



Amorphous copper cobalt carbonate hydroxide prepared by SILAR on copper foam for non-enzymatic glucose sensing

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ABSTRACT

Amorphous copper cobalt carbonate hydroxide (CuCoCH) was prepared on copper foam (CF) by successive ionic layer adsorption and reaction (SILAR) method for non-enzymatic glucose sensing. The binder-free approach facilitates the transfer of electrons in the CuCoCH/CF electrode, its hierarchical porous network structure promotes the diffusion of glucose and its large surface area provides abundant catalytic sites for electrocatalysis oxidation of glucose. Moreover, the easily controllable Cu/Co ratio and the synergistic effect of copper and cobalt in CuCoCH increase the electrocatalytic activity for glucose oxidation. As a result, the CuCoCH/CF electrode exhibits a linear range of 0.005–3.47 mM, a sensitivity of 1.5167 mA·mM⁻¹·cm⁻² and a detection limit of 2.3 μM (S/N = 3) for glucose detection. Meanwhile, it also demonstrates satisfactory selectivity, reproducibility, stability and practical applicability, indicating the CuCoCH/CF electrode prepared by this facile method is promising in non-enzymatic glucose sensing.

Introduction

As a common chronic disease worldwide, diabetes causes physical disability like stroke, kidney failure, heart disease, etc. and even death [1, 2]. The content

of glucose in blood is an indicator for clinical diagnosis and monitoring of diabetes. In order to control the disease, it is very important for diabetics to detect changes in blood glucose concentration multiple times a day. Therefore, it is of great significance to develop an efficient and reliable glucose sensor. Most

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of the commercially available glucose meters are glucose oxidase (GOD) enzyme-based electrochemical sensors [3]. Despite its excellent selectivity, this enzyme has the drawbacks of high cost, complicated immobilization process and chemical instability [4]. Therefore, researchers have tried to prepare enzyme-free glucose electrochemical sensors with various materials including noble metals [5–7], transition metals and their compounds [8–10], conductive polymers [11], carbon [12, 13] and composites of above materials [14–16].

Among them, transition metals have been widely studied due to their high electrocatalytic activity, high electroactivity, low cost and environmental friendliness. Copper, cobalt and nickel are commonly used transition metal nanozymes for glucose sensors, including their metals and alloys [17–19], oxides [20–23], hydroxides [24–27], sulphides [28–31], etc. Different types of transition metal nanozymes have different properties such as conductivity, catalytic activity and sensitivity, which lead to their different performance in sensors. For example, the oxides have received extensive attention due to their high catalytic activity, while sulphides can obtain high sensitivity [30]. Therefore, it is of great significance to develop new types of transition metal-based non-enzymatic glucose sensors. The using of bimetallic nanozymes is an efficient strategy to improve the sensing performance of nanozymes and various bimetallic nanozymes were designed [32–34]. For instance, Li et al. prepared MCo (M=Cu, Fe, Ni and Mn) bimetallic nanoparticle-doped carbon nanofibers (MCo-CFs) for non-enzymatic glucose detection. The large surface area of CuCo-CFs and synergistic effect of the CoIII/IV and CuII/III redox make CuCo-CFs the best catalytic activity with a large sensitivity of $507 \mu\text{A}\cdot\text{cm}^{-2}\cdot\text{mM}^{-1}$ and a wide linear range of 0.02–11 mM [35].

In recent years, bimetallic carbonate hydroxides have been used in the field of electrochemistry such as supercapacitors, water splitting due to their rich redox reaction, favourable synergistic effects and superior electrochemical stability [36–38]. Despite their excellent electrochemical properties, bimetallic carbonate hydroxides are rarely used in electrochemical sensors. Zhao et al. prepared a layer of cobalt copper carbonate hydroxide nanowires (CCCH) with a large specific surface on copper foam (CF) by hydrothermal method to increase the loading of NiCo layered double metal hydroxide

(NiCo-LDH), which formed a NiCo-LDH/CCCH/CF structure for enzyme-free glucose detection and exhibited high sensitivity of $10.78 \mu\text{A}\cdot\mu\text{M}^{-1}\cdot\text{cm}^{-2}$, large linear concentration range of 0.001–1.5 mM and fast response–recovery time of 2.0 s [39].

To study the catalytic effect of bimetallic carbonate hydroxides on glucose oxidation, we prepared copper cobalt carbonate hydroxide (CuCoCH) on copper foam by SILAR for non-enzymatic glucose sensing. In the SILAR process, a substrate is immersed in one precursor solution to adsorb the ions; after removing the excess ions, the substrate is immersed in the other precursor solution, and ions of opposite charge are adsorbed and react to obtain the target product on the substrate. Different substrates have obvious effects on the performance of electrochemical sensors [9]. Copper foam (CF) was used as a substrate for electrochemical sensors because of its good electrical conductivity, large specific surface area and good supporting properties [39]. In the SILAR process, the large specific surface area and rough surface of copper foam can increase the adsorption capacity of ions. At the same time, the in situ preparation can make good contact between the material (CuCoCH) and the substrate (CF), which is conducive to the transfer of electrons. Most importantly, the ratio of Cu/Co can be easily tuned and the synergistic effect of copper and cobalt can increase the electrocatalytic activity of CuCoCH towards glucose oxidation. Therefore, this facile prepared CuCoCH/CF electrode is expected to show good sensing performance for glucose detection.

Experimental

Reagents and materials

NaOH, Na_2CO_3 , $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and L-ascorbic acid (AA) were provided by Tianjin Fuchen reagent Co. Ltd. D-(+)-Glucose and L-cysteine (L-cys) were obtained from Shanghai Yuanye Bio-technology Co., Ltd. Dopamine hydrochloride (DA) and uric acid (UA) were purchased from Sigma-Aldrich. Acetone, ethanol and methanol were bought from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as received without further dispose. Copper foam ($\delta = 1.0 \text{ mm}$, 90 ppi) was provided by Yiyang Form-metal new material Co., Ltd. Deionized water was

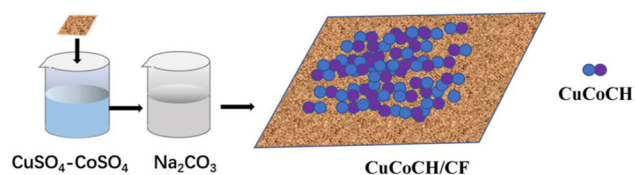
produced by a Millipore ultrapure water system. The simulated human serum was purchased from Acme Biochemical Company.

Preparation of CuCoCH/CF electrode

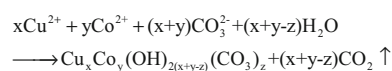
Copper foam with the area of $1.2 \times 0.8 \text{ cm}^2$ was sonicated with acetone, deionized water and absolute ethanol sequentially and dried in air. SILAR method was used to prepare CuCoCH/CF electrode. As shown in Scheme 1, copper foam was immersed in a mixed solution of 0.2 M $\text{CuSO}_4\text{-CoSO}_4$ (Cu/Co molar ratio: 1:3) for 1 min, which was then rinsed with deionized water to remove the excess ions and immersed in a solution of 0.2 M Na_2CO_3 for another 1 min. After that, it was washed with deionized water and dried at $50 \text{ }^\circ\text{C}$ for 20 min to obtain the CuCoCH/CF electrode. The proposed reaction scheme of the formation of CuCoCH material is shown in Scheme 2. A mixed solvent of water and methanol ($V_{\text{water}}/V_{\text{methanol}} = 4:1$) was used for the two solutions in order to enhance the hydrophilicity of copper foam. For comparison, bare copper foam (CF) was used as electrode after cleaning.

Characteristics

The morphology of CuCoCH was observed by Hitachi model SU 8020 UHR field emission scanning electron microscope (FESEM) (Japan), and the element composition analysis was performed by the equipped energy-dispersive X-ray spectroscopy (EDS). The ESCALAB 250Xi (Thermo Fisher Scientific, USA) was used to conduct X-ray photoelectron spectroscopy (XPS) test with a monochromatized Al K α line source. The Fourier transform infrared (FTIR) spectroscopy of the CuCoCH sample was tested on a FTIR-8400S (Shimadzu, Japan) spectrometer.



Scheme 1 Schematic diagram of preparing CuCoCH/CF electrode by SILAR method.



Scheme 2 Proposed reaction scheme of the formation of CuCoCH.

Electrochemical measures

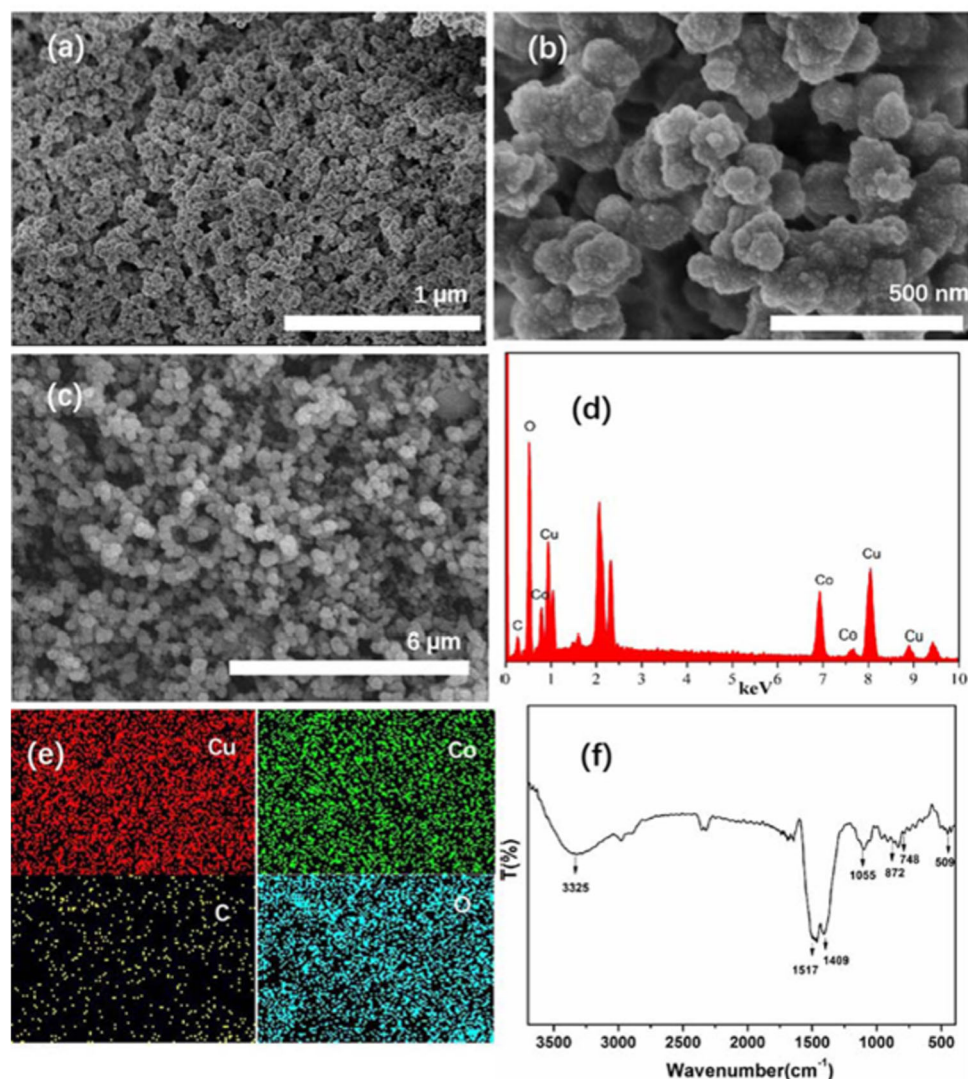
The electrochemical measurements were taken on a CHI 660E electrochemical workstation (Chenhua Inc., China) with a three-electrode system. The CuCoCH/CF electrode (active area of 0.8 cm^2), Pt wire and Ag/AgCl electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. NaOH (0.1 M) was used as the electrolyte. For EIS measurements, the electrolyte was 1 M KOH. The EIS measurements were taken under open-circuit potential with the frequency range from 0.01 to 100 kHz at an amplitude of 5 mV.

Results and discussions

Structure and morphology analyses

The CuCoCH/CF electrode was characterized by SEM, EDS and FTIR, and the results are shown in Fig. 1. From the SEM image shown in Fig. 1a, the amorphous CuCoCH has a hierarchical porous network structure, which is composed of many nanoflowers about 100–200 nm in size. These nanoflowers are connected to each other, forming many large pores that are favourable for glucose diffusion and electrolyte infiltration, which facilitates the transfer of electrons in the CuCoCH/CF electrode. Figure 1b shows that there are a large number of smaller nanoparticles on the surface of the nanoflowers, which can increase the specific surface area of the material, thereby increasing the electrocatalytic active sites of the electrode. Elemental scan analysis was performed on the CuCoCH sample (Fig. 1c). The EDS is shown in Fig. 1d, indicating the existence of Cu, Co, C and O, and the atomic ratio of Cu to Co was estimated to be 2.5:1. From the elemental mapping shown in Fig. 1e, the four elements distributed homogeneously, revealing the uniform structure of the electrode. The CuCoCH sample was also characterized by the FTIR spectrum over the range of $4000\text{--}400 \text{ cm}^{-1}$. As shown in Fig. 1f, the broad peak centred at approximately 3325 cm^{-1} can be ascribed to the stretching vibration of O–H. The

Figure 1 **a** SEM image of CuCoCH/CF at 1 μm scale, **b** SEM image of CuCoCH/CF at 500 nm scale, **c** scan area, **d** EDS, **e** elemental mapping and **f** FTIR spectrum of CuCoCH.



two peaks at $1517, 1409\text{ cm}^{-1}$ are assigned to the stretching vibrations of νOCO_2 and the asymmetrical stretching vibration of CO_3^{2-} , respectively. The ownership of the peak at 1055 cm^{-1} remains controversial. It was considered as the symmetrical stretching vibration of CO_3^{2-} [40] or assigned to metal–OH bond [41]. The peaks at 872 and 748 cm^{-1} are due to the in-plane and out-of-plane bending vibration of CO_3^{2-} . The band below 600 cm^{-1} are associated with metal–oxygen bonds. Our results are similar to previous report [40], indicating the formation of CuCoCH.

The chemical states of the CuCoCH sample were investigated by X-ray photoelectron spectroscopy (XPS) and are shown in Fig. 2. Figure 2a shows a full

survey of the CuCoCH sample, indicating the existence of Co, Cu, C and O elements in the sample. Figure 2b shows that the peaks corresponding to C 1s are located at 284.9 eV and 288.4 eV . The former corresponds to the C=C originates from carbon contamination in the test, and the latter corresponds to the C–O in the sample [42]. Figure 2c shows the peak of O1s at 531.2 eV which can be ascribed to hydroxyl group (O–H) [43]. According to Fig. 2d, the peaks at 936.0 eV (Cu2p $_{3/2}$) and 956.0 eV (Cu2p $_{1/2}$) correspond to Cu^{2+} [34, 40, 44], and the peaks at 943.7 eV and 963.5 eV are satellite peaks. From Fig. 2e, the peaks at 781.8 eV (Co2p $_{3/2}$) and 797.7 eV (Co2p $_{1/2}$) correspond to Co^{2+} [34, 40, 44], and the peaks at 787.0 eV and 802.9 eV are satellite peaks.

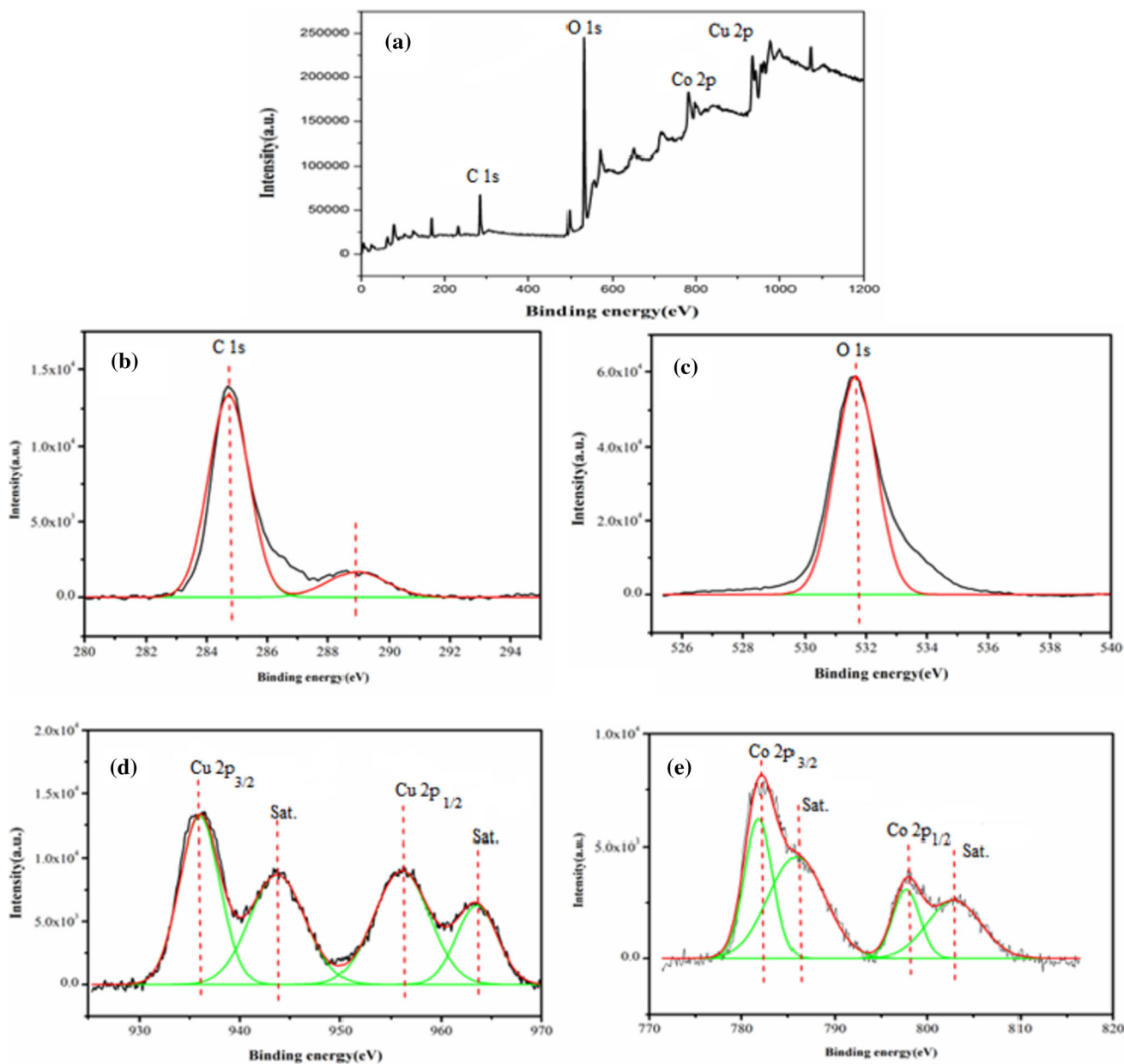


Figure 2 XPS spectra of CuCoCH sample: **a** full scanning, **b** C 1 s, **c** O 1 s, **d** Cu 2p and **e** Co 2p.

Electrochemical characterization of CuCoCH/CF electrode

The electrochemical behaviours of CF and CuCoCH/CF electrodes in 0.1 M NaOH with or without 0.5 mM glucose were investigated by cyclic voltammetry. As shown in Fig. 3a, the oxidation peak of CuCoCH/CF electrode towards glucose is significantly larger than that of CF. It also shows the current responses around 0.4–0.6 V of CuCoCH/CF electrode increase obviously with the addition of glucose compared those without glucose, indicating the

electrode has good electrocatalytic activity for glucose. Figure 3b shows the CV curves of CuCoCH/CF electrode towards various concentration of glucose, the current responses increases gradually and linearly with the increased concentration of glucose in the range of 0 to 3 mM (shown in the inset of Fig. 3b), revealing its high sensitivity to glucose content, which could be attributed to the synergistic effect produced by the copper–cobalt bimetallic material. The mechanism of the electrocatalytic reaction between CuCoCH/CF and glucose on the electrode

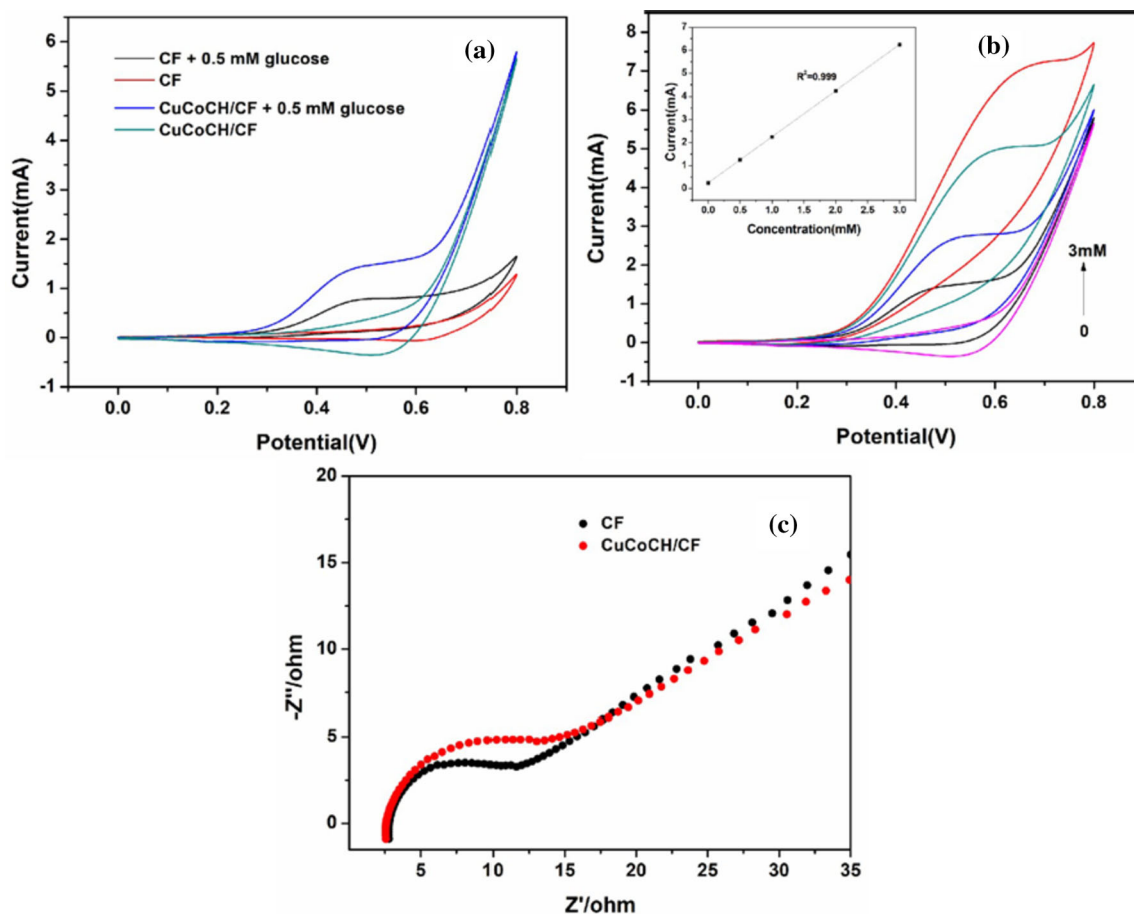
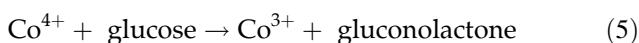
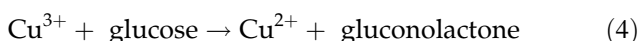
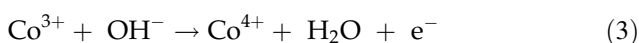
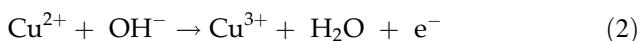
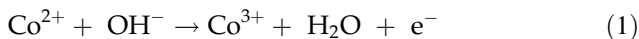


Figure 3 a CV curves of bare CF and CuCoCH/CF electrodes in the absence and presence of 0.5 mM glucose in 0.1 M NaOH at 20 mV s⁻¹. b CV curves of CuCoCH/CF electrode in 0.1 M

NaOH with different glucose concentrations (0–3.0 mM). c Nyquist plots of bare CF and CuCoCH/CF electrodes.

surface is speculated as follows: Co²⁺ was first oxidized to Co³⁺ (Eq. (1)), then Cu²⁺ was oxidized to Cu³⁺ (Eq. (2)) and Co³⁺ was oxidized to Co⁴⁺ (Eq. (3)), which finally oxidized the glucose into gluconolactone at about 0.5 V (Eq. (4) and (5))[35, 45].



The electrochemical performance of CuCoCH/CF electrode was further investigated by EIS. Figure 3c shows the Nyquist plots of bare CF and CuCoCH/CF electrodes. The value of charge transfer resistance (R_{ct}) at the surface of the electrode can be obtained from the diameter of the semicircle in high frequency

region of EIS plot [43]. From Fig. 3c, a small semicircle of bare CF electrode was observed, and the semicircle of CuCoCH/CF electrode was only slightly larger than that of bare CF electrode due to the coating of CuCoCH, implying the R_{ct} of CuCoCH/CF electrode was small and close to that of bare CF electrode, which reveals its good conductivity and fast electron transfer ability. The ratio of Cu to Co had obviously influence on the catalytic activity of CuCoCH/CF electrode. The CV curves of CuCoCH/CF electrodes with different Cu/Co feed ratios (Fig S1) showed that the electrode with the Cu/Co feed ratio of 1:3 exhibited high electrocatalytic activity and obvious oxidation peak for glucose oxidation. As cobalt-based material showed higher current responses than copper-based material towards glucose oxidation, with the increase in the cobalt content, the current responses increased; with further increase in the cobalt content, the CV curve showed

the characteristic of cobalt with two pairs of redox peaks of CoII/III and CoIII/IV and the oxidation peak at about 0.5 V became less obvious. Therefore, the Cu/Co feed ratio of 1:3 was used in subsequent experiments.

The kinetic control mechanism of a sensor can be investigated by cyclic voltammeter (CV) measurement under different scan rate. The CV curves of CuCoCH/CF electrode with different scan rate are shown in Fig. 4a. The redox peaks at about 0.5 V increase with the increase of scan rate. It was also observed that the other pair of redox peaks at about 0.2 V become apparent with the increase of scan rate, further verified the existence of two pairs of redox peaks of cobalt. From Fig. 4b, the oxidation and reduction peak currents show good linear relationship with the square root of the scan rate in the range of 20–120 mV/s, implying a diffusion-controlled process in the redox reaction.

Detection performance of the as-prepared sensor

In order to test the linear range of the as-prepared CuCoCH/CF electrode for glucose detection, amperometric measurement was taken by successive addition of glucose into 0.1 M NaOH at a potential of 0.6 V. The amperometric responses of the electrode is shown in Fig. 5a. The corresponding linear relationship between the response current and the glucose concentration is shown in Fig. 5b. The CuCoCH/CF electrode exhibits good linearity in the range of 0.005–3.47 mM. The linear equation is:

$y = 1.51664x + 0.05339$ ($R^2 = 0.993$), the sensitivity is $1.517 \text{ mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$, and the detection limit is $2.3 \text{ }\mu\text{M}$. The sensing performances of CuCoCH/CF-based sensor were compared with some reported CuCo bimetallic material-based non-enzymatic glucose sensors and are listed in Table 1. In general, the sensitivity and linear range is similar or better than the reported results, and the detection limit is similar or lower than the reported results, demonstrating the as-prepared CuCoCH/CF sensor exhibited a good sensing performance.

Selectivity, reproducibility and stability of the as-prepared sensor

Selectivity is of great importance in glucose detection for practical application. The common interfering species existing in human blood serum, such as uric acid, ascorbic acid, dopamine and cysteine, were studied in the glucose detection process. As the glucose concentration in normal human blood is almost ten times higher than interfering species, the selectivity of CuCoCH/CF-based sensor was evaluated by comparing the current responses of $100 \text{ }\mu\text{M}$ glucose and $10 \text{ }\mu\text{M}$ of UA, AA, DA and cysteine in 0.1 M NaOH. As shown in Fig. 6a, $100 \text{ }\mu\text{M}$ glucose produces a remarkable current response, while the successive addition of $10 \text{ }\mu\text{M}$ interferences produced no evident response, after the final addition of glucose, the current response increased obviously again and was almost the same as before, implying that CuCoCH/CF-based sensor has good selectivity towards glucose.

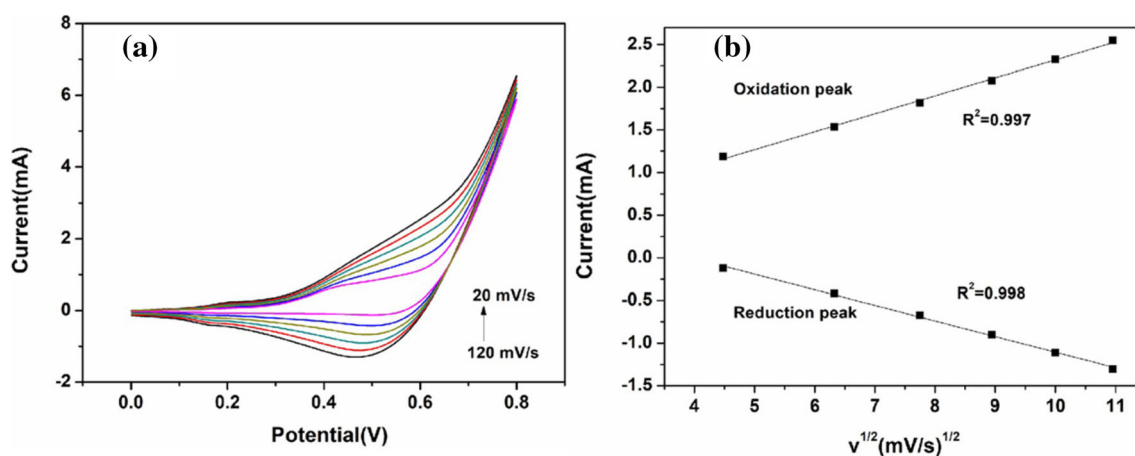


Figure 4 a CV curves of CuCoCH/CF electrode at varying scan rates ($20\text{--}120 \text{ mV s}^{-1}$), b linear relationships between anodic/cathodic peak currents and square root of the scan rate ($v^{1/2}$).

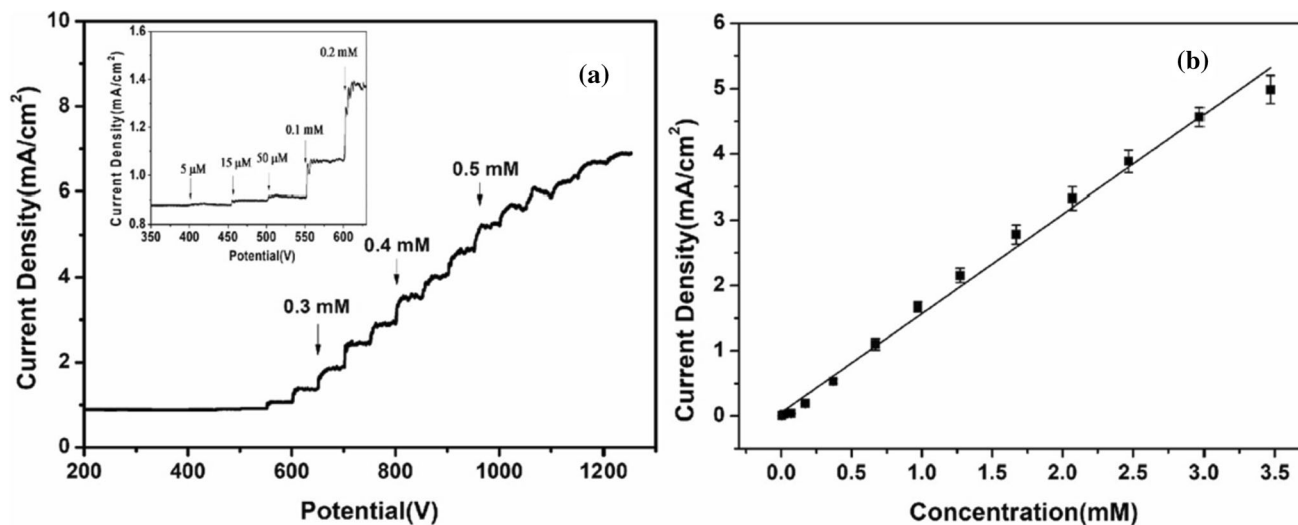


Figure 5 **a** Amperometric response curve of CuCoCH/CF electrode with an amplified inset, **b** the calibration curve of CuCoCH/CF electrode with successive addition of different concentrations of glucose to 0.1 M NaOH solution at 0.6 V.

Table 1 Comparison of sensing performances of the CuCoCH/CF electrode with other CuCo bimetallic material-based non-enzymatic glucose sensors

Electrode	Sensitivity ($\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$)	Linear range (mM)	Detection limit (μM)	Ref
Co(OH) ₂ nanosheets/Cu(OH) ₂ nanorods	2366	0.25–2	170	[27]
CuCo-600	567	0.005–0.825	3	[44]
CuCo ₂ O ₄ /CF	3930	0.001–0.93	0.5	[46]
CuCo/rGO/PGE	240	0.001–4	0.15	[47]
PTBA/CuCo ₂ O ₄ -CNFs	2932	0.01–0.5	0.15	[48]
	708	0.5–1.5		
CuCo bimetallic nanoparticles	1632	0.1–1	-	[49]
CoCuCH/CF	1517	0.005–3.47	2.3	This work

In order to evaluate the reproducibility, amperometric responses of five independent CuCoCH/CF electrodes were measured towards 0.5 M glucose under the same condition. From Fig S2, the current responses were almost the same and the calculated relative standard deviation (RSD) was 4.1%, implying the excellent reproducibility of the as-prepared electrodes. In addition, the stability of the sensors was investigated by storing CuCoCH/CF electrodes in a refrigerator at 4 °C and then examining amperometric responses towards 1 M glucose every 5 days. As shown in Fig. 6b, the CuCoCH/CF electrodes still retained 88% of the initial current after 25 days, indicating their good stability.

Real sample analysis

To verify the feasibility of the developed glucose sensor, the performance of CuCoCH/CF-based sensor was tested in simulated human serum sample. The simulated serum (20 μL) was added into 0.1 M NaOH (20 mL) and different standard glucose solution was added to the diluted serum sample and the recovery of glucose was calculated. As shown in Table S1, the relative standard deviations (RSDs) were less than 5% and the recovery was in range of 98–103%, demonstrating the CuCoCH/CF-based sensor is feasible and reliable in the detection of glucose level in actual samples.

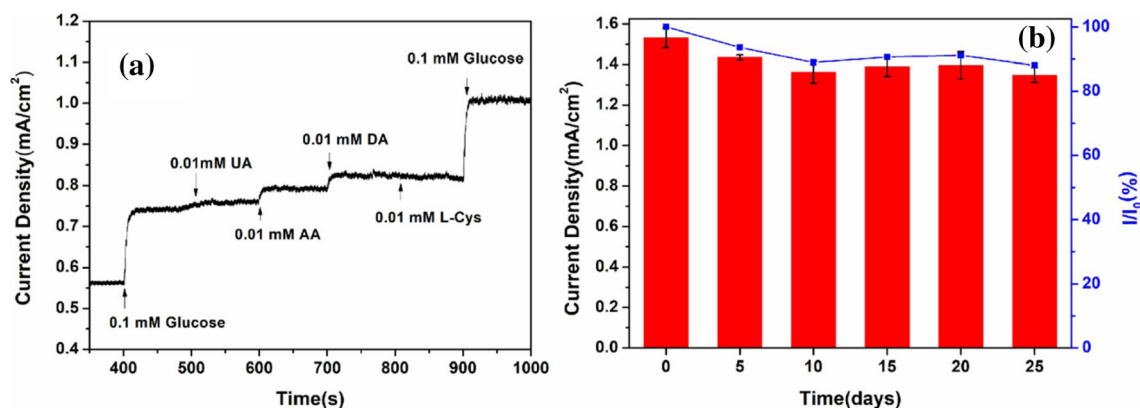


Figure 6 **a** Amperometric response of CuCoCH/CF electrode to 100 μM glucose, 10 μM interferent species (UA, AA, DA and cysteine) at 0.6 V in 0.1 M NaOH. **b** Stability of CuCoCH/CF electrodes measured over 25 days.

Conclusion

In conclusion, CuCoCH was prepared on copper foam by SILAR method and its morphology, structure and electrochemical properties were characterized. The in situ preparation, the good conductivity of the electrode, the hierarchical porous network structure, the large surface area and the synergistic effect of copper and cobalt in CuCoCH increased the electrocatalytic activity and facilitated electron transfer for glucose oxidation. Therefore, the CuCoCH/CF electrode had good electrocatalytic activity for glucose detection in 0.1 M NaOH, which exhibited good performances such as a linear range of 0.005–3.47 mM, a sensitivity of $1.5167 \text{ mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ and a detection limit of 2.3 μM . The sensor had good selectivity, reproducibility and stability. It also showed its feasibility in the detection of real samples. The preparation method of CuCoCH/CF electrode is simple, fast and easily controllable, and can be extended to other metal compound-based non-enzymatic glucose sensors.

Data and code availability

All data generated or used during the study are available from the corresponding author by request.

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Declarations

Conflicts of interest The authors declared they have no conflict of interest to declare in this work.

Ethical approval Not involved.

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