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# Ultra-small dispersed Cu<sub>x</sub>O nanoparticles on graphene fibers for miniaturized electrochemical sensor applications†

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A graphene microfiber (GF) modified with ultrafine Cu<sub>x</sub>O nanoparticles (Cu<sub>x</sub>ONPs/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 H<sub>2</sub>O<sub>2</sub> sensing. Benefiting from the unique microfiber architecture and synergetic effects, as well as strong coupling between components with many active sites and boosted electron transport, the Cu<sub>x</sub>ONPs/GF electrode shows prominent sensitivity, selectivity and long-term operational stability for the detection of H<sub>2</sub>O<sub>2</sub>. Further work successfully applied this Cu<sub>x</sub>ONPs/GF electrode to detection of H<sub>2</sub>O<sub>2</sub> in real samples such as milk and human serum. These results indicate that the Cu<sub>x</sub>ONPs/GF is a promising mini-sized sensor in electrochemical analysis.

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## 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,<sup>1</sup> 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.<sup>2–12</sup> Copper oxide nanoparticles (Cu<sub>x</sub>ONPs) are an attractive alternative electroactive species due to their abundance, low cost, good chemical stability and unique electronic properties.<sup>13,14</sup> Hybridizing graphene with Cu<sub>x</sub>ONPs 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,<sup>15</sup> ion exchange,<sup>16</sup> wet chemistry,<sup>17</sup> microwave,<sup>18</sup> template growth,<sup>19</sup> and anion-assisted approaches<sup>20</sup> have been employed to prepare Cu<sub>x</sub>ONPs/graphene hybrids. Unfortunately, as-prepared Cu<sub>x</sub>ONPs 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 Cu<sub>x</sub>ONPs/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 Cu<sub>x</sub>ONPs/graphene fiber-based microsensor with a high number of active sites and highly efficient electrocatalytic activity.

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is indispensable to ecosystems and is widely used in foodstuffs, the environment, medicine and industry. Excess H<sub>2</sub>O<sub>2</sub> can lead to toxicity for humans and to the environment.<sup>21–24</sup> 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

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a graphene microfiber electrode modified by well-dispersed and ultrafine  $\text{Cu}_x\text{O}$  nanoparticles ( $\text{Cu}_x\text{ONPs}/\text{GF}$ ) derived from copper-based metal organic frameworks (HKUST-1) by a direct electrodeposition self-assembly technique for nonenzymatic electrochemical  $\text{H}_2\text{O}_2$  detection. The unique nanoarchitecture and synergetic effect as well as strong coupling between components endows 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  $0.023 \mu\text{M}$  and a rapid response time of 1 s. Our work provides a straightforward method for synthesizing highly efficient nonenzymatic micro-sensing electrodes for  $\text{H}_2\text{O}_2$  detection.

## Experimental

### Synthesis of graphene fiber (GF)

Graphene oxide (GO) was synthesized by oxidation of graphite powder according to the modified Hummers' method.<sup>25</sup> Then, graphene oxide fibers (GOF) were prepared by a wet spinning strategy. Typically, 3 mL GO ( $20 \text{ mg mL}^{-1}$ ) was spun into a methanol solution saturated by potassium chloride (KCl) with a speed of  $0.1 \text{ m s}^{-1}$  by an injector (with a diameter of 0.25 mm), followed by drying. To obtain GF, the GOF was heated to  $200 \text{ }^\circ\text{C}$  for 2 h at first and then further heated to  $1000 \text{ }^\circ\text{C}$  for 2 h with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2/\text{H}_2$  ( $v/v = 4 : 1$ ) 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 ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), 0.2102 g of 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ) and 0.7748 g of tetrabutylammonium hexafluorophosphate ( $\text{NBu}_4\text{PF}_6$ ) were dispersed in 20 mL of *N,N*-dimethylformamide (DMF) solution, and the mixture was treated by ultrasound for 30 min to obtain a homogeneous 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  $\text{N}_2$  for 30 min) at  $-1.5 \text{ V}$  for 60 s, the obtained sample is denoted  $\text{HNPs}_{60}/\text{GF}$ . 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  $\text{HNPs}_{30}/\text{GF}$ ,  $\text{HNPs}_{90}/\text{GF}$  and  $\text{HNPs}_{120}/\text{GF}$ , respectively.

### Synthesis of $\text{Cu}_x\text{ONPs}/\text{GF}$

The  $\text{Cu}_x\text{ONPs}/\text{GF}$  was synthesized by direct annealing of HNPs/GF ( $\text{HNPs}_{30}/\text{GF}$ ,  $\text{HNPs}_{60}/\text{GF}$ ,  $\text{HNPs}_{90}/\text{GF}$  and  $\text{HNPs}_{120}/\text{GF}$ ) samples from room temperature to  $400 \text{ }^\circ\text{C}$  in  $\text{N}_2$  with a ramp rate of  $10 \text{ }^\circ\text{C min}^{-1}$  and stabilized for 2 h, then cooled to room temperature naturally, and denoted  $\text{Cu}_x\text{ONPs}_{30}/\text{GF}_{400}$ ,  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$ ,  $\text{Cu}_x\text{ONPs}_{90}/\text{GF}_{400}$  and  $\text{Cu}_x\text{ONPs}_{120}/\text{GF}_{400}$ , respectively.

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

### Synthesis of $\text{Cu}_x\text{ONPs}/\text{GF}$ electrode

The  $\text{Cu}_x\text{ONPs}/\text{GF}$  was glued with silver conductive adhesive onto stainless steel sheets ( $2.5 \times 0.5 \text{ cm}$ ). The end of the tip was sealed with molten paraffin. The exposed  $\text{Cu}_x\text{ONPs}/\text{GF}$  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  $\text{Cu}_x\text{ONPs}/\text{GF}$  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  $44 \mu\text{m}$  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 ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) and 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ), in which HNPs grew *in situ* on the surface of GF after 60 s of electrodeposition ( $\text{HNPs}_{60}/\text{GF}$ , Fig. 1d), which was confirmed by X-ray diffraction (XRD, Fig. S2†). As shown in Fig. 2a, the obtained  $\text{HNPs}_{60}/\text{GF}$  shows fiber features with a diameter of  $45 \mu\text{m}$ , larger than that of the bare GF. Fig. 2b demonstrates that the  $\text{HNPs}_{60}$  with an octahedral structure have a uniform size of 200 nm and are well distributed over the surface of GF. Further annealing at  $400 \text{ }^\circ\text{C}$  led to pyrolysis of  $\text{HNPs}_{60}$  with simultaneous formation of  $\text{Cu}_x\text{O}$

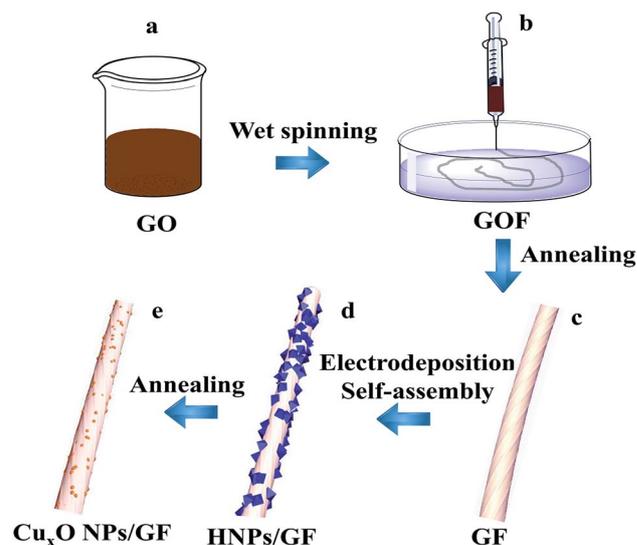
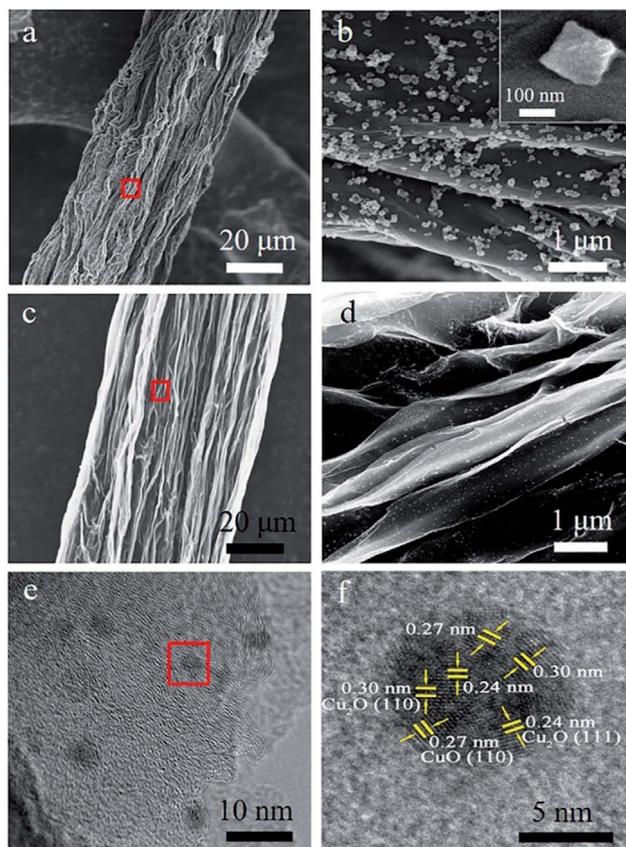


Fig. 1 Schematic illustration of the preparation of  $\text{Cu}_x\text{ONPs}/\text{GF}$ . (a) GO solution, (b) GOF, (c) GF, (d) HNPs/GF, (e)  $\text{Cu}_x\text{ONPs}/\text{G}$ .





**Fig. 2** (a) Scanning electron microscopy (SEM) images of HNP<sub>60</sub>/GF. (b) The enlarged view of the rectangle area in (a). The inset in (b) is an enlarged SEM image of a single HNP<sub>60</sub>. (c) SEM image of Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub>. (d) The enlarged view of the rectangle area in (c). (e) Transmission electron microscopy (TEM) image of sheets within the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub>. (f) The enlarged view of the rectangle area in (e).

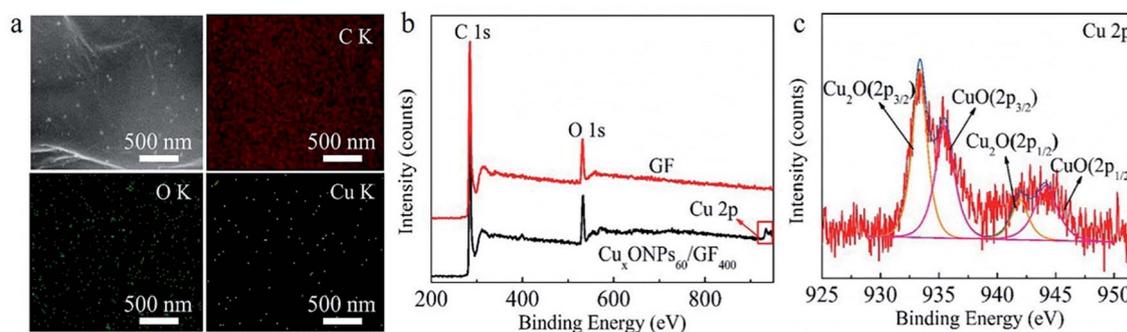
nanoparticles (Cu<sub>x</sub>ONPs<sub>60</sub>, the size is about 10 nm) well distributed on the sheets of GF (Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub>, Fig. 2c–e). High-resolution transmission electron microscopy (HR-TEM) of Cu<sub>x</sub>ONPs/GF (Fig. 2f) indicates clear lattice fringes with a spacing of 0.24, 0.27 and 0.30 nm, corresponding to the Cu<sub>2</sub>O(111), CuO(110) and Cu<sub>2</sub>O(110), respectively.<sup>26–30</sup> Element mapping reveals the coexistent and uniform distribution of C, O and Cu elements for Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> (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 Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> shows the two apparent Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> features at 934.2 eV and 944.4 eV with a Cu atomic percentage of 0.76% (Fig. 3b), indicating the presence of Cu<sub>x</sub>ONPs<sub>60</sub>, 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 (Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub>), demonstrating an increase in the oxygen content resulting from the introduction of Cu<sub>x</sub>O. In addition, the chemical states of copper in Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> are revealed by the high-resolution XPS spectra (Fig. 3c). The signals of Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> can each be deconvoluted into two peaks of Cu<sub>2</sub>O (933.4 eV and 935.4 eV) and CuO (941.9 eV and 944.2 eV)<sup>31</sup> ascribed to the oxidation products of HNPs after annealing.

### H<sub>2</sub>O<sub>2</sub>-sensing properties

The electrochemical properties of the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode are investigated in 0.1 M PBS saturated with N<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup>. Considering the electrodeposition self-assembly time has a significant effect on the content and size of Cu<sub>x</sub>ONPs, as well as the catalytic performance of the Cu<sub>x</sub>ONPs/GF electrode, various Cu<sub>x</sub>ONPs/GF electrodes were obtained by adjusting the electrodeposition self-assembly time (30 s, 90 s and 120 s), which were denoted Cu<sub>x</sub>ONPs<sub>30</sub>/GF<sub>400</sub>, Cu<sub>x</sub>ONPs<sub>90</sub>/GF<sub>400</sub>, and Cu<sub>x</sub>ONPs<sub>120</sub>/GF<sub>400</sub>, respectively. The SEM images and EDS analysis of the Cu<sub>x</sub>ONPs/GF samples (Fig. S4 and Table S1†) imply that with the increasing time of electrodeposition self-assembly, the content and size of the Cu<sub>x</sub>ONPs increase. As a result, there is almost no reductive peak at the Cu<sub>x</sub>ONPs<sub>30</sub>/GF<sub>400</sub> electrode (Fig. 4a), which can be attributed to only trace amounts of Cu<sub>x</sub>O 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 Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode, which was attributed to the successful electrode surface reaction process.

A further increase of electrodeposition self-assembly time causes severe agglomeration of Cu<sub>x</sub>ONPs 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 Cu<sub>x</sub>ONPs and performance of



**Fig. 3** (a) Scanning transmission electron microscopy (STEM) and C-, O- and Cu-element mappings for the sheets within the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub>. (b) XPS spectra of the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> and the bare GF. (c) High-resolution Cu 2p XPS spectrum of Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub>.



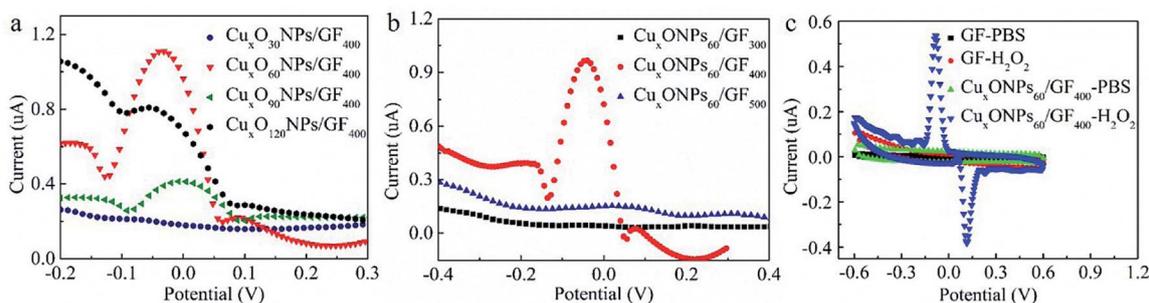


Fig. 4 (a) Differential pulse voltammograms (DPVs) of the  $\text{Cu}_x\text{ONPs}_{30}/\text{GF}_{400}$ ,  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$ ,  $\text{Cu}_x\text{ONPs}_{90}/\text{GF}_{400}$  and  $\text{Cu}_x\text{ONPs}_{120}/\text{GF}_{400}$  in 0.1 M phosphate buffer solution (PBS) with 0.2 mM  $\text{H}_2\text{O}_2$  (pH = 7.15). (b) DPVs of the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{300}$ ,  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  and  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{500}$  in 0.1 M PBS with 0.2 mM  $\text{H}_2\text{O}_2$  (pH = 7.15). (c) Cyclic voltammograms (CVs) of the bare GF and the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrodes in 0.1 mM PBS (pH = 7.15) without and with 0.2 mM  $\text{H}_2\text{O}_2$ .

the final  $\text{Cu}_x\text{ONPs}/\text{GF}$  electrode. For comparison, a series of  $\text{Cu}_x\text{ONPs}/\text{GF}$  electrodes were prepared by annealing the precursors of HNP/GF derived from the optimal electrodeposition time at different temperatures (300 °C and 500 °C, which were denoted  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{300}$  and  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{500}$ , respectively). Apparently, the current response signal of the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode is obviously higher than that of the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{300}$  and the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{500}$  electrodes (Fig. 4b). This may be attributed to the incomplete decomposition of the HNP<sub>60</sub> precursor for the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{300}$  electrode (Fig. S5a†). The residual non-conductive HNP<sub>60</sub> inhibit electron transport on the surface of GF, leading to poor electrocatalytic activity towards  $\text{H}_2\text{O}_2$  sensing. For the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{500}$  electrode, an increase of  $\text{Cu}_x\text{ONPs}_{60}$  size can be observed as shown in Fig. S5b,† hence reducing the utilization of active sites and leading to a decrease in electrocatalytic performance.<sup>32</sup>

As a result, compared with the bare GF (no redox peaks, Fig. 4c), the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode displays a couple of sharp redox peaks, indicating an excellent electrocatalytic activity of the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode towards  $\text{H}_2\text{O}_2$  detection. Meanwhile, the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  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  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode for  $\text{H}_2\text{O}_2$  were measured by differential pulse voltammetry (DPV). As shown in Fig. 5a, the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode displays two linear responses with a good sensitivity of  $56.25 \mu\text{A mM}^{-1} \text{cm}^{-2}$  and a low detection limit of  $0.023 \mu\text{M}$  in the range of  $0.07\text{--}1.13 \mu\text{M}$  (Fig. 5b), whilst displaying an ultrahigh sensitivity of  $3437.5 \mu\text{A mM}^{-1} \text{cm}^{-2}$  in the range of  $1.20\text{--}133 \mu\text{M}$  (Fig. 5c). The reason for two linear relationships herein was probably caused by the different  $\text{H}_2\text{O}_2$  absorption and activation on the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode catalyst under different  $\text{H}_2\text{O}_2$  concentrations.<sup>32</sup> At extremely low  $\text{H}_2\text{O}_2$  concentration, the electrocatalytic process is dominated by  $\text{H}_2\text{O}_2$  absorption, but at high  $\text{H}_2\text{O}_2$  concentration, the process is dominated by  $\text{H}_2\text{O}_2$  activation. Accordingly, the low detection limit obtained at the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode was estimated to be  $0.023 \mu\text{M}$  (S/N = 3). As a contrast, the sensing performances of recently reported  $\text{H}_2\text{O}_2$  sensors based on copper-based electrodes are shown in Table

S2.†<sup>32–41</sup> Detection limit of  $0.023 \mu\text{M}$  and linear range of  $0.07\text{--}133 \mu\text{M}$  achieved by using the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$ . The overall performance of  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  exceed the most of copper-based electrodes, which benefiting from the unique

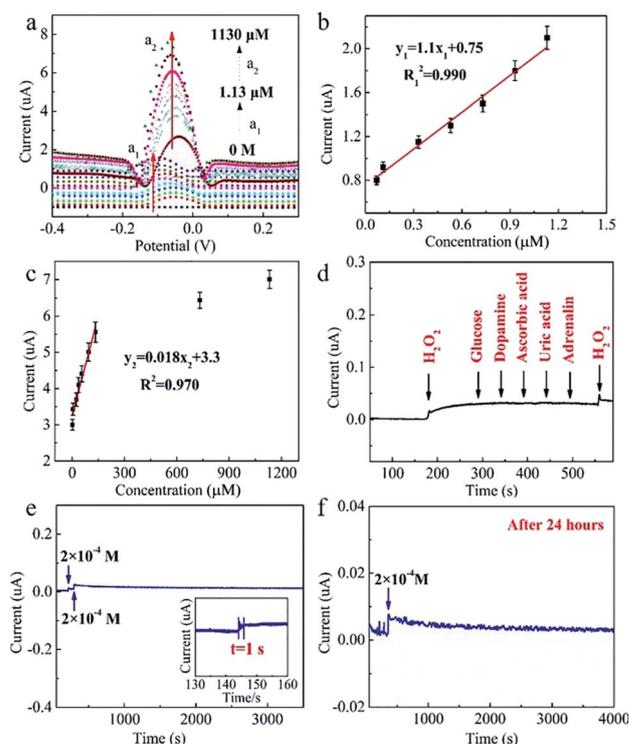


Fig. 5 (a) DPVs of the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode in PBS (pH = 7.15) of various  $\text{H}_2\text{O}_2$  concentrations. The concentration of  $\text{H}_2\text{O}_2$  is from  $0.07 \mu\text{M}$  to  $1.13 \text{mM}$ , scan rate:  $50 \text{mV s}^{-1}$ . (b) The fitting curves of reductive current vs. concentration of  $\text{H}_2\text{O}_2$  ( $0.07, 0.09, 0.11, 0.13, 0.33, 0.53, 0.73, 0.93, 1.13 \mu\text{M}$ ). (c) The fitting curve of current response vs.  $\text{H}_2\text{O}_2$  concentration ( $1.2, 5.2, 9.2, 13.2, 53.2, 93.2, 133, 733, 1130 \mu\text{M}$ ). (d) Amperometric responses of  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  electrode at potential of  $-0.15 \text{V}$  in the 0.1 M PBS with 0.2 mM  $\text{H}_2\text{O}_2$ , 0.04 mM glucose, 0.04 mM dopamine, 0.04 mM ascorbic acid, 0.04 mM uric acid and 0.04 mM adrenalin. (e) Amperometric curve of the  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  consistently adding 0.2 mM  $\text{H}_2\text{O}_2$  under gentle agitation. (f) The amperometric curve of the same  $\text{Cu}_x\text{ONPs}_{60}/\text{GF}_{400}$  after 24 h with addition of 0.2 mM  $\text{H}_2\text{O}_2$ .



**Table 1** Determination of H<sub>2</sub>O<sub>2</sub> in real samples at the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> microelectrode ( $n = 3$ )

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 Serum	0.47	0.48	102.1	3.34
	0.60	0.57	95.0	2.08
	5.30	6.11	115.3	4.10
	94.10	95.06	101.0	4.05

microfiber architecture and synergetic effect as well as strong coupling between components with countless active sites and boosted electrons transport. In addition, few group attempt for electrochemical detection of H<sub>2</sub>O<sub>2</sub> on fiber electrode.

The selectivity test of the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode was carried out in 0.1 M phosphate buffer solution (PBS). 0.2 mM H<sub>2</sub>O<sub>2</sub> was added, followed by 0.04 mM glucose, 0.04 mM dopamine, 0.04 mM ascorbic acid, 0.04 mM uric acid and 0.04 mM adrenalin, respectively. As shown in Fig. 5d, after adding 0.2 mM H<sub>2</sub>O<sub>2</sub>, a distinct current response was observed, and there was almost no change in the peak current in the presence of the interferents. In addition, when a further 0.2 mM H<sub>2</sub>O<sub>2</sub> was added, the current signal showed the same response as after the first H<sub>2</sub>O<sub>2</sub> addition, indicating the excellent selectivity of the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode. The Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode shows a response time of H<sub>2</sub>O<sub>2</sub> detection within 1 s, indicating it tracks very quickly (Fig. 5e inset). The peak current barely changed after 3500 s (Fig. 5e), and after storing at room temperature for 24 h, the response signal of the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode remains 98% of its original response for H<sub>2</sub>O<sub>2</sub> detection (Fig. 5f), revealing a good operational stability of the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode.

### Detection of H<sub>2</sub>O<sub>2</sub> in milk and human serum

The Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode was used for the determination of 0.47, 0.60, 5.30, and 94.10  $\mu\text{M}$  H<sub>2</sub>O<sub>2</sub> in diluted milk and diluted human serum samples (Table 1 and Fig. S7 and S8<sup>†</sup>), respectively. The recovery rates calculated according to the calibration curves (Fig. 5b and c) were 104.3%, 96.7%, 101.7% and 100.8% for milk, and 102.1%, 95.0%, 115.3% and 101.0% for human serum, respectively, the relative standard deviation were less than 4.10% for  $n = 3$ , indicating that the Cu<sub>x</sub>ONPs<sub>60</sub>/GF<sub>400</sub> electrode is effective for H<sub>2</sub>O<sub>2</sub> detection in a biological system.

## Conclusions

In summary, we have fabricated a graphene fiber electrode modified with well-dispersed and superfine copper oxide nanoparticles derived from electrodeposition self-assembly of a copper-based metal organic frameworks. The as-prepared Cu<sub>x</sub>ONPs/graphene fiber electrode exhibits a high number of

active sites and enhanced electrode exhibits a high number of active sites and enhanced electron-transfer ability. It shows highly efficient electro-catalytic activity for nonenzymatic electrochemical H<sub>2</sub>O<sub>2</sub> detection, greater than any previously reported Cu<sub>x</sub>ONPs-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.

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