Hierarchical Co$_3$O$_4$/CuO nanorod array supported on carbon cloth for highly sensitive non-enzymatic glucose biosensing

Siyi Cheng$^{a,b,c}$, Steven DelaCruz$^{a,b}$, Chen Chen$^{c}$, Zirong Tang$^{c}$, Tielin Shi$^{c}$, Carlo Carraro$^{a,b}$, Roya Maboudian$^{a,b,*}$

$^a$ Berkeley Sensor & Actuator Center, University of California, Berkeley, California 94720, United States of America

$^b$ Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States of America

$^c$ State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

Email: maboudia@berkeley.edu

Highlights

- Hierarchical core-shell Co$_3$O$_4$/CuO nanorod arrays were fabricated.
- The uniform core-shell structure offers abundant electro-active sites.
- The heterostructure favors electron transport within the electrode.
- Co$_3$O$_4$/CuO on carbon cloth can be directly used as non-enzymatic glucose sensor.
- The glucose sensor shows a high sensitivity and good selectivity.

Abstract

A hierarchical core-shell Co$_3$O$_4$/CuO nanorod array (NRA) anchored on flexible carbon cloth (CC) has been fabricated through a stepwise process consisting of magnetron sputtering of Cu, its anodic oxidation, and chemical bath deposition of
Co$_3$O$_4$. The structure, composition and morphology of the synthesized Co$_3$O$_4$/CuO NRA on CC were characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The glucose sensing performance of the Co$_3$O$_4$/CuO NRA on CC electrode was investigated by cyclic voltammetry and chronoamperometry. The sensor exhibited a high sensitivity of 5405 μA mM$^{-1}$ cm$^{-2}$ with a fast response time ($t_{90} = 1.9$ s) and a low detection limit of 0.38 μM. The electrode also showed outstanding selectivity toward various interferences. These results indicate that the Co$_3$O$_4$/CuO nanocomposites may be promising electrode materials for electrochemical biosensing.

Keywords
Hierarchical; Co$_3$O$_4$@CuO; core-shell structure; Carbon cloth; Non-enzymatic biosensor; Glucose sensor

1. Introduction
Rapid and accurate glucose detection can provide critical information in a variety of contexts, including diabetes monitoring, fermentation, and environmental protection [1-3]. To date, tremendous efforts have been made to develop glucose sensors with high sensitivity, good selectivity, fast response time, good reliability, and low cost [4, 5]. Many methods have been developed for glucose detection, including ones based on electrochemical, fluorescence, surface plasmon resonance, and optical methods [3, 6-
Among these, electrochemical methods have attracted significant attention due to such advantages as high sensitivity and selectivity, simple operation, and cost effectiveness [9, 10]. Among different types of electrochemical glucose sensors, enzymatic glucose sensors, which catalyze glucose using glucose oxidase, show high sensitivity and selectivity [11]. However, low chemical stability, complicated immobilization processes and high cost limit the practical application of enzyme-based glucose sensors [12, 13]. Hence, it is highly desirable to develop non-enzymatic sensors for the direct detection of glucose.

Owing to great progress in nanotechnology, various nanostructures based on metals and metal oxides have been applied for the construction of non-enzymatic glucose sensors with high performance [10, 14, 15]. Over the past decade, several noble metals, such as gold [16], platinum [17], silver [18] and their alloys [19], have been widely studied for glucose detection due to their high catalytic properties. However, their high cost, relatively low selectivity, and proneness to poisoning hinder their practical applications [20]. In contrast, transition metal oxides, such as CuO, NiO, Co$_3$O$_4$ and MnO$_2$ have drawn increasing attention due to their low cost, enhanced selectivity, and high stability [21-24]. Among these nanomaterials, CuO possesses a high isoelectric point and excellent electrochemical performance. Hence, various CuO-based nanostructures, including nanowires [25], nanosheets [20], nanoflowers [26] and nanorods [27], have been fabricated for glucose sensing applications. However, the poor intrinsic electrical conductivity of CuO limits charge carrier transport, resulting in low sensitivity. Therefore, constructing an electrode from multiple nanomaterials and
leveraging synergistic effects between its components is believed to be a promising way to improve the conductivity, electro-active surface area, and contact area between the sensing material and the substrate, leading to improved ion/electron transport inside the electrodes and better electrochemical performance. Recently, various CuO-based composite nanomaterials have been reported for glucose detection [20, 28-30]. However, most of these studies have focused on the sensing performance of nanomaterials on glassy carbon electrodes, which may limit their practical applications.

It was recently demonstrated that CuO-based nanostructures can be directly grown on conductive substrates without any binder [31]. This approach can reduce the resistance between the sensing materials and the substrate. Therefore, fabricating composite nanomaterials directly on conductive substrates may open a new avenue toward achieving enhanced glucose sensing performance.

Herein, we report on the synthesis of a Co$_3$O$_4$/CuO hierarchical core-shell nanorod array (NRA) directly on flexible and conductive carbon cloth via a stepwise approach. The integration of Co$_3$O$_4$ nanoflakes on CuO nanorods can increase the electro-active surface area and improve the contact area between the sensing materials and the substrate, which lead to more active sites for redox reactions and faster reaction kinetics. We demonstrate that the composite nanostructures on carbon cloth exhibit high electrochemical performance with high sensitivity, fast response time, low detection limit, and good selectivity, thus proving promising for non-enzymatic glucose sensors.

2. Experimental

2.1. Fabrication of hierarchical Co$_3$O$_4$/CuO NRA/CC
All chemicals were analytical grade and were used without further purification. Carbon cloth, purchased from Cetech Co. Ltd., was cleaned in acetone, ethanol and deionized (DI) water for 10 min each. After drying in air, carbon cloth was placed into a magnetron sputtering system. A Cu layer was sputtered on both sides of carbon cloth by using a magnetron sputtering system (TPR-450) at a power of 100 W for 30 min. Subsequently, the as-obtained sample was cut into 10 mm × 10 mm pieces and anodized in a 3 M NaOH solution at a current density of 10 mA cm\(^{-2}\) to form a Cu(OH)\(_2\) NRA on carbon cloth. Then, 0.075 M cobalt sulfate hydrate and 1.134 M urea were dissolved in 20 ml of DI water in a 25 mL vial and stirred to form a clear pink solution. The as-prepared Cu(OH)\(_2\) NRA/CC sample was immersed in the solution and held for 1 h at 85 °C in an oil bath. The sample was then taken out of the solution, washed with DI water, and annealed at 350 °C in air for 2 h to prepare hierarchical Co\(_3\)O\(_4\)/CuO NRA/CC. For comparison, the CuO NRA/CC sample was prepared by directly annealing Cu(OH)\(_2\) NRA/CC in air at 350 °C.

2.2. Materials Characterization

The structures of the as-synthesized samples were characterized by X-ray diffraction (XRD, Bruker AXS D8 Discover with GADDS) using a Co K\(_{\alpha}\) radiation source and by transmission electron microscopy (TEM) using a FEI Tecnai G2 S-TWIN. The chemical compositions of the samples were analysed by X-ray photoelectron spectroscopy (XPS, Omicron Dar400 system with an achromatic Al K\(_{\alpha}\) X-ray source) and Raman spectroscopy (Horiba LabRAM confocal Raman spectrometer with an excitation laser of 632.8 nm). The morphologies and
microstructures of the samples were probed by field-emission scanning electronic microscopy (FE-SEM Quanta 3D FEG).

2.3. Electrochemical measurements

All electrochemical experiments were performed at room temperature with a CHI 600D electrochemical workstation. The electrochemical measurements were performed in 0.1 M NaOH using a conventional three-electrode configuration: carbon cloth samples as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. For amperometric tests, the solution was stirred to facilitate mixing.

3. Results and discussion

Scheme 1 illustrates the fabrication process of hierarchical Co$_3$O$_4$/CuO core-shell structures on carbon cloth. A highly ordered Cu(OH)$_2$ NRA was first synthesized on flexible carbon cloth via magnetron sputtering of copper and subsequent anodic oxidation [32]. Then chemical bath deposition and a follow-up calcination process were used to form a hierarchical Co$_3$O$_4$/CuO core-shell nanorod array. The formation mechanism of the Co$_3$O$_4$ shell can be described by the “self-assembly” and “oriented attachment” processes [33]. In our case, the Cu(OH)$_2$ nanorod array acts as the backbone which guides the Co-based precursor deposition.

XRD and Raman measurements were carried out to investigate the structure and composition of the as-synthesized materials. Figure 1a shows representative XRD spectra obtained on CuO NRA and Co$_3$O$_4$/CuO NRA on carbon cloths. The broad diffraction peaks at around 25.6° demonstrate the graphitized carbon phase originating
from the carbon cloth. The peaks located at 43.2° can be ascribed to copper (JCPDS 04-0836), revealing that the as-deposited copper layer was not fully transformed into CuO during the anodic oxidation and annealing processes. The formation of CuO is evidenced by the peaks at 32.4, 35.5, 38.7, 48.9, 53.5, 58.2, 61.4, 66.3 and 67.9°, which correspond to the (110), (002), (111), (-202), (020), (202), (-113), (022) and (113) planes of the monoclinic CuO structure (JCPDS No. 89-5899), respectively [34]. The chemical bath deposition and calcination processes lead to the formation of the Co$_3$O$_4$/CuO NRA on carbon cloth. The peaks centered at 18.9, 31.1, 36.6 and 65.2° correspond to the (111), (220), (311) and (440) planes of the Co$_3$O$_4$ spinel phase (JCPDS No. 42-1467), respectively [35]. The XRD result of the sample after 1 h immersion in 0.075 M cobalt sulfate hydrate and 1.134 M urea solution at 85 °C is shown in Figure S1. The peak located at 22.1° can be attributed to Co(OH)$_2$ (JCPDS 04-0836), while the peaks located at 32.7, 38.8, and 45.7° can be ascribed to CoCO$_3$ (JCPDS 11-692). The remaining peaks can be attributed to those of carbon cloth (25°), copper (43°), and Cu(OH)$_2$. Therefore, the Co precursors appear to be in the form of Co(OH)$_2$ and CoCO$_3$, and this result corresponds to previous reported precursors for Co$_3$O$_4$[36]. Raman spectroscopy was carried out to examine the difference between the CuO and the Co$_3$O$_4$/CuO core-shell nanostructures. Figure 1b displays the Raman spectra of the CuO NRA and Co$_3$O$_4$/CuO NRA on carbon cloth. Two strong bands at 1325 and 1603 cm$^{-1}$ can be indexed to the characteristic peaks of the D-band (indicative of the presence of defects in the hexagonal graphitic layers) and G-band (first-order scattering of the E$_{2g}$ mode observed for sp$^2$ carbon domains) of carbon cloth [37, 38]. The Raman spectrum of
CuO shows three peaks at 291, 347 and 623 cm\(^{-1}\), corresponding to the \(A_g\), \(B_g^{(1)}\) and \(B_g^{(2)}\) modes of CuO backbone, respectively [39]. As shown in the spectrum of the Co\(_3\)O\(_4\)/CuO NRA on carbon cloth, four peaks detected at around 190, 480, 520 and 680 cm\(^{-1}\) correspond to \(E_g\), \(F_{2g}^1\), \(F_{2g}^2\) and \(A_{1g}\) modes of Co\(_3\)O\(_4\) [40]. After the growth of Co\(_3\)O\(_4\), the relative peak intensity of CuO is reduced, suggesting that the CuO core is covered by the Co\(_3\)O\(_4\) shell.

The near-surface elemental composition and oxidation state of the Co\(_3\)O\(_4\)/CuO NRA/CC as well as the presence of absorbed species were analyzed by XPS. The survey spectrum (Figure 2a) shows a series of characteristic peaks associated with copper, cobalt, oxygen and carbon elements. It is worth mentioning that the C 1s peak is weak, which may be due to the uniform growth of sensing material on the surface of the carbon substrate. In the high-resolution Co 2p XPS spectrum (Figure 2b), the two characteristic peaks centered at 780.3 and 795.4 eV correspond to Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\), respectively, with a spin-orbit separation of around 15 eV [41, 42]. The Gaussian fitted peaks positioned at the binding energies around 780.5 and 795.5 eV can be ascribed to Co\(^{3+}\), whereas the peaks at 781.6 and 797.4 eV confirm the presence of Co\(^{2+}\) [43, 44]. In addition, the two shakeup satellite peaks located around 788.2 and 803.9 eV indicate that the cobalt has a spinel structure [45]. Figure 2c displays the core level Cu 2p spectrum of the composite material. Two peaks located at the binding energies of 934.3 and 954.6 eV can be assigned to Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\), while the shakeup satellite peak at 942.6 eV can be indexed to Cu\(^{2+}\) [46]. Figure 2d shows the high-resolution spectrum of the O 1s region, demonstrating the co-existence of three oxygen species marked as
O1, O2 and O3. The O1 component located at a binding energy of 529.8 eV is consistent with the typical metal-oxygen bond, and the O2 component at a binding energy of 531.4 eV can be ascribed to the large density of defects with low oxygen coordination in the composite material [6]. The O3 component at a binding energy of 532.4 eV corresponds to multiplicity of physically absorbed and chemisorbed species onto and within the surface layer [47]. These results clearly show that the surface of the as-synthesized Co$_3$O$_4$/CuO NRA contains Co$^{2+}$, Co$^{3+}$ and Cu$^{2+}$ ions, indicating the composition consists of CuO and Co$_3$O$_4$.

Carbon cloth, which consists of interconnected carbon fibers with an average diameter of ~10 μm (Figure S2a), was used as the conductive substrate. As shown in Figure S2b, the bare carbon cloth possesses high flexibility under bending, making it a good substrate for flexible sensing applications. The morphologies of the CuO NRA and core-shell Co$_3$O$_4$/CuO NRA on carbon cloth were examined by SEM. Figure 3a shows that the CuO nanorods were grown uniformly and vertically on carbon fiber. The magnified SEM image (Figure 3b) indicates that the as-synthesized CuO nanorods possess lengths of a few micrometers and an average diameter of ~100 nm. Figures 3c-d present the SEM images of the core-shell Co$_3$O$_4$/CuO NRA under different magnifications. It can be seen that the deposited Co$_3$O$_4$ layer consists of nanoflakes which are interconnected to each other and form a highly ordered 3D nanostructure. The detailed structures of the Co$_3$O$_4$/CuO NRA were recorded by TEM. Figure 3e shows the TEM image of the Co$_3$O$_4$/CuO NRA. It can be seen that the CuO nanorod is compactly wrapped by interconnected Co$_3$O$_4$ nanoflakes. Figure 3f displays the TEM
image of $\text{Co}_3\text{O}_4$ at high resolution, revealing lattice fringes with the interplanar gap of 0.24 nm, corresponding well to the (311) plane of $\text{Co}_3\text{O}_4$.

Electrochemical tests for different working electrodes were performed in a three-electrode cell system. Figures 4 display the cyclic voltammograms (CVs) of different electrodes in 0.1 M NaOH solution in the absence and presence of 0.5 mM glucose under a scan rate of 50 mV s$^{-1}$. The bare carbon cloth electrode shows a much smaller CV curve area than that of the CuO NRA/CC and $\text{Co}_3\text{O}_4$/CuO NRA/CC electrodes, and exhibits no redox peak after the addition of glucose (see enlarged CVs in Figure S3), implying that the contribution of the carbon cloth toward the detection of glucose can be neglected. The bare CC electrode exhibits a large oxidative tail corresponding to the onset of water breakdown observed for potentials above 0.65 V [48]. This behavior can also be observed in the CV curves of the CuO NRA/CC and $\text{Co}_3\text{O}_4$/CuO NRA/CC electrodes. The CV result on the CuO NRA/CC shows a broad reduction peak at ~0.42 V in the blank alkaline solution. This peak may be ascribed to the CuOOH/CuO transition [32]. However, the corresponding oxidation peak related to CuO/CuOOH is not clearly observed, which may be due to overshadowing by the oxidation peak of water-splitting [48, 49]. After the addition of 1 mM glucose, an oxidation peak appears at ~0.3 V, corresponding to the irreversible glucose oxidation reactions [32]. In comparison, on the $\text{Co}_3\text{O}_4$/CuO NRA/CC electrode, two pairs of redox peaks, one at 0.58 and 0.38 V, and one at 0.25 and 0.12 V, are observed prior to the addition of glucose, which can be ascribed to the $\text{Co}_3\text{O}_4$/CoOOH and CoOOH/CoO$_2$ redox couples, respectively [50]. After the addition of 1 mM glucose, the oxidative peak at 0.58 V shift
to 0.5 V and its magnitude increases, while the current at 0.25 V remains nearly constant. The oxidative peak at 0.5 V can be attributed to the transitions of CuO/CuOOH and CoOOH/CoO₂, and the oxidative peak at 0.25 V can be assigned to the Co³O₄/CoOOH transition [23]. This phenomenon indicates that the CoOOH/CoO₂ couple on Co³O₄ is the dominant redox reaction for the glucose catalysis process [50]. In the cathodic scan, the broad peak at 0.38 V may be attributed to the combination of CoO₂/CoOOH and CuOOH/CuO transitions, while the broad peak at 0.12 V could be attributed to the Co³O₄/CoOOH transition [31, 51]. We hypothesize that the mechanism of the glucose oxidation in Co³O₄/CuO NRA/CC electrode is similar to that of individual CuO and Co³O₄ electrodes and can be explained as follows [51, 52]:

\[
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \rightarrow 3\text{CoOOH} + e^- \quad (1)
\]

\[
\text{CoOOH} + \text{OH}^- \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (2)
\]

\[
2\text{CoO}_2 + \text{glucose} \rightarrow 2\text{CoOOH} + \text{gluconolactone} \quad (3)
\]

\[
\text{CuO} + \text{OH}^- \rightarrow \text{CuOOH} + e^- \quad (4)
\]

\[
2\text{CuOOH} + \text{glucose} \rightarrow 2\text{CuO} + \text{gluconolactone} + \text{H}_2\text{O} \quad (5)
\]

In addition, the oxidation and reduction peaks of the Co³O₄/CuO NRA/CC electrode show higher intensity than those of the CuO NRA/CC electrode, demonstrating that the composite electrode has better electrochemical behavior toward the electro-oxidation of glucose. The improved electrochemical performance can be ascribed to the large amount of Co³O₄ nanoflakes firmly and uniformly fixed to the surface of the CuO NRA electrode, providing greater electroactive surface area for the detection of glucose.
The electrochemical surface area (ECSA) of the Co$_3$O$_4$/CuO NRA/CC and CuO NRA/CC electrodes were estimated through electrical double-layer capacitance (EDLC) tests in 0.1 M NaOH solution as the double-layer capacitance ($C_{dl}$) is proportional to the ECSA [53]. The CV plots were obtained within ±0.05 V of open circuit potential, where the current response should only be due to the charging of the double layer [54]. The CV curves of Co$_3$O$_4$/CuO NRA/CC and CuO NRA/CC electrodes at various scan rates (in 2 to 10 mV/s range) are shown in Figures S4a and b, respectively. At each scan rate, the Co$_3$O$_4$/CuO NRA/CC electrode exhibits much higher anodic ($j_a$) and cathodic ($j_c$) current densities than the CuO NRA/CC electrode. As shown in the reported works, the linear slope in such plots is equal to $2C_{dl}$ [55]. The calculated capacitance of the Co$_3$O$_4$/CuO NRA/CC electrode (0.03 mF/cm$^2$) is much higher than that of CuO NRA/CC electrode (0.0035 mF/cm$^2$), indicating the higher electrochemical surface area of the Co$_3$O$_4$/CuO NRA/CC electrode (Figure S4c).

To better understand the electrochemical behavior of the Co$_3$O$_4$/CuO NRA/CC electrode, CV tests were also conducted at different scan rates. Figure 5a displays the CVs of the Co$_3$O$_4$/CuO NRA/CC electrode in the presence of 1 mM glucose with scan rates ($\nu$) of 5, 10, 20, 30, 40, 50 mV s$^{-1}$. It can be seen that the anodic ($j_{pa}$) and the cathodic ($j_{pc}$) peak current densities increase with increasing scan rate. The redox peak current shows good linearity with the scan rate, and the regression equations for the anodic and cathodic peak current can be expressed as $j_{pa}$ (mA cm$^{-2}$) = 1.16 + 0.53$\nu$ (mV s$^{-1}$) ($R^2$=0.999) and $j_{pc}$ (mA cm$^{-2}$) = -0.11 - 0.27$\nu$ (mV s$^{-1}$) ($R^2$=0.998), respectively. This linearity indicates that the electro-oxidation of glucose on the Co$_3$O$_4$/CuO NRA/CC
electrode is a diffusion-controlled process [56, 57].

Figure 6a shows the amperometric response curves of the CuO NRA/CC and Co$_3$O$_4$/CuO NRA/CC electrodes after successive injection of glucose into 0.1 M NaOH under continuous stirring at an applied potential of 0.55 V. After glucose addition, the Co$_3$O$_4$/CuO NRA/CC electrode exhibits a larger response current compared to the CuO NRA/CC electrode. The slope of the calibration curve (Figure 6b) also confirms the higher sensitivity of the Co$_3$O$_4$/CuO NRA/CC electrode. The amperometric results are consistent with the CV results. The improved response current achieved with the Co$_3$O$_4$/CuO NRA/CC could be ascribed to the larger electro-active surface area, which provides more active sites for the oxidation of glucose. Thus, Co$_3$O$_4$/CuO core-shell nanostructures possess better electrochemical performance than the bare CuO nanorods, making them promising materials for the detection of glucose.

Figure 7a shows a typical amperometric response of the Co$_3$O$_4$/CuO NRA/CC electrode to the successive addition of glucose into 0.1 M NaOH with an applied potential of 0.55 V. After the injection of glucose, the current increases, reaching 90% of its steady-state value ($t_{90}$) in 1.9 s (Figure S5), demonstrating the rapid response of the Co$_3$O$_4$/CuO core-shell structure. The corresponding calibration curve of the Co$_3$O$_4$/CuO NRA/CC electrode is displayed in Figure 7b. The peak current increases linearly with increasing glucose concentration within the range of 1 to 500 μM ($R^2=0.997$), and the electrode demonstrates a high sensitivity of 5405 μA mM$^{-1}$ cm$^{-2}$ and a low detection limit of 0.38 μM (S/N = 3). When the glucose concentration is above 500 μM, the slope of the fitting curve is slightly reduced (Figure S6), which may
be ascribed to a condition where the glucose diffusion rate exceeds the consumption rate at high glucose concentration [58]. The Co$_3$O$_4$/CuO NRA/CC electrode exhibits excellent glucose sensing performance, with the highest sensitivity, lower detection limit and response time, and a comparable linear range, when compared to the performance of recently reported CuO and Co$_3$O$_4$ based glucose sensors (Table S1). The superior performance can be attributed to the following aspects: (1) The Co$_3$O$_4$ shell can act as a stable matrix to encapsulate and connect the core CuO nanorods, thereby generating more channels for electron transport between the CuO nanorods and the substrate; (2) The uniform hierarchical Co$_3$O$_4$/CuO core-shell nanostructures can offer electro-active sites for glucose oxidation; (3) The core-shell structures are supported on highly conductive carbon cloth without binder, which can further improve the electron transportation efficiency.

Selectivity is one of the most important aspects for judging the performance of a glucose sensor. The selectivity of the Co$_3$O$_4$/CuO NRA/CC electrode was investigated by adding sucrose, fructose, uric acid (UA), ascorbic acid (AA), and dopamine (DA) into the 0.1 M NaOH solution at a potential of 0.55 V. Additionally, the influence of chloride ions was studied because they can poison non-enzymatic glucose sensors and lower the activity significantly [20]. The ratio of glucose and interferences in the human blood is more than 30:1 at a physiological level [59]. In order to evaluate the selectivity of the glucose sensor, a 10:1 concentration ratio of glucose to interferences was used to simulate the physiological level. Herein, the interference test was conducted by first adding 1 mM glucose and then adding 100 μM of the various interfering substances.
sequentially. As shown in Figure 8, with the addition of glucose, the current density increased significantly, whereas negligible current responses can be observed following the injection of the interferences. Therefore, it can be concluded that the Co$_3$O$_4$/CuO NRA/CC electrode possesses excellent selectivity as a non-enzymatic glucose sensor. The stability of the Co$_3$O$_4$/CuO NRA/CC electrode was evaluated by measuring the amperometric current response of Co$_3$O$_4$/CuO NRA/CC electrode with the addition of 0.1 mM glucose during a period of 20 days at a time interval of 2 days, as shown in Figure S7. After 20 days storage in air, the Co$_3$O$_4$/CuO NRA/CC electrode maintained approximately 97.6% of its original current response, implying a good stability of the Co$_3$O$_4$/CuO core-shell nanostructure. The Co$_3$O$_4$/CuO NRA/CC electrode shows better stability than some recently reported CuO based glucose sensors [60-62].

4. Conclusions

In summary, the hierarchical core-shell Co$_3$O$_4$/CuO NRA were synthesized on carbon cloth via a stepwise fabrication process including magnetron sputtering, anodic oxidation and chemical bath deposition. This core-shell nanostructure favors mass ion/electron transport and reversible redox reactions. The as-obtained sensor showed excellent electrochemical performance with a fast response time of 1.9 s, a low detection limit of 0.38 μM and a high sensitivity of 5405 μA mM$^{-1}$ cm$^{-2}$. These sensing properties are comparable to or better than many recently reported non-enzymatic glucose sensors. The results demonstrate that the Co$_3$O$_4$/CuO NRA/CC is promising for biosensing applications.

Acknowledgements
The authors thank Jinhu Fan for help with the magnetron sputtering. The support of the industrial members of the Berkeley Sensor & Actuator is gratefully acknowledged. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. S.C. acknowledge additional support through the China Scholarship Council. C.C., Z.T. and T.S. acknowledge the National Basic Research Program of China with Project No. 2015CB057205, the Program for Changjiang Scholars and Innovative Research Team in University (Grant No. IRT13017), and the National Science Foundation of China (No. 51775218).
References


Siyi Cheng received the B.S. degree from Beijing University of Chemical Technology in 2010, and the M.S. degree from Beijing University of Chemical Technology in 2014, he is working toward the Ph.D. degree in Mechanical Engineering in Huazhong University of Science and Technology. Currently he is working as a visiting graduate student in Department of Chemical Engineering at the University of California Berkeley. His research focuses on synthesis of semiconductor nanostructures for gas sensing and electrochemical applications.

Steven DelaCruz received his B.S. in Chemical Engineering from University of Nevada-Reno in 2015. He is currently a graduate student researcher in Chemical Engineering at the University of California Berkeley. His research concerns the development and characterization of electrode materials for thermionic energy converters.

Chen Chen received the B.Sc. degree in Engineering Machinery from Chang’an University in 2016. Currently She is working towards her Ph.D degree in Mechatronics Engineering at Huazhong University of Science and Technology. Her current research activities are the fabrication of micro/nano-materials.

Zirong Tang is a professor in the State Key Laboratory for Digital Manufacturing Equipment and Technology at Huazhong University of Science and Technology. He obtained his Ph.D. in Material Science and Engineering in 2001 from the University of California, Irvine, USA. His current interests are in MEMS, electrochemical sensors, biosensors and micro/nanofabrication technologies.
Tielin Shi is the director of the State Key Laboratory for Digital Manufacturing Equipment and Technology at Huazhong University of Science and Technology. He obtained his Ph.D in Mechanical Engineering in 1999 from Huazhong University of Science and Technology. His interests are in micro/nanofabrication technologies and developing advanced fabrication systems for microelectronic industry.

Carlo Carraro is a researcher and a lecturer in the Department of Chemical and Biomolecular Engineering at the University of California, Berkeley. He received his bachelor's degree from the University of Padua, Padua, Italy, and his Ph.D. degree from California Institute of Technology in Pasadena, California. His research interests are in the physics and chemistry of surfaces and synthesis of novel thin-film materials and processes.

Roya Maboudian is a Professor of chemical engineering at the University of California, Berkeley. She received her Ph.D. in applied physics from California Institute of Technology. Her current research interests are in the areas of surface/interfacial science and engineering of micro-/nanosystems, and thin-film science and technology.
**Figure 1** (a) X-ray diffraction and (b) Raman spectra of the CuO NRA (black) and Co$_3$O$_4$/CuO NRA (red) on carbon cloth.

**Figure 2** (a) Survey scan, and (b) Co 2p, (c) Cu 2p and (d) O 1s regions of the XPS spectrum obtained on Co$_3$O$_4$/CuO NRA/CC.
Figure 3 (a, b) SEM images of CuO NRA on carbon cloth with different magnifications.

(c, d) SEM images of Co$_3$O$_4$/CuO NRA on carbon cloth with different magnifications.

(e, f) TEM images of Co$_3$O$_4$/CuO NRA.
Figure 4 Cyclic voltammetry curves obtained on CC, CuO NRA/CC and Co$_3$O$_4$/CuO NRA/CC in the absence and presence of 1 mM glucose in 0.1 M NaOH solution at a scan rate of 50 mV s$^{-1}$. 
Figure 5 (a) CV responses of Co$_3$O$_4$/CuO NRA/CC electrode in 0.1 M NaOH with different scan rates. (b) Corresponding calibration curve of current vs. scan rate.

Figure 6 (a) Amperometric responses of the CuO NRA/CC (red) and Co$_3$O$_4$/CuO NRA/CC (black) electrodes under the successive addition of 50 µM glucose at the applied potential of 0.55 V. (b) Corresponding calibration curves for glucose detection.
Figure 7 (a) Amperometric response of the Co$_3$O$_4$/CuO NRA/CC electrode upon successive additions of glucose with select concentrations marked. Inset: the enlarged view in low concentrations. (b) Calibration curve for glucose of the Co$_3$O$_4$/CuO NRA/CC electrode.

Figure 8 Amperometric responses of the Co$_3$O$_4$/CuO NRA/CC electrode to the successive addition of glucose and interference species.
Scheme 1 Schematic illustration of the fabrication process for the Co$_3$O$_4$/CuO NRA on carbon cloth.