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Ultrasensitive binder-free glucose sensors based on the pyrolysis of in situ grown Cu MOF*

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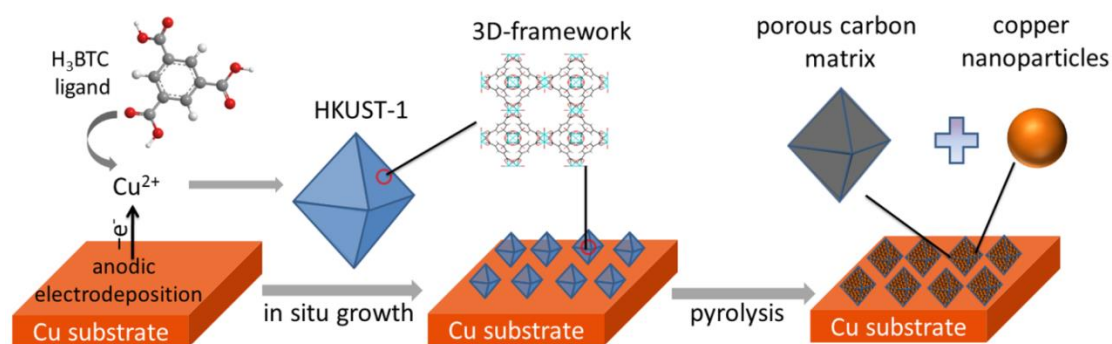
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Graphical abstract



A non-enzymatic glucose sensor based on carbon/Cu composite materials was developed by the in-situ growth and subsequent pyrolysis of metal-organic frameworks (MOFs) on Cu foam. After pyrolysis, the Cu nanoparticles are uniformly embedded in the carbon matrix, attached on the carbon layer closely. The resulting Cu@porous carbon matrix electrode displays ultrahigh sensitivity ($10.1 \text{ mA cm}^{-2} \text{ mM}^{-1}$), low detection limit ($< 1 \text{ } \mu\text{M}$), short response time (less than 2 s) and good stability, indicating that the developed electrode is a promising candidate material for glucose sensors.

Highlights

HKUST-1 (Cu-BTC) was directly grown on different copper substrates by anodic electrodeposition.

Cu nanoparticles embedded in the porous carbon matrix (Cu@porous carbon material) were successfully fabricated on the Cu foam without any binder.

The as-prepared Cu@porous carbon matrix electrode displays ultrahigh sensitivity, low detection limit, short response time and long stability for glucose sensors.

Abstract

A non-enzymatic glucose sensor based on carbon/Cu composite materials was developed by the in-situ growth and subsequent pyrolysis of metal-organic frameworks (MOFs) on Cu foam. After pyrolysis, SEM, HRTEM and STEM-EELS were employed to clarify the hierarchical Cu@porous carbon electrode. It is found that the Cu nanoparticles are uniformly embedded in the carbon matrix, attached on the carbon layer closely. The electrocatalytic activity of the Cu@porous carbon matrix electrode for glucose sensing was explored by cyclic voltammetry (CV) and chronoamperometry. The resulting Cu@porous carbon matrix electrode displays ultrahigh sensitivity ($10.1 \text{ mA cm}^{-2} \text{ mM}^{-1}$), low detection limit ($< 1 \text{ }\mu\text{M}$), short response time (less than 2 s) and good stability, indicating that the developed electrode is a promising candidate material for glucose sensors.

Keywords: metal-organic frameworks, electrodeposition, pyrolysis, carbon-metal composite materials, glucose sensors, ultrasensitive.

Introduction

Diabetes has become one of the biggest health problems in the world with more than 370 million people affected.¹ Currently, glucose sensors constitute 85% of the market share of all biosensor products for detecting diabetes. As more and more people are affected by diabetes, a safe, efficient and noninvasive ultra-sensitive glucose monitoring biosensor is a way to improve patient's adherence and health. Therefore, the development of better and cheaper

glucose sensors has drawn a lot of attention.²⁻⁴ Because traditional enzyme-based biosensors are easily affected by temperature, pH and humidity, glucose sensors based on transition metals (Pt, Au, Ag, Cu, Ni, Fe, Co, Mn, etc.) as well as their oxides and sulfides in alkaline solutions have been extensively explored as promising candidates for next-generation glucose sensors.⁵⁻¹² Among these materials, Cu (or CuO) is an interesting material for glucose sensor due to the fact that it is inexpensive, non-toxic and environmentally stable. More importantly, the electrochemical glucose oxidation shows fast kinetics on Cu (or CuO).^{13, 14}

It is well known that the electrocatalytic active surface area plays a critical role in enzymeless analysis. In order to increase the electrocatalytic active surface area, encouraging results have been shown by Cu nanomaterials (nanoparticles, nanocluster, nanobelts, nanocubes, etc.) for glucose sensors recently.¹⁵⁻¹⁹ Moreover, in order to avoid the aggregation of nanomaterials and enhance the catalytic activity of Cu materials, great efforts have been made to combine copper or copper oxides with carbon-based nanomaterials such as carbon nanotubes and graphene. For example, Ding et al. synthesized copper nanoparticles (NPs) decorated nitrogen-doped graphene (Cu-N-G) by thermal treatment. Compared with pure Cu NPs, the Cu-N-G showed enhanced electrocatalytic activity for the glucose oxidation (*e.g.* the oxidation peak current increased a lot).²⁰ Nevertheless, in the typical fabrication process of glucose sensor, the polymer binders such as Nafion, polyvinylidene fluoride (PVDF) or chitosan are used to immobilize active materials. These binders have been shown to increase the electrical resistance, hinder the electrolyte diffusion and decrease the effective active surface area.²¹⁻²³ Thus, plenty of researchers focus on in-situ synthesis of nanostructured Cu directly on the substrate. For instance, Li et al. successfully prepared free-standing porous CuO nanowire electrodes on a Cu foil. The in-situ engineered electrodes show higher sensitivity than “reconstituted” electrodes (electroactive materials that are pasted on an electrode with the addition of a binder).¹³ Furthermore, Zhang et al. used Cu foam as the precursor for in-situ growth of CuO nanowires by anodic electrodeposition.²⁴ However, the

preparation of electrodes based on binder-free carbon/Cu composite materials remains challenging.

Metal-organic frameworks (MOFs) are highly porous coordination polymers formed by combining organic linkers and metal ions. Due to their unique structures, nano-scale cavities and open channels, MOFs are considered as promising candidates for synthesizing porous carbon materials and nano-sized metal particles.²⁵⁻³¹ For example, Song et al. produced 3D anthill-like Cu@carbon nanocomposites successfully by pyrolysis of HKUST-1. The resultant materials shown good catalytic performance towards the oxidation of glucose with a wide range (up to 8 mM) and low detection limit (29.8 μ M).²⁸ However, complex steps for immobilization of catalyst and polymer binder were still involved. In order to prepare binder-free electrode, multi-step hydrothermal or solvothermal are normally used in traditionally methods, which are both time and resource consuming.³²⁻³⁴ Very recently, a new method (patented by BASF) proposed the electrochemical synthesis of MOFs, avoiding the use of salts and saving synthesis time.³⁵ Besides, Ameloot et al. reported that densely packed crystalline Cu-based MOF layers could be synthesized on pure copper electrodes by anodic electroprecipitation.³⁶ Furthermore, the mechanism of the electrochemical nucleation and growth of HKUST-1 layers have been proposed by our group.³⁷

Taking the above considerations into account, we propose a facile method to prepare binder-free electrodes based on carbon/Cu composite materials (**Figure 1**). Firstly, the archetypal MOF HKUST-1 (Cu-BTC) was directly grown on copper foam by anodic electroprecipitation. After pyrolysis, the Cu nanoparticles embedded in the porous carbon matrix (Cu@porous carbon material) were successfully fabricated on the Cu foam. The resulting Cu@porous carbon matrix electrode was tested as a non-enzymatic electrochemical glucose sensor electrode. The Cu@porous carbon matrix electrode displayed much better electrochemical catalytic performance towards glucose than Cu foam and flat copper electrodes.

2. Results and discussions

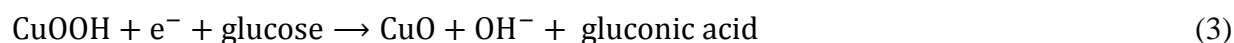
HKUST-1 was successfully deposited on the copper foam substrate, as shown by the XRD pattern of materials scratched from the substrate (**Figure S1**). The characteristic peaks of Cu-BTC framework at $2\theta \approx 9.5^\circ$, 11.5° and 13.4° can be clearly identified, which agree well with previous literature.³⁸ Furthermore, HKUST-1 can be deposited on different copper substrates such as plate (**Figure 2a**), wire (**Figure 2b**) and foam (**Figure 2c**). The HKUST-1 grows conformably on the surface of the different copper substrates. This advantage can meet the need of commercial electronic devices. At higher magnification, the typical octahedral morphology of HKUST-1 can be observed (inset of **Figure 2c**). The crystal sizes range from 2 μm to 8 μm . The result of EDS is illustrated in **Figure. S2**, confirming the existence of C, O and Cu (from HKUST-1) and Pt (from Pt sputtered for SEM imaging). After pyrolysis, the “octahedral unit” remains while the pyrolyzed MOF still covers the surface of the copper foam (**Figure 3**). The pyrolytic carbon is expected to act as an electron pathway between the copper nanoparticles and the copper substrate. According to thermogravimetric analysis (TGA) (**Figure S3**), there are three main weight loss events during pyrolysis. Events A and B probably correspond to the loss of guest molecules of ethanol (b.p. = 78°C) and DMF (b.p. = 153°C), respectively. After that, there is a plateau (event C) from 210°C to 250°C , indicating that the framework of HKUST-1 is stable up to 250°C . Event D starts from 250°C and is attributed to the thermal decomposition of the linker molecules. After the thermal decomposition, copper particles can be found dispersed on the surface. Most copper particles are below 300 nm (**Figure 3c** and **3d**). However, there are some large Cu particles on the surface of the porous carbon matrix. These particles probably arise from outer surface decomposition of MOF units, especially for the overlap of MOF units as shown in **Figure 2c**. This phenomenon has been observed before by Song et al. as well.²⁸ The EDS measurements (**Figure S4**) confirm three elements: C from the carbon matrix, Cu from nanoparticles and O from the CuO thin layer (oxidized in the air), respectively. These results are in good

agreement with the XRD measurement results. As shown in **Figure S5**, three characteristic peaks for Cu were observed at $2\theta = 43.3^\circ$, 50.4° and 74.2° , corresponding to Miller indices (111), (200) and (220), respectively. Moreover, a small peak at $2\theta = 36.8^\circ$ can be clearly observed, which corresponds to (111) reflection peak of cubic CuO phase.^{39,40} In this work, copper foam is used as both substrate and copper source. In addition, the photograph of the Cu foam, HKUST-1-covered and Cu@porous carbon matrix electrodes (**Figure S6a**) show that the Cu@porous carbon matrix is in close contact with the Cu foam. In this work, copper foam is used as both substrate and copper source. The 3D structure of the copper foam provides high surface area, which will increase the sensitivity. Moreover, copper foam shown stronger adhesive for Cu@porous carbon materials compared with copper plate substrate as displayed in Fig. S6 (a) and (b).

To further explore the structure of single nanoparticles, TEM and STEM-EELS mappings have been conducted. As shown in Figure 4 (a), the nanoparticles are supported by carbon sheets. HRTEM analysis and corresponding reduced FFT (fast Fourier transform) spectra (**Figure 4b, 4c** and **4d**) show that the outer shell of nanoparticles are cubic CuO phase, [FM3-M]-Space group 225, with lattice parameters of $a = 0.4245$ nm, and $\alpha = 90^\circ$ as visualized along the [112] direction, which perfectly agree with the XRD observations (**Figure S5**). The RGB composition of IFFT (Inverse fast Fourier transform) from CuO further confirms the HRTEM analysis (**Figure 4e**). To figure out the chemical composition of Cu@porous carbon matrix materials, STEM-EELS has been conducted (**Figure 5**). The general view and magnified details of the HAADF-STEM images are displayed in **Figure 5**, which also show that the nanoparticles are supported by carbon sheets. The geometrical shape of the nanoparticles is spherical. Moreover, the relative compositions of Cu, O and C elements of these nanoparticles have been mapped by means of EELS analysis using Hartree-Slater model for signal quantification and power law for background removal.⁴¹ Clearly, the nanoparticle is embedded in the carbon layer. Around the outer shell of the nanoparticles, there is a thin

layer with a relatively high O concentration, which is probably due to the oxidation of the Cu nanoparticles in air.⁴² In addition, Cu dominates the main region of the nanoparticles. These results are in good agreement with EDS (**Figure S4**), TEM (**Figure 4**) and XRD observations (**Figure S5**). After glucose sensor performance tests, the structure and chemical compositions of the Cu@porous carbon matrix materials were analyzed again by TEM and STEM-EELS composition maps extracted from the obtained spectrum images (SIs). It was found that after the performance test, the nanoparticles were still attached to the carbon layer (**Figure 6a**). After the tests, the structure of the nanoparticles changed to urchin-like particles, which is probably caused by the electrochemical oxidation of Cu into CuO. A similar change has been observed for the transformation of Cu₂O into CuO nanostructures.⁴³ However, the hierarchical structure of the nanoparticles embedded in the carbon matrix units remains unchanged (**Figure S7a**). The HRTEM and corresponding reduced FFT spectra (**Figure 6b**, **6c** and **6d**) indicate that the nanoparticle crystallizes in the form of a cubic CuO phase ([FM3-M]-Space group 225, with lattice parameters of $a = 0.4245$ nm, and $\alpha = 90^\circ$ as visualized along the [011] direction). Furthermore, the relative O content of the particles increased significantly due to the presence of cubic CuO phase after the sensor test (**Figure 6e**), which is confirmed by EDS results (**Figure S6b**). It is worth noting from the relative C content of the nanoparticles that each particle is covered by a thin carbon layer and connected by a carbon layer to each other. This unique structure might be the reason for the transport of charge and the protection of the nanoparticles from aggregation and degradation during glucose oxidation. Combining XRD patterns (**Figure S5**), TEM observations (**Figure 4**, **5** and **6**) and the electrochemical information (as shown in **Figures 7** and **8**) of Cu@porous carbon matrix materials for the glucose sensor, the possible electro-oxidation mechanism of glucose on the Cu@porous carbon matrix surface in an alkaline solution can be assumed as follows:^{44, 45}





The reactions (1) and (2) occur in activated process before test.^{46,47} After addition of glucose, the oxidative Cu(III) could catalyze glucose oxidation to generate gluconolactone and then gluconolactone is further oxidized to glucose acid. The reaction catalyzed by Cu@porous carbon matrix electrode was assisted by the Cu(II)/Cu(III) redox couple.

The CV curves of the Cu@porous carbon matrix electrode in 0.1 M NaOH with different concentrations of glucose at a scan rate of 50 mV s⁻¹ is shown in **Figure 7a**. In the absence of glucose (curve A), there is no obvious oxidation peak. When glucose was added to the 0.1 M NaOH solution, a clear increase of the oxidative peak current was observed in the potential range between +0.4 V and +0.7 V (*vs.* Hg/HgO), corresponding to the irreversible oxidation of glucose. The optimal detection potential was determined from the amperometric responses of the Cu@porous carbon matrix electrode at different potentials from +0.45 to +0.65 V with the addition of 1 mM glucose (**Figure 7b**). The Cu@porous carbon matrix electrode shows only a slightly lower current response at +0.55 V than +0.6 V. However, at higher potentials the influence of interferences and polarization of the oxygen evolution are larger. Therefore, the potential is subsequently fixed at +0.55 V for amperometric *i-t* tests. The amperometric responses of the Cu plate, Cu foam, AO-Cu foam and Cu@porous carbon matrix electrode to 1 mM glucose at +0.55 V in 0.1 M NaOH are shown in **Figure 7c**. The copper foam shows a 100% increase in current compared to the copper plate due to its larger surface area. After anodic oxidation, the AO-Cu foam electrode showed 55% higher current response than copper foam due to surface structure change of copper foam as exhibited in Figure. S8. The 3D structure skeleton of Cu foam can be remaining well after anodic oxidation process (Figure. S8a and Figure. S8d). However, the smooth surface of Cu foam was changed to porous nest structure, which probably caused by oxygen evolution bubble during anodic oxidation

process,⁴⁸⁻⁵⁰ and the diameter of these pores is around 3 μm as displayed in Figure. S8(e). At high magnification, it is can be seen that porous nanostructure constructed the nest structure. Then the copper foam was further decorated by Cu@porous carbon matrix, the resulting electrode shown even 20% higher current response for 1 mM glucose than AO-Cu foam electrode.

Figure 8a displays an amperometric $i-t$ test measured in 0.1 M NaOH at +0.55 V under stepwise addition of glucose. When the current was stable, different concentrations of glucose solutions were successively injected into the solution under stirring, which induced an increase in the current within 2 s. The low-concentration part is magnified and shown in the inset above the amperometric $i-t$ curve. Another inset is the amperometric response of the Cu@porous carbon matrix electrode to the addition of 1 μM and 2.5 μM glucose solutions. An increase of current can be clearly identified even for 1 μM glucose. Moreover, as shown in Figure S9, the AO-Cu foam electrode and Cu@porous carbon matrix decorated copper foam show highest current response for 10 μM glucose than bare copper foam or copper plate. Besides, there is no obviously current increase for the bare copper foam or copper plate electrode with the addition of 1 μM of glucose. The calibration curves based on the results of the amperometric $i-t$ test is presented in **Figure 8b**. The current (i) is correlated with the glucose concentration (c) in the range of 1 μM – 6000 μM with a correlation coefficient of 0.9998 using the following equation:⁴⁵

$$i = \frac{12.1c}{928.9 + c} \quad (5)$$

Between 1 μM and 300 μM glucose, the response is linear ($R^2 = 0.9947$) as shown in the inset of **Figure 8b**. In this concentration range (linear part), the sensitivity is 10.1 $\text{mA cm}^{-2} \text{mM}^{-1}$ based on projected geometrical electrode area. The limit of detection is estimated to be 0.6 μM at a signal-to-noise ratio of 3. Cu@porous carbon matrix electrode showed a comparable

sensing performance to previous reports (Table S1), especially showing an ultrahigh sensitivity as shown in **Figure 9**.

As there are various oxidizable species present in human body fluids, such as uric acid (UA), ascorbic acid (AA), sucrose, fructose, the ability to discriminate these interferences is an important factor for glucose sensors. Under stepwise addition of the same amount (0.1 mM) of glucose, UA, AA, sucrose, fructose, the interferences showed obvious current responses as shown in curve A (**Figure 10a**). Considering in human blood the concentration of these interferences are much smaller ($< 1/30$) than the concentration of glucose,⁵¹⁻⁵⁴ generally speaking, the ratio of glucose concentration and interference concentration are 1:10 or at physiological concentration level (around 1:30) in selectivity test.⁵⁵⁻⁶¹ When the concentration of the interferences was decreased from 0.1 mM to 0.01 mM (curve B, **Figure 10a**) or physiological concentration level (curve C and , **Figure 10a**), no current response can be observed for species other than glucose. These results suggest that the Cu@porous carbon matrix electrode shown reliable anti-interference property at physiological concentration level. Furthermore, the stability of the Cu@porous carbon matrix electrode was investigated by recording the continuous or intermittent amperometric responses to 0.1 mM glucose. The longtime current response of the Cu@porous carbon matrix electrode indicates that around 89% can be retained during a period of 1800 s (**Figure 10b**). Furthermore, after storage at room temperature in ambient atmosphere for 25 days, the sensitivity of the electrode decreased only slightly compared with its initial response as shown in the inset of **Figure 10b**.

3. Conclusions

In summary, HKUST-1 can be easily synthesized on the different kinds of copper substrates. After pyrolysis, carbon-Cu composite materials can be grown in-situ on the Cu foam. The resulting electrode shows high sensitivity, low detection limit and good stability for the non-enzymatic detection of glucose. The excellent electrochemical performance of the Cu@porous carbon matrix electrode can be attributed to the multidimensional hierarchical

structure of the electrode and the synergistic effect between Cu and carbon. These results indicate that the Cu@porous carbon matrix electrode could be a promising candidate for the construction of non-enzymatic glucose sensors, especially for saliva-based glucose sensors due to the very high sensitivity.

4. Experimental section

Electrodeposited MOF: All reagents were of analytical purity without further purification. Three kinds of copper substrates were used to prepared MOF-covered electrodes: copper plate (thickness: 1 mm, 99% purity, Testas, Belgium), copper wire (diameter: 1.5 mm) and copper foam (thickness: 1 mm, pore density: 90 ppi, Cu>99.5%, Changsha LYRUN New Material China Co., Ltd.). Before electrodeposition, the copper substrate was carefully cleaned with dilute hydrochloric acid, acetone and ultrapure water several times, respectively. Unless stated otherwise, the anodic MOF deposition was performed on different kinds of copper substrates under the same conditions. Copper plates were used as the cathode, and different copper substrates were used as the anode. The electrodeposition was performed in a solution containing 1 g 1,3,5-benzenetricarboxylic acid (H₃BTC) and 0.5 g methyltributylammonium methyl sulfate (MTBS) per 100 mL solvent (67 mL ethanol and 33 mL Milli-Q[®] water). By applying a current density of 4 mA cm⁻² at room temperature until the total passed charge reached 36 C cm⁻², MOFs were grown on the copper substrates. The current densities were determined by projected geometric area. After MOF growth, the MOF-covered electrode was washed with ethanol and dimethylformamide (DMF) to remove excess ligand and MTBS.

Preparation of Cu@porous carbon matrix electrode: The MOF-covered copper foam electrodes were pyrolyzed at 850 °C in flowing argon gas (99.998%) with a flow rate of 300 cm³ min⁻¹. The temperature inside the furnace was gradually increased from room temperature to the target temperature at a heating rate of 3 °C min⁻¹. After the target temperature was reached, the MOF-covered copper foam electrode was annealed for 8 h and then cooled down to room temperature at a rate of 5 °C min⁻¹. The as-prepared electrode is

denoted as Cu@porous carbon matrix electrode. For comparison, Cu foam was directly anodic oxidation without H₃BTC at the same current density and total passed charge, which named as AO-Cu foam. Besides, a copper plate and a copper foam were used for comparative experimental as well.

Material characterizations: X-ray diffraction (XRD) data of the samples were collected on a Bruker AXS D8 diffractometer using Cu K α radiation (wavelength $\lambda = 0.15405$ nm) and Ni filter from 5° to 50° in 2θ with a step of 0.02° (2 s per step). TGA was performed in an argon atmosphere on a thermogravimetric analyzer (AutoTGA 2950HR V5.4A, TA Instruments) using platinum pans at a heating rate of 3 °C min⁻¹. For the XRD and TGA tests, the sample was scratched off from the copper substrate. The morphology of the samples and energy dispersive spectroscopy (EDS) were observed on a FEI/Philips XL30 FEG microscope (SEM). In order to improve the electronic conductivity of the MOF samples, a 5 nm layer of Pt was sputtered on top of the samples. The onset temperature of the weight loss in the TGA was used as the decomposition temperature (T_d). High resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) images were obtained by using an FEI Tecnai F20 field emission gun microscope operated at 200 kV with a point-to-point resolution of 0.19 nm, which is equipped with high angle annular dark field (HAADF) and electron energy loss spectroscopy (EELS) detectors. The obtained images and spectra were analyzed by means of Gatan Digital Micrograph software.

Electrochemical characterizations: The electrochemical performance of the samples was characterized by chronoamperometry ($i-t$) and cyclic voltammetry (CV) techniques with an Autolab electrochemical workstation at room temperature in a three-electrode system. The as-prepared electrode with an immersed area of 1×1 cm², platinum gauze and an Hg/HgO electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. For comparative experimental, all the electrodes are fixed at same

immersed area ($1 \times 1 \text{ cm}^2$). In this paper, all the current densities were normalized by the projected geometrical electrode area. The working electrode was used after being activated for several cycles of cyclic voltammetry from 0 to 0.65V at a scan rate of 50 mV s^{-1} until CV curves are stable. The supporting electrolyte in all electrochemical experiments is 0.1 M NaOH.

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Prof. Joan Ramon Morante received his PHD from University of Barcelona in 1980. He is full professor of the Faculty of Physics, University of Barcelona and director of the Catalanian Institute for Energy Research, IREC. His activities were centred in electronic materials and devices; semiconductors and electronics ceramics. He was also involved on nanomaterials for sensors, actuators and Micro and Nano systems, especially on chemical sensors. He is now focussed on “nano energy” addressing effort to the energy transfer mechanisms in solid interfaces involving electrons, photons and phonons as well as chemicals and photoelectrochemical processes. He has taken part in many R&D EU projects (>30) as well as in private industrial projects. He has co-authored more than 600 works in international specialized journals with more of 13800 citations, several proposal patents (15) and he has been advisor of more than 35 PhD students; he is member of international committees and editorial boards of scientific journals. He has been general chairman of international events and has been guest editor of many special issues. He has been awarded the Narcís Monturiol

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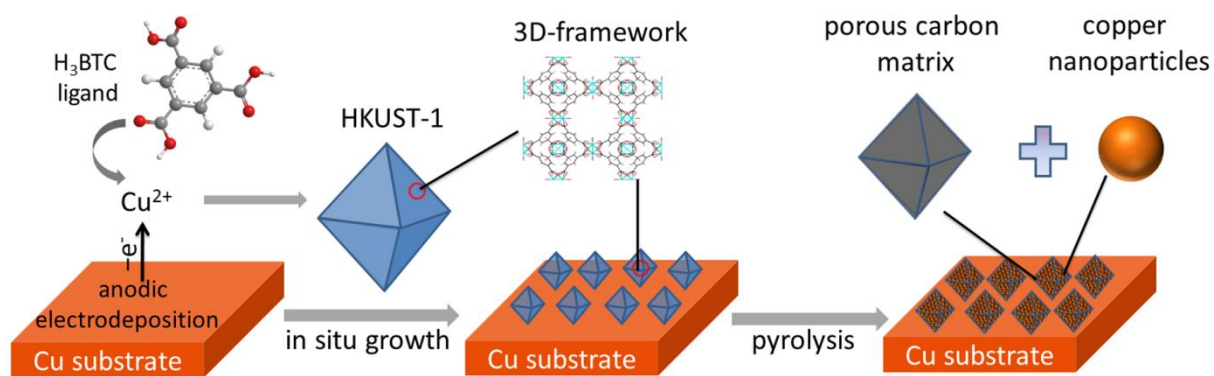


Figure 1. Schematic illustration of the synthesis of Cu@porous carbon matrix on the copper foam substrates.

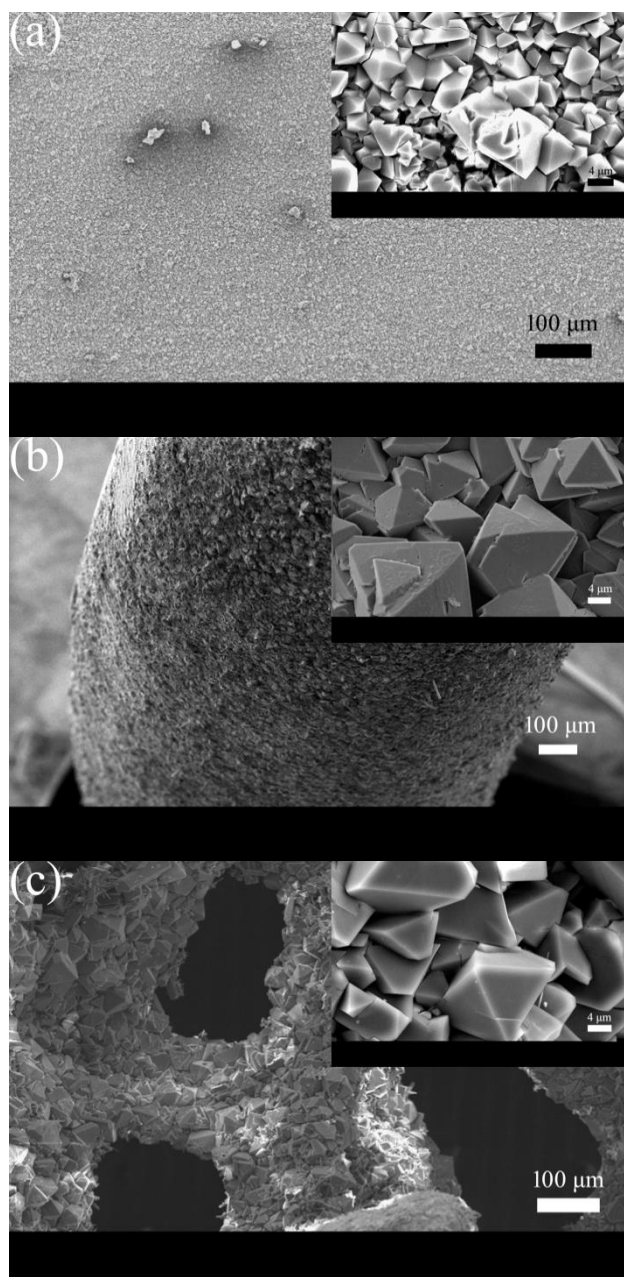


Figure 2. SEM images of different MOF-covered copper substrates: (a) copper plate; (b) copper wire and (c) copper foam. Insets are the corresponding magnifications with a scale bar of 4 μm.

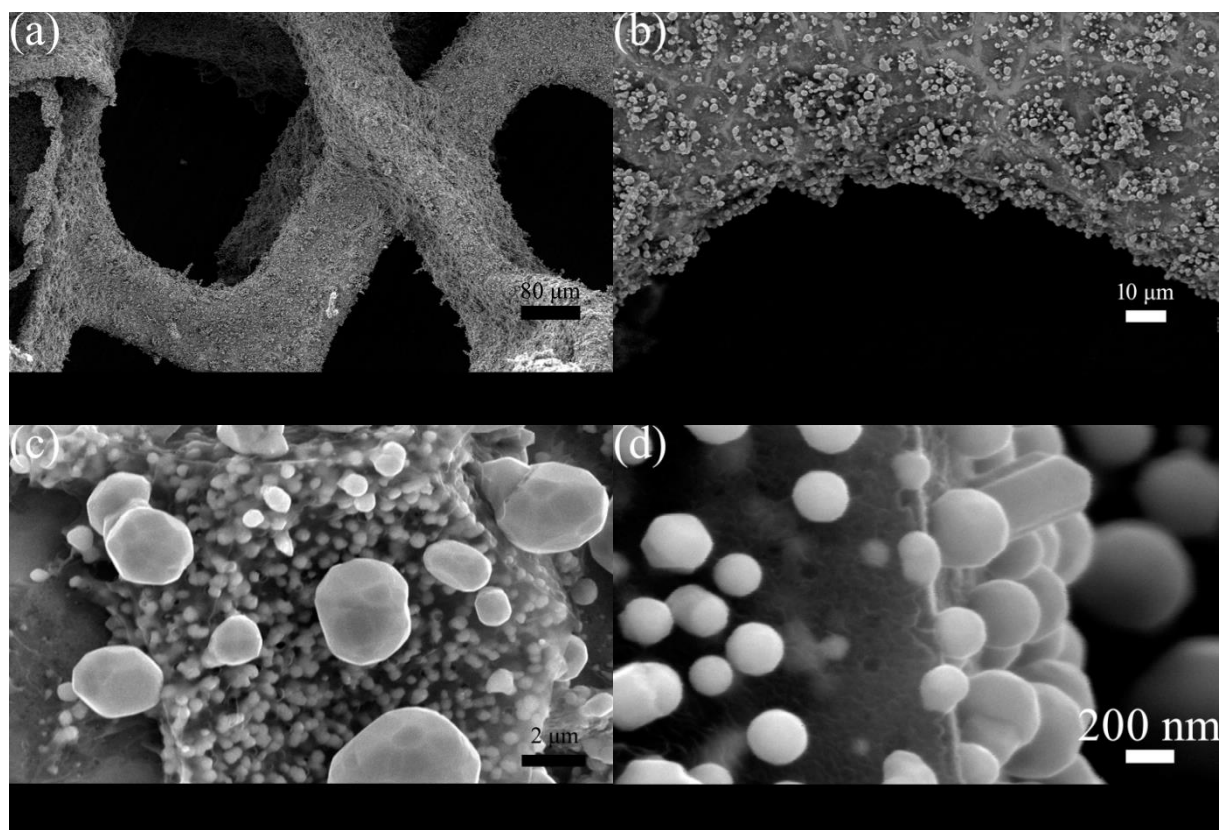


Figure 3. SEM images of the Cu@porous carbon matrix electrode at different magnifications. The scale bars are (a) 80 μm (b) 10 μm , (c) 2 μm and (d) 200 nm, respectively.

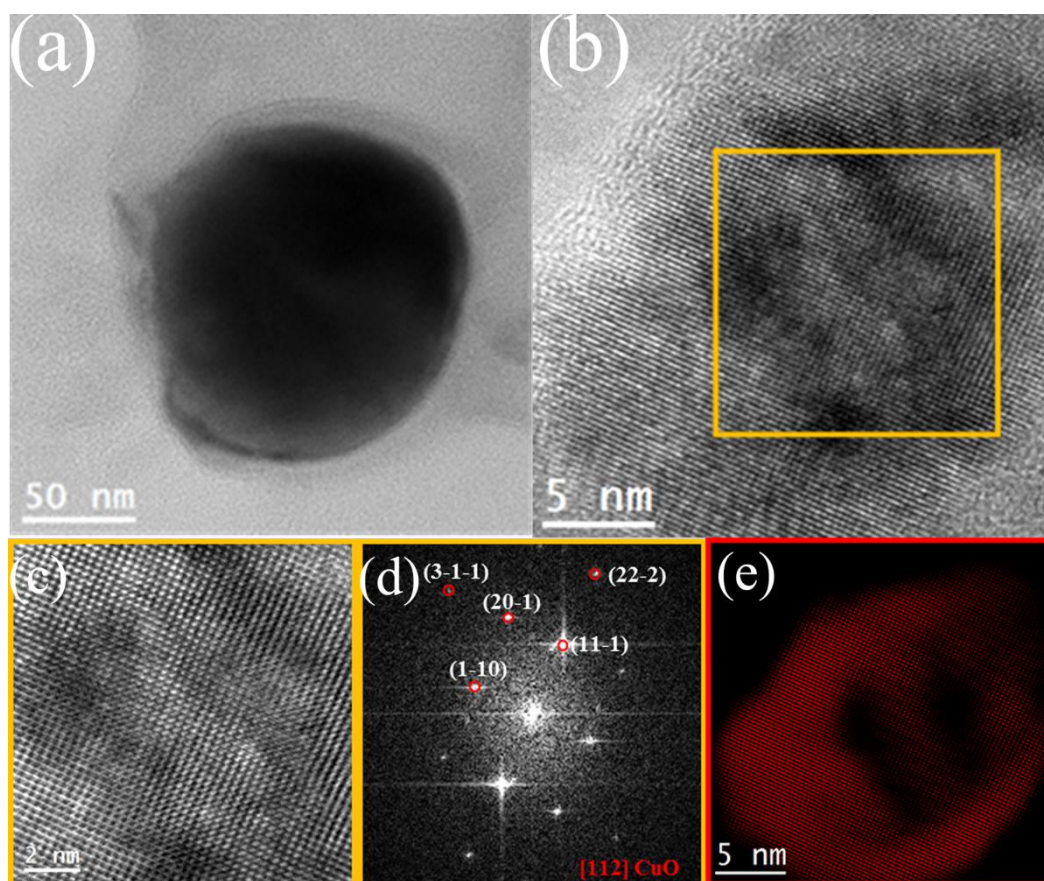


Figure 4. TEM images of Cu@porous carbon matrix materials (removed from the Cu foam) at the resolution of 50 nm (a) and 5 nm (b), respectively. (c) Details of the region squared in yellow and (d) the corresponding indexed power spectrum. (e) The RGB composition of IFFT from CuO.

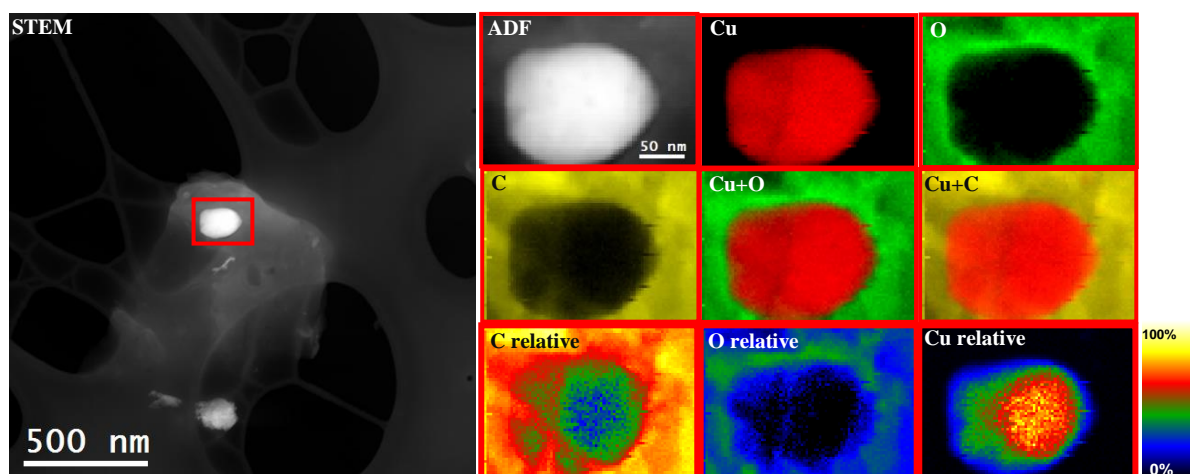


Figure 5. EELS chemical composition maps of Cu@porous carbon matrix materials (removed from the Cu foam) obtained from the area squared in red on the ADF-STEM micrograph. Right top and right middle: Individual Cu (red), O (green), C (yellow) maps and their composites; Right bottom: the relative composition map of C, O and Cu elements.

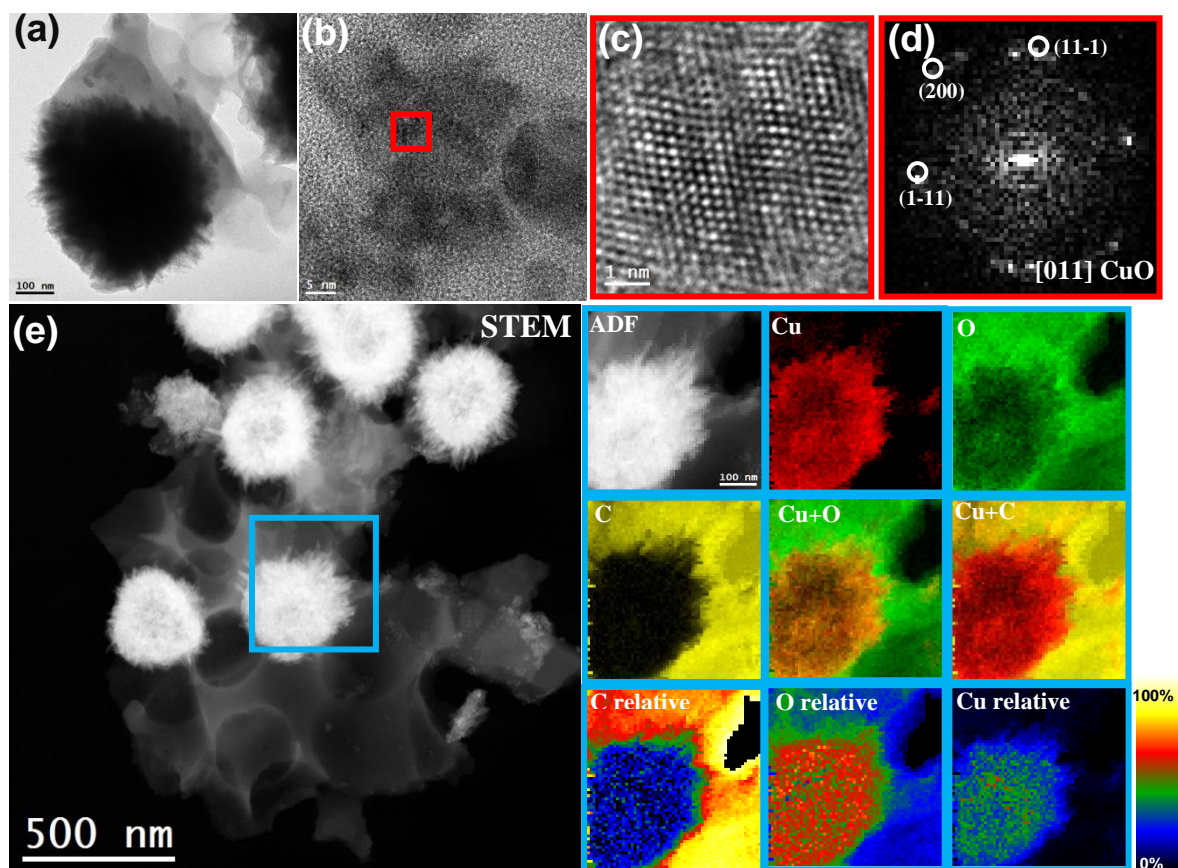


Figure 6. (a) and (b) TEM images of Cu@porous carbon matrix materials after sensor test (removed from the Cu foam). (c) details of the squared region in red line and (d) their corresponding indexed power spectrum. (e) EELS chemical composition maps of Cu@porous carbon matrix materials after glucose sensor test (scratched from Cu foam) obtained from the area squared in indigo on the ADF-STEM micrograph. Right top and right middle: Individual Cu (red), O (green), C (yellow) maps and their composites; Right bottom: the relative composition map of C, O and Cu elements.

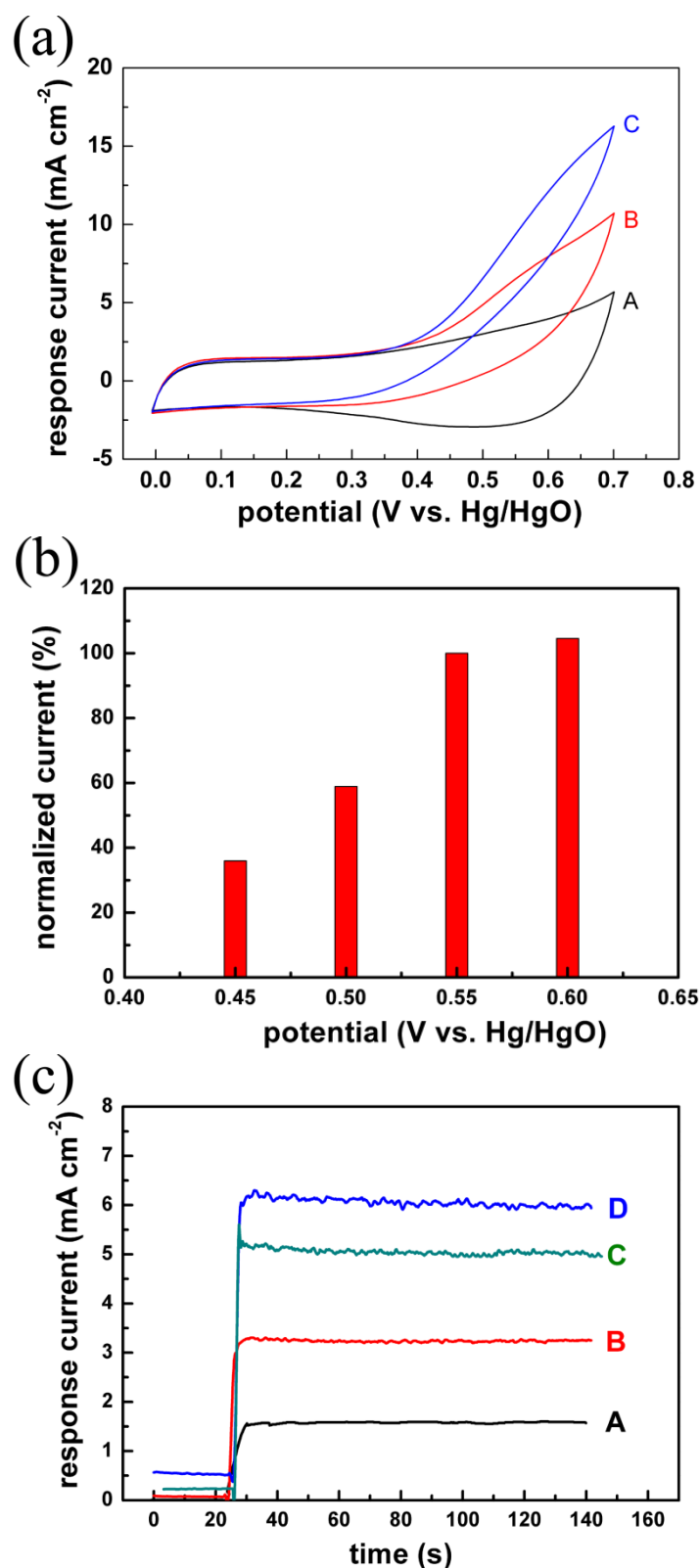


Figure 7. (a) CV curves of Cu@porous carbon matrix electrode in the absence (A) and presence of glucose (B: 1 mM glucose; C: 2 mM glucose) at a scan rate of 50 mV s^{-1} , respectively. (b) Amperometric responses of Cu@porous carbon matrix electrode at potentials from +0.45 V to +0.6 V vs. Hg/HgO to the addition of 1 mM glucose (normalized by the amperometric response at +0.55 V vs. Hg/HgO). (c) Amperometric responses of the copper plate electrode (A), copper foam electrode (B) and Cu@porous carbon matrix electrode (C) to the addition of 1 mM glucose at +0.55 V vs. Hg/HgO.

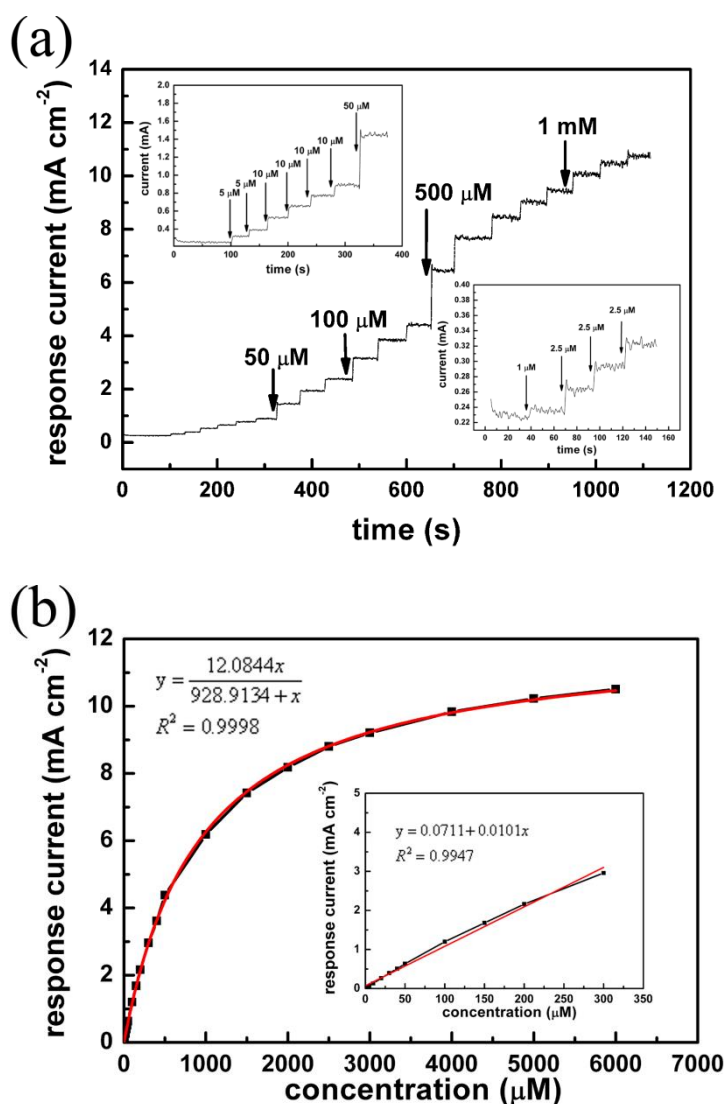


Figure 8. (a) Amperometric response of the Cu@porous carbon matrix electrode to successive additions of increased concentrations of glucose solutions to 0.1 M NaOH solution at an applied potential of +0.55 V (vs. Hg/HgO). The low-concentration part is magnified and shown in the inset in the upper left corner. The inset curve in the lower right corner is amperometric response of Cu@porous carbon matrix electrode to successive addition of glucose solution with smaller concentrations. (b) Corresponding calibration curve for **Figure 8 (a)**.

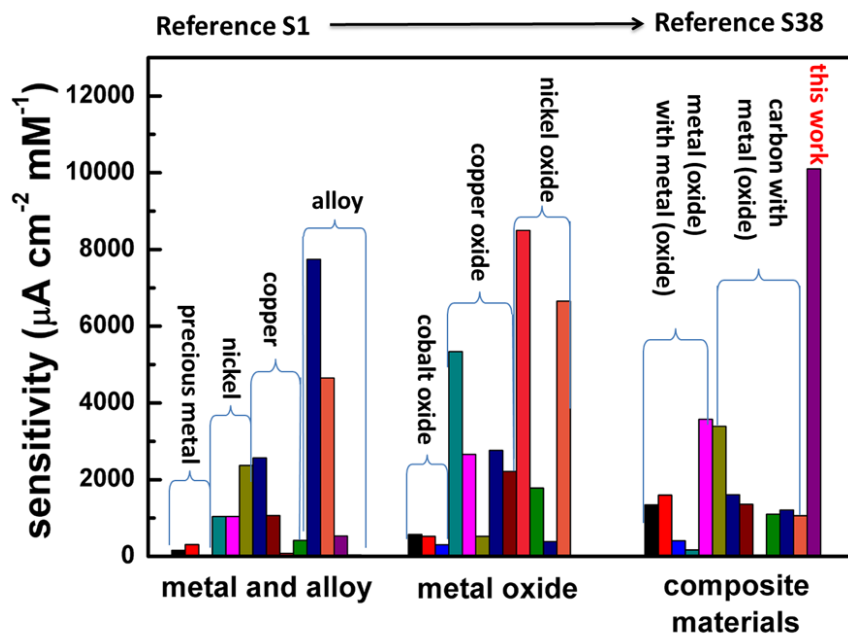


Figure 9. Comparison of the sensitivity of Cu@porous carbon matrix electrode with other electrodes reported in the literature (the related references S1~S38 are listed in the supplementary information).

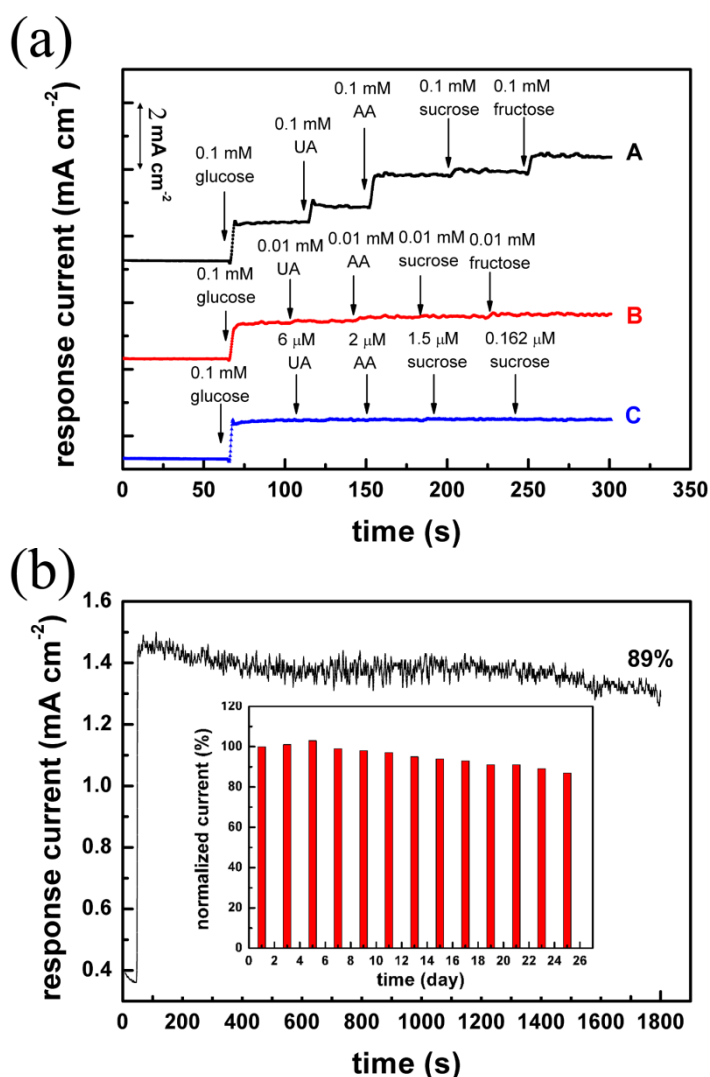


Figure 10. (a) The selectivity study of Cu@porous carbon matrix electrode with addition of different concentrations of UA, AA, sucrose, fructose and glucose at an applied potential of +0.55 V. (b) Long term stability of Cu@porous carbon matrix electrode at +0.55 V for 1800 s. Inset shows the normalized sensitivity of Cu@porous carbon matrix electrode to glucose tested every two days by amperometric measurement over 25 consecutive days.