarahomi, M. Fayazi, M. Ghanei-Motlagh and B. Maleki, *Appl. Surf. Sci.*, 2019, **478**, 87–93.
12. J. Cai, S. Ding, G. Chen, Y. Sun and Q. Xie, *Appl. Surf. Sci.*, 2018, **456**, 302–306.
13. K. Zhang, N. Zhang, H. Cai and C. Wang, *Microchim. Acta*, 2012, **176**, 137–142.
14. L. Lu and X. Huang, *Microchim. Acta*, 2011, **175**, 151–157.
15. J. Huang, Y. Zhu, H. Zhong, X. Yang and C. Li, *ACS Appl. Mater. Interfaces*, 2014, 6, 7055–7062.
16 L. Zhou, L. Kuai, W. Li and B. Geng, ACS Appl. Mater. Interfaces, 2012, 4, 6463–6467.
17 R. Agarwal, K. Verma, N. K. Agrawal, R. K. Duchaniya and R. Singh, Appl. Therm. Eng., 2016, 102, 1024–1036.
18 C. Yang, X. Su, F. Xiao, J. Jian and J. Wang, Sens. Actuators, B, 2011, 158, 299–303.
19 X. Zhang, S. Sun, J. Lv, L. Tang, C. Kong, X. Song and Z. Yang, J. Mater. Chem. A, 2014, 2, 10073–10080.
20 C. Kong, L. Tang, X. Zhang, S. Sun, S. Yang, X. Song and Z. Yang, J. Mater. Chem. A, 2014, 2, 7306–7312.
21 Y. Sun, M. Luo, Y. Qin, S. Zhu, Y. Li, N. Xu, X. Meng, Q. Ren, L. Wang and S. Guo, ACS Appl. Mater. Interfaces, 2017, 9, 34715–34721.
22 Y. Hu, Z. Zhang and C. Yang, Anal. Chim. Acta, 2007, 601, 95.
23 X. Zhu, X. Niu, H. Zhao and M. Lan, Sens. Actuators, B, 2014, 195, 274–280.
24 M. Zhang, Y. Wang, L. Huang, Z. Xu, C. Li and G. Shi, Adv. Mater., 2016, 27, 6708–6713.
25 V. Gupta, P. Mahbub, P. N. Nesterenko and B. Paull, Anal. Chim. Acta, 2018, 1005, 81–92.
26 A. A. M. Abdurhman, Y. Zhang, G. Zhang and S. Wang, Anal. Bioanal. Chem., 2015, 407, 8129–8136.
27 M. L. Huffman and B. J. Venton, Analyst, 2009, 134, 18–24.
28 Y. T. Liao, Y. Y. Huang, H. M. Chen, K. Komaguchi, C. H. Hou, J. Henzie, Y. Yamauchi, Y. Ide and K. C. W. Wu, ACS Appl. Mater. Interfaces, 2017, 9, 42425–42429.
29 M. Zhang, Y. Wang, L. Huang, Z. Xu, C. Li and G. Shi, Adv. Mater., 2015, 27, 6708–6713.
30 T. Baran, S. Wojtyla, C. Lenardi, A. Vertova, P. Ghigna, E. Achilli, M. Fracchia, S. Rondinini and A. Minguzzi, ACS Appl. Mater. Interfaces, 2016, 8, 21250–21260.
31 X. Sun, S. Guo, Y. Liu and S. Sun, Nano Lett., 2012, 12, 4859–4863.
32 W. Meng, S. Xu, L. Dai, Y. Li, J. Zhu and L. Wang, Electrochim. Acta, 2017, 230, 324–332.
33 F. Xu, M. Deng, G. Li, S. Chen and L. Wang, Electrochim. Acta, 2013, 88, 59–65.
34 H. Song, C. Ma, L. You, Z. Cheng, X. Zhang, B. Yin, Y. Ni and K. Zhang, Microchim. Acta, 2015, 182, 1543–1549.
35 B. B. Jiang, X. W. Wei, F. H. Wu, K. L. Wu, L. Chen, G. Z. Yuan, C. Dong and Y. Ye, Microchim. Acta, 2014, 181, 1463–1470.
36 M. Liu, R. Liu and W. Chen, Biosens. Bioelectron., 2013, 45, 206–212.
37 C. Zhang, M. Wang, L. Liu, X. Yang and X. Xu, Electrochem. Commun., 2013, 33, 131–134.
38 S. Li, Y. Zheng, G. W. Qin, Y. Ren, W. Pei and L. Zuo, Talanta, 2011, 85, 1260–1264.
39 Y. K. Hsu, Y. C. Chen and Y. G. Lin, Appl. Surf. Sci., 2015, 354, 85–89.
40 A. Gu, G. Wang, J. Gu, X. Zhang and B. Fang, Electrochim. Acta, 2010, 55, 7182–7187.
41 J. Huang, Y. Zhu, H. Zhong, X. Yang and C. Li, ACS Appl. Mater. Interfaces, 2014, 6, 7055–7062.