Electrochemical Cycling-Induced Spiky CuₓO/Cu Nanowire Array for Glucose Sensing
Hsin-Hsin Fan, Wei-Lun Weng, Chi-Young Lee, and Chien-Neng Liao*

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, 30013 Taiwan, ROC

Supporting Information

ABSTRACT: The glucose level is an important biological indicator for diabetes diagnosis. In contrast with costly and unstable enzymatic glucose sensing, oxide-based glucose sensors own the advantages of low fabrication cost, outstanding catalytic ability, and high chemical stability. Here, we fabricate a self-supporting spiky CuₓO/Cu nanowire array structure by electrochemical cycling treatment. The spiky CuₓO/Cu nanowire is identified to be a Cu core passivated by a conformal Cu₂O layer with extruded CuO petals, which provides abundant active sites for electrocatalytic reaction in glucose detection. An interruptive potential sweeping experiment is presented to elucidate the growth mechanism of the spiky CuₓO/Cu nanostructure during the potential cycling treatment. The spiky CuₓO/Cu nanowire array electrode exhibits a sensitivity of 1210 ± 124 μA·mM⁻¹·cm⁻², a wide linear detection range of 0.01–7 mM, and a short response time (<1 s) for amperometric glucose sensing. The study demonstrates a route to modulate oxide phase, crystal morphology, and electrocatalytic properties of metal/oxide core–shell nanostructures.

INTRODUCTION

A timely and accurate detection of glucose levels in biological fluids is essential for diabetes care. Traditional glucose sensing is based on the enzymatic functionalization of immobile glucose oxidase (GOx) in a gel on an electrode. Although enzymatic glucose sensors have been brought to practical medical diagnostic applications, yet the stability and durability of GOx still remains to be improved for enzymatic glucose sensing because they can be easily affected by test environments such as temperature, pH value, oxygen content, and humidity. Recently, a non-enzymatic glucose sensing based on the electrocatalytic oxidation of glucose on noble metals, metal oxides, complexes, and carbon materials has been actively researched to resolve the reliability and durability problems encountered for enzymatic glucose sensing. Among these non-enzymatic glucose sensing materials, semiconductor metal oxides appear to be highly attractive by considering the fabrication cost, synthesis complexity, biocompatibility, chemical stability, and electrocatalytic performance.

Copper oxide is a promising glucose sensing material because of the advantages of natural abundance, low cost, nontoxicity, and excellent electrocatalytic properties. A tremendous research effort has been dedicated to the development of enzyme-free glucose sensors based on Cu oxides. Generally, Cu oxides in the form of nanoparticles (NPs) or nanowires (NWs) are preferred forms because their catalytic efficiency and charge transfer capability are greatly enhanced due to the presence of plentiful active sites on the surface of NPs and NWs. To form a functional sensing electrode, Cu oxide NPs or NWs synthesized from solutions must be transferred onto a conducting substrate such as a glassy carbon electrode (GCE). However, the charge transport from oxide to the conducting electrode may be hindered by huge contact resistance between the NPs or NWs. Zhang et al. prepared a glucose sensor with CuO NPs/GCE configuration, showing a high sensitivity of 2555 μA·mM⁻¹·cm⁻² and a low detection limit of 72 nM but a narrow linear detection range of 0.1–3 mM. Moreover, Cu NWs with extruded Cu₂O nanosheets have been synthesized and implemented onto a GCE, showing a glucose sensing performance of 1420 μA·mM⁻¹·cm⁻² in sensitivity, 40 nM in detection limit, and 0.7–2.0 mM in the linear detection range.
The main issue associated with the NPs/GCE or NWs/GCE type glucose sensors is the narrow linear range that is likely attributed to the resistive transport path of charge carriers from Cu oxide NPs (NWs) to the electrode. Li et al. have electrodeposited Cu NPs on a Cu foil directly, followed by an appropriate anodic oxidation treatment, to form a Cu$_2$O/Cu glucose sensor, showing a wide linear detection range up to 6 mM. In summary, a direct growth of nanostructured Cu oxide on a conducting electrode shall be able to provide the best overall glucose detection performance.

A cyclic voltammetric deposition technique, also known as the potential cycling method, has been used to grow various metal oxides including ruthenium oxide and manganese oxide by controlling composition and pH value of electrolyte and potential sweeping range and cycles. In this study, a spiky Cu$_x$O/Cu NW array structure was grown on a Ni thin film electrode through template-assisted electrodeposition followed by potential cycling treatment, as shown in Scheme 1. The oxide phase and crystal structure of the Cu$_x$O/Cu NWs were characterized. The growth mechanism of the spiky Cu$_x$O/Cu nanostructure during the potential cycling treatment is elucidated based on the ex situ microstructure characterization in an interruptive potential sweeping experiment. Finally, the glucose sensing performance of the spiky Cu$_x$O/Cu NW array was evaluated by amperometric measurement.

**RESULTS AND DISCUSSION**

**Synthesis of the Spiky Cu$_x$O/Cu NW Array.** An array of Cu NWs grown on a Ni thin film was released from the anodic alumina oxide (AAO) template and consequently treated in an alkaline solution by sweeping the potential back and forth in a three-electrode cell. The scanning electron microscopy (SEM) images show that the as-released Cu NWs exhibit a smooth surface (Figure 1a,c) and transform into a spiky morphology after the potential cycling treatment (Figure 1b,d). An X-ray diffraction (XRD) analysis indicates that only cuprous oxide (Cu$_2$O) is present in the as-released Cu NWs, whereas both Cu$_2$O and cupric oxide (CuO) appear on the post-treated Cu NWs (Figure 1e). Furthermore, an enlarged transmission electron microscopy (TEM) image reveals that the Cu NW indeed is passivated by a conformal Cu$_2$O layer with extruded CuO petals extruding out of the Cu$_2$O layer (Figure 2a). The Cu/Cu$_2$O/CuO composite nanostructure was further confirmed by the high-resolution TEM (HRTEM) images and their corresponding fast Fourier transform (FFT) diffraction patterns (Figure 2b–d).

Now, one question may be raised whether the unique spiky CuO/Cu$_2$O/Cu nanostructure is specifically associated with the electrochemical potential cycling treatment. It has been attempted to grow CuO on the Cu NWs in the same alkaline electrolyte by applying a constant oxidation potential of +0.6 V (vs SCE) with the same duration as the potential cycling treatment. Interestingly, the Cu NWs only formed a thick and rough Cu$_2$O layer rather than the spiky CuO according to the XRD and TEM analyses (Figure 3). A static anodic oxidation environment is apparently unable to grow spiky CuO on the Cu NWs. Thus, an in-depth understanding of the growth...
mechanism of spiky CuO during the potential cycling treatment becomes the subject of interest.

**Growth Mechanism of Spiky CuO/Cu NWs.** The spiky CuO/Cu NW array was obtained by sweeping the potential with respect to the saturated calomel electrode (SCE) from +0.6 to −0.7 V and back to +0.6 V several times at a scan rate of 2.5 mV/s in a 0.1 M NaOH solution. Each cyclic voltammetry (CV) curve behaves differently with potential sweeping cycles (Figure 4). Considering the sweeping potential in between −0.2 and +0.6 V of the oxidation half-cycle (upper part), the current peak is most significant in the first CV cycle, then becomes two individual small peaks in the second CV cycle, and finally decreases down to a negligible level in the following CV cycles. It implies that the growth of CuO phase mainly occurs in the first CV cycle, becomes less significant in the second cycle, and is almost negligible in the following cycles.

Here, an ex situ experiment was performed by interrupting the potential sweeping process at different stages of the first CV cycle to clarify the microstructural evolution of the Cu NWs during the potential cycling process (Figure 5a). First, by sweeping the potential from +0.6 to 0 V in the reduction half-cycle (Segment I), a large oxidation current was developed and decreased to a negligible level rapidly. Some tiny CuO particles formed on the Cu NW surface as shown in the TEM image (Figure 5b). Second, by sweeping the potential from +0.6 to −0.7 V directly in the reduction half-cycle (Segment I + II), there is a clear reduction of current peak in between −0.4 to −0.6 V. A TEM analysis indicates that Cu2O becomes the major oxide phase in the electrochemically treated Cu NW (Figure 5c). The Cu2O phase is mainly ascribed to the reduction of CuO NPs formed in the previous stage because the sweeping potential covers the Cu(II) → Cu(I) reduction peak at −0.55 V. Consequently, by sweeping the potential from +0.6 to −0.7 V and back to −0.4 V (Segment I + II + III), the Cu2O/Cu NWs showed no significant change in morphology and oxide phase (Figure 5d). Although the sweeping potential covers the Cu → Cu(I) transformation at −0.5 V in the oxidation half-cycle, the oxidation peak in the CV curve is barely detectable (Figure 5a) and no gross oxide formation is observed in this stage. Finally, when the Cu NWs were treated with a complete CV cycle (Segment I + II + III + IV)

**Figure 3.** (a) Low-magnification TEM image of the Cu NW subject to static-potential oxidation treatment; (b) HRTEM image of Cu2O obtained from the red square in (a); (c) XRD patterns of the as-released and post-treated Cu NW arrays.

**Figure 4.** CV curves of the Cu NW array measured by sweeping the potential with respect to the SCE from +0.6 to −0.7 V and back to +0.6 V five times at a scan rate of 2.5 mV/s in a 0.1 M NaOH electrolyte.

**Figure 5.** (a) Potential sweeping process interrupted at different stages of the first CV cycle. Low-magnification TEM images of the CuO/Cu NW and HRTEM images of Cu oxide in red square (insets) after the sweeping process along (b) Segment I, (c) Segment I + II, (d) Segment I + II + III, and (e) Segment I + II + III + IV.
IV), they evolved into spiky Cu/Cu2O NWs (Figure 5e). It is noted that a large current peak in the potential between −0.2 and +0.3 V of the oxidation half-cycle may reflect a gross formation of Cu oxide associated with the Cu(I) → Cu(II) and Cu → Cu(II) transformations. The Cu(I) → Cu(II) transformation may involve two possible oxidation reactions, as given below.

$$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{Cu(OH)}_2 + 2\text{e}^- \quad (1)$$

$$\text{Cu}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{CuO} + \text{H}_2\text{O} + 2\text{e}^- \quad (2)$$

The above two reactions reveal that Cu2O can be oxidized to form Cu(OH)2 or CuO when the sweeping potential is in between −0.2 and 0 V.

Although Cu(OH)2 formation is the dominant reaction in the electrochemical cell,25,26 the Cu(OH)2 can further transform into CuO in a basic solution through the dehydration reaction with an intermediate of Cu(OH)42−.27 Therefore, the previously formed Cu2O extrusions would transform into CuO in this stage. When the potential was swept further to the range of +0.1 to +0.3 V, the Cu → Cu(II) transformation becomes active and favors the formation of copper hydroxide from elemental Cu.

$$\text{Cu}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{Cu(OH)}_2 + 2\text{e}^- \quad (3)$$

In this reaction, Cu atoms are first ionized into Cu2+ ions under the applied potential. The Cu2+ ions would diffuse through the previously formed Cu2O layer and react with OH− ions to sustain the growth of Cu(OH)2. Actually, the Cu2+ ionized at the inner Cu tend to out-diffuse along some fast paths such as grain boundaries and surface of the extruded Cu2O. Assuming the diffusion of Cu2+ ions as the rate-limiting step, dendritic Cu(OH)2 is expected to form because the replenishment flux of Cu2+ ions varies from site to site on the Cu2O/Cu NW. Finally, the dendritic Cu(OH)2 would transform into spiky CuO after the dehydration reaction. The morphological evolution of Cu NWs during the potential cycling is depicted in Scheme 2.

Scheme 2. Schematic Representation of the Transformation from a Cu/Cu2O Core−Shell NW to a Flowerlike Cu/Cu2O/CuO Structure

Effects of Potential Scan Rate and NaOH Concentration on the CuO/Cu NW Morphology. Although both CuO and Cu(OH)2 belong to Cu(II) species, they do exhibit distinct crystal morphology and color. The Cu(OH)2 phase appears to be blue, while the CuO looks black (Figure S1). The relative portion of these two Cu(II) species in the Cu2O/Cu NW array can be modulated by changing the scan rate of potential cycling treatment and NaOH concentration in the electrolyte. Figure 6 shows the SEM images of the Cu2O/Cu NWs treated in a 0.1 M NaOH solution after three potential cycling with different scan rates: (a) 100, (b) 50, (c) 5, and (d) 2.5 mV/s.

Figure 6. SEM images of the Cu2O/Cu NWs treated in a 0.1 M NaOH solution after three potential cycling with different scan rates: (a) 100, (b) 50, (c) 5, and (d) 2.5 mV/s.

that the specimens with high scan rates (>5 mV/s) show many needlelike crystallites among the Cu2O/Cu NWs without spiky morphology. The needlelike crystallites were identified to be the Cu(OH)2 phase according to the TEM analysis (Figure S2). As we mentioned earlier, Cu(OH)2 is a precursor for CuO formation during the potential cycling treatment. Under a high scan rate, newly formed Cu(OH)2 cannot be completely transformed into CuO due to the slow dehydration reaction. Instead, some Cu(OH)2 would grow into needlelike crystallites. Thus, the spiky CuO only grows at a slow scan rate during potential cycling. The growth kinetics of Cu(OH)2 can also be tailored by varying the NaOH concentration in the electrolyte.

Figure 7 shows the SEM images of the Cu2O/Cu NWs treated in a solution of different NaOH concentrations (0.001–2 M) after three potential cycling at a scan rate of 2.5 mV/s. It is found that the thin CuO petals transform into thick CuO plates around the Cu2O/Cu NWs with increasing NaOH concentration in the electrolyte. It is noted that no spiky CuO was developed in the Cu2O/Cu NWs prepared in

Figure 7. SEM images of the Cu2O/Cu NWs treated in an electrolyte of (a) 0.001, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.5, and (f) 2 M NaOH after three potential cycling at a scan rate of 2.5 mV/s.
0.001 M NaOH electrolyte (Figure 7a) due to the suppressed Cu(OH)₂ formation under an extremely low NaOH concentration. The enhanced growth of Cu(OH)₂ in an electrolyte of high NaOH concentration gives rise to thick Cu(OH)₂ dendrites that turn into coarse CuO plates after the dehydration reaction (Figure 7b−f). It is worth mentioning that the gross growth of Cu(OH)₂ or CuO may also cause the cavitation of Cu NWs due to the Kirkendall effect.28 The electrochemical process condition must be carefully controlled to achieve the desired morphology and structural integrity of the spiky CuₓO/Cu NWs.

**Glucose Sensing Performance of the Spiky CuₓO/Cu NW Array Electrode.** The self-supporting CuₓO/Cu NW array electrode is subject to amperometric measurement for glucose sensing performance evaluation. All the samples were prepared by three potential cycling between +0.6 and −0.7 V at a scan rate of 2.5 mV/s in a 0.1 M NaOH solution. Prior to the glucose response measurements, a CV measurement was performed on the samples in the 0.1 M NaOH electrolyte with different glucose concentrations of 0, 1, 2, and 5 mM (Figure 8a). The oxidation current in the potential range of +0.2 to +0.6 V increases with the glucose concentration. The increase of the oxidation current is mainly ascribed to the transformation of CuO to CuOOH or Cu(OH)₄⁻ on the CuO surface, as shown below.2

\[
\text{CuO} + \text{OH}^- \rightarrow \text{CuOOH} + e^- 
\]

(4)

\[
\text{CuO} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_4^- + e^- 
\]

(5)

Because the Cu(III) species, CuOOH and Cu(OH)₄⁻, tend to oxidize glucose into gluconolactone in the solution, the measured current is expected to increase with the amount of glucose molecules on the surface of the spiky CuₓO/Cu NW array electrode. The amperometric measurement was performed at a fixed potential of +0.6 V with recurrent glucose addition. Prior to the determination of glucose sensing sensitivity, an interference test has been performed to confirm the specificity of the spiky CuₓO/Cu NW array electrode to glucose. Several potential interference species were sequentially added during the amperometric measurements. The concentrations of interference species were selected based on their nominal values in human blood. The normal physiological level of glucose is about 3−7 mM in human blood. The concentrations of chloride ions, ascorbic acid (AA), dopamine (DA), and uric acid (UA) are approximately in the range of 1/10−1/20 of the blood glucose concentration.29 By adding 1 mM NaCl and 0.1 mM of UA, AA and DA into the solution sequentially, the formation of CuO to CuOOH or Cu(OH)₄⁻ on the CuO surface, as shown below.2

**Table 1. Summarized Glucose Sensing Performance of Various Copper Oxide Electrodes**

| electrode                  | self-supporting electrode | sensitivity (μA·mM⁻¹·cm⁻²) | detection limit (μM) | linear range (mM) | refs |
|----------------------------|---------------------------|-----------------------------|----------------------|--------------------|------|
| Cu@Cu₂O NS-NW coaxial NW   | no                        | 1420                        | 0.04                 | na                 | 22   |
| porous Cu₂O microcubes     | no                        | 70.8                        | 0.8                  | −0.5               | 12   |
| Cu₂O/Cu                    | yes                       | 62.29                       | 37                   | 0.05−6.75          | 30   |
| CuO NWs                    | no                        | 648.2                       | 2                    | NA                 | 31   |
| CuO NWs@GCE               | no                        | 0.49                        | 0.049                | 0.0004−2           | 32   |
| CuO nanofibers            | no                        | 431.3                       | 0.8                  | 0.006−2.5          | 33   |
| CuO NWs                   | yes                       | 1886.3                      | 0.05                 | 2−3.56             | 34   |
| candocklike CuO           | yes                       | 3252                        | 0.6                  | 0.005−2            | 35   |
| CuₓO/Cu NWs               | yes                       | 1620                        | 49                   | −4                 | 29   |
| spiky CuₓO/Cu NPs         | yes                       | 1210                        | 10                   | 0.01−7             | this work |

0.001 M NaOH electrolyte (Figure 7a) due to the suppressed Cu(OH)₂ formation under an extremely low NaOH concentration. The enhanced growth of Cu(OH)₂ in an electrolyte of high NaOH concentration gives rise to thick Cu(OH)₂ dendrites that turn into coarse CuO plates after the dehydration reaction (Figure 7b−f). It is worth mentioning that the gross growth of Cu(OH)₂ or CuO may also cause the cavitation of Cu NWs due to the Kirkendall effect.28 The electrochemical process condition must be carefully controlled to achieve the desired morphology and structural integrity of the spiky CuₓO/Cu NWs.
current responses to these interference species were barely detectable as compared with that of 1 mM glucose (Figure 8b). Moreover, we also found that the glucose detection limit for the spiky Cu₂O/Cu NW array electrode is around 10 μM (Figure 8c). By plotting the measured current density versus the added glucose concentration, we can determine the sensitivity of the Cu₂O/Cu NW array electrode to be around 1300 μA·mM⁻¹·cm⁻². If we took the sample-to-sample variation into account, the sensitivity averaged from five different samples is around 1210 ± 124 μA·mM⁻¹·cm⁻² (Figure 8d). All the samples exhibit a wide linear range of 0.01–7 mM and a short response time (<1 s).

Table 1 lists the summarized glucose sensing performance of various copper oxide electrodes reported in the literature.12,20,22,23,30–35 It is worth mentioning that the Cu₂O/Cu NW array electrode in this work may not have the highest sensitivity and the lowest detection limit compared to other works published in the literature. However, the glucose sensor developed in this study indeed shows a widest linear range together with a competitively high sensitivity. The spiky CuO/Cu NW array electrode shows no significant changes in glucose sensing performance and morphology (Figure S3) after long storage in ambient air. The results suggest that the spiky Cu₂O/Cu nanostructure prepared by the potential cycling treatment not only preserves decent glucose sensing properties but also excellent chemical stability. Moreover, we also found that the spiky Cu₂O/Cu NW array electrode to be around 1210 ± 124 μA·mM⁻¹·cm⁻² and a linear detection range of 0.01–7 mM. This study paves a way to produce chemically stable and functional nanostructured Cu oxide through a simple and fast potential cycling method.

![Figure 9](image.png)

**Figure 9.** Amperometric response to glucose addition for the as-fabricated Cu₂O/Cu NW array electrode (red circle) and the same sample after keeping in ambient air for 6 months (blue square).

electrode shows no significant changes in glucose sensing performance and morphology (Figure S3) after long storage in ambient air. The results suggest that the spiky Cu₂O/Cu nanostructure prepared by the potential cycling treatment not only preserves decent glucose sensing properties but also excellent chemical stability.

One of the intriguing findings for the spiky Cu₂O/Cu NW array is its superior chemical stability, which is likely associated with the conformal Cu₂O layer in the Cu/Cu₂O/CuO composite nanostructure. We have shown that the Cu₂O layer grown on Cu NWs with high-density nanoscale twin boundaries can maintain its structural integrity in ambient air for more than 1 year.37 The twin-modified surface enables the epitaxial growth of Cu₂O layer on nanotwinned Cu NWs (same in this study). The epitaxial Cu₂O layer will suppress the out-diffusion of Cu cations and prevent continued Cu oxidation due to lack of fast diffusion paths. Here, the spiky CuO/Cu₂O/Cu composite nanostructure was obtained by the potential cycling method. The spiky CuO phase was mainly formed in the first two CV cycles (Figure 4). No significant redox peaks and morphological changes were observed for the spiky CuO/Cu₂O/Cu nanostructure after two cycles of potential sweeping (Figure 4). It accounts for why the spiky CuO/Cu NW array electrode is so stable over a long storage period.

**EXPERIMENTAL SECTION**

**Preparation of the Cu₂O/Cu NW Array.** Copper NWs were deposited into a porous AAO template (60–80 nm in pore size) by pulse-current electrodeposition, which had a Ni layer evaporated at one side to serve as a contact electrode.38 After dissolving the AAO in a NaOH solution, the released Cu NW array evolved into a bush of spiky Cu₂O/Cu NWs through a potential cycling treatment using an electrochemical working station (CHI602E, CH Instruments). In a standard three-electrode cell, the Cu NW array was connected to the working electrode in conjunction with a Pt counter electrode and a reference SCE. The Cu oxide was grown on the Cu NWs by sweeping the working electrode potential with respect to the SCE from +0.6 to −0.7 V and back to +0.6 V repeatedly at different scan rates and NaOH concentrations in electrolyte.

**Microstructure Characterization.** X-ray diffractometry (XRD, D2 Phaser, Bruker) was used to analyze the oxide phase and crystal structure of the Cu₂O/Cu NWs. The sample was glued on a glass substrate for Bragg–Brentano XRD measurements with 2θ angle ranging from 15° to 75°. The morphology and dimension of Cu₂O/Cu NWs were examined by a field-emission SEM system (SU-8010, Hitachi). Finally, a TEM (JEM-ARM200FTH, JEOL) analysis was performed to reveal the microstructural information of Cu₂O/Cu NWs. Samples for TEM observation were prepared by separating the Cu₂O/Cu NWs from the array electrode through ultrasonic vibration in ethanol solution and dispersing the suspension onto a Mo-grid TEM holder (Formvar/Carbon 200 mesh, Ted Pella).

**Evaluation of Glucose Sensing Performance.** An amperometric measurement was performed by recording the electric current at a fixed potential with consecutive addition of desired amount of glucose solution. The electrolyte used for glucose detection evaluation is 40 mL of 0.1 M NaOH solution with magnetic stirring at a rate of 100 rpm. The electric current was recorded with consecutive glucose addition under a constant potential of +0.6 V (vs SCE) applied on the Cu₂O/Cu NW array electrode.
Cu NW array electrode. The measured current shows a stepwise rising profile with time due to the recurrent addition of glucose. The sensitivity and linear range of glucose sensing were obtained from the plot of current density versus glucose concentration. The detection limit and selectivity of glucose sensing were, respectively, determined from the amperometric response to the addition of minimum glucose amount and appropriate dosage of interference species into the solution.

**REFERENCES**

(1) Clark, L. C.; Lyons, C. Electrode systems for continuous monitoring in cardiovascular surgery. *Ann. N.Y. Acad. Sci.* 2006, 102, 29–45.

(2) Zhu, H.; Li, L.; Zhou, W.; Shao, Z.; Chen, X. Advances in non-enzymatic glucose sensors based on metal oxides. *J. Mater. Chem. B* 2016, 4, 7333–7349.

(3) Yoo, E.-H.; Lee, S.-Y. Glucose biosensors: an overview of use in clinical practice. *Sensors* 2010, 10, 4558–4576.

(4) Park, S.; Chung, T. D.; Kim, H. C. Nonenzymatic glucose detection using mesoporous platinum. *Anal. Chem.* 2003, 75, 3046–3049.

(5) Jena, B. K.; Raj, C. R. Enzyme-Free amperometric sensing of glucose by using gold nanoparticles. *Chem. Eur. J.* 2006, 12, 2702–2708.

(6) Ye, J.-S.; Chen, C.-W.; Lee, C.-L. Pd nanocube as non-enzymatic glucose sensor. *Sens. Actuators, B* 2015, 208, 569–574.

(7) Song, Y.-Y.; Zhang, D.; Gao, W.; Xia, X.-H. Nonenzymatic glucose detection by using a three-dimensionally ordered, macroporous platinum template. *Chem. Eur. J.* 2005, 11, 2177–2182.

(8) Cherevko, S.; Chung, C.-H. Gold nanowire array electrode for non-enzymatic voltammetric and amperometric glucose detection. *Sens. Actuators, B* 2009, 142, 216–223.

(9) Mu, Y.; Jia, D.; He, Y.; Miao, Y.; Wu, H.-L. Nano nickel oxide modified non-enzymatic glucose sensors with enhanced sensitivity through an electrochemical process strategy at high potential. * Biosens. Bioelectron.* 2011, 26, 2948–2952.

(10) Le, W.-Z.; Liu, Y.-Q. Preparation of nano-copper oxide modified glassy carbon electrode by a novel film plating/potential cycling method and its characterization. *Sens. Actuators, B* 2009, 141, 147–153.

(11) Zhang, X.; Wang, G.; Liu, X.; Wu, J.; Li, M.; Gu, J.; Liu, H.; Fang, B. Different CuO nanostructures: synthesis, characterization, and applications for glucose sensors. *J. Phys. Chem. C* 2008, 112, 16845–16849.

(12) Zhang, L.; Li, H.; Ni, Y.; Li, J.; Liao, K.; Zhao, G. Porous cuprous oxide microcubes for non-enzymatic amperometric hydrogen peroxide and glucose sensing. *Electrochem. Commun.* 2009, 11, 812–815.

(13) Li, X.; Yao, J.; Liu, F.; He, H.; Zhou, M.; Mao, N.; Xiao, P.; Zhang, Y. Nickel/Copper nanoparticles modified TiO₂ nanotubes for non-enzymatic glucose biosensors. *Sens. Actuators, B* 2013, 181, 501–508.

(14) Jin, Z.; Li, P.; Zheng, B.; Yuan, H.; Xiao, D. CuO–Ag₂O nanoparticles grown on a AgCuZn alloy substrate in situ for use as a highly sensitive non-enzymatic glucose sensor. *Anal. Methods* 2014, 6, 2215–2220.

(15) Özcan, L.; Şahin, Y.; Türk, H. Non-enzymatic glucose biosensor based on oxidized polypyrrole nanofiber electrode modified with cobalt (II) phthalocyanine tetrasulfonate. *Biosens. Bioelectron.* 2008, 24, 512–517.

(16) Wang, X.; Zhang, Y.; Banks, C. E.; Chen, Q.; Ji, X. Non-enzymatic amperometric glucose biosensor based on nickel hexacyanoferrate nanoparticle film modified electrodes. *Colloids Surf., B* 2010, 78, 363–366.

(17) Luo, D.; Wu, L.; Zhi, J. Fabrication of boron-doped diamond nanorod forest electrodes and their application in nonenzymatic amperometric glucose biosensing. *ACS Nano* 2009, 3, 2121–2128.

(18) Kang, X.; Mai, Z.; Zou, X.; Cai, P.; Mo, J. A sensitive nonenzymatic glucose sensor in alkaline media with a copper nanocluster/multiwall carbon nanotube-modified glassy carbon electrode. *Anal. Biochem.* 2007, 363, 143–150.

(19) Park, S.; Boo, H.; Chung, T. D. Electrochemical non-enzymatic glucose sensors. *Anal. Chim. Acta* 2006, 556, 46–57.

(20) Li, C.; Su, Y.; Zhang, S.; Lv, X.; Xia, H.; Wang, Y. An improved sensitivity nonenzymatic glucose biosensor based on a CuO modified electrode. *Biosens. Bioelectron.* 2010, 26, 903–907.

(21) Zhang, X.; Sun, S.; Lv, J.; Tang, L.; Kong, C.; Song, X.; Yang, Z. Nanoparticle-aggregated CuO nanoliposphids for high-performance non-enzymatic glucose detection. *J. Mater. Chem. A* 2014, 2, 10073–10080.

(22) Zhao, Y.; Fan, L.; Zhang, Y.; Zhao, H.; Li, X.; Li, Y.; Wen, L.; Yan, Z.; Huo, Z. Hyper-Branched Cu@CuO coaxial nanowires mesh electrode for ultra-sensitive glucose detection. *ACS Appl. Mater. Interfaces* 2015, 7, 16802–16812.

(23) Jow, J.-J.; Lee, H.-J.; Chen, H.-R.; Wu, M.-S.; Wei, T.-Y. Anodic, cathodic and cyclic voltammetric deposition of ruthenium oxides from aqueous RuCl₃ solutions. *Electrochim. Acta* 2007, 52, 2625–2633.

(24) El-Deab, M. S.; Awad, M. I.; Mohammad, A. M.; Ohsaka, T. Enhanced water electrolysis: electrocatalytic generation of oxygen gas at manganese oxide nanorods modified electrodes. *Electrochem. Commun.* 2007, 9, 2082–2087.

(25) Sillén, L. G. Stability constants of metal-ion complexes; The Chemical Society: London, 1964.

(26) Ambrose, J.; Barradas, R.; Shoesmith, D. Investigations of copper in aqueous alkaline solutions by cyclic voltammetry. *J. Electroanal. Chem/Interfacial Electrochem.* 1973, 47, 47–64.

(27) Cudennec, Y.; Lecerf, A. The transformation of Cu(OH)₂ into Cu₂O with time due to the recurrent addition of glucose. *Ann. N.Y. Acad. Sci.* 2009, 112, 16845–16849.

(28) Yun, Y.; Rioux, R. M.; Erondezn, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. Formation of hollow nanocrystals through the nanoscale Kirkendall effect. *Science* 2004, 304, 711–714.

(29) Dong, J.; Ren, L.; Zhang, Y.; Cui, X.; Hu, P.; Xu, J. Direct electrodeposition of cable-like CuO@Cu nanowires array for non-enzymatic sensing. *Talanta* 2015, 132, 719–726.
(30) Wang, L.; Fu, J.; Hou, H.; Song, Y. A facile strategy to prepare Cu$_2$O/Cu electrode as a sensitive enzyme-free glucose sensor. *Int. J. Electrochem. Sci.* 2012, 7, 12587–12600.

(31) Zhang, Y.; Liu, Y.; Su, L.; Zhang, Z.; Huo, D.; Hou, C.; Lei, Y. CuO nanowires based sensitive and selective non-enzymatic glucose detection. *Sens. Actuators, B* 2014, 191, 86–93.

(32) Zhuang, Z.; Su, X.; Yuan, H.; Sun, Q.; Xiao, D.; Choi, M. M. F. An improved sensitivity non-enzymatic glucose sensor based on a CuO nanowire modified Cu electrode. *Analyst* 2008, 133, 126–132.

(33) Wang, W.; Zhang, L.; Tong, S.; Li, X.; Song, W. Three-dimensional network films of electrospun copper oxide nanofibers for glucose determination. *Sens. Actuators, B* 2014, 191, 86–93.

(34) Ni, P.; Sun, Y.; Shi, Y.; Dai, H.; Hu, J.; Wang, Y.; Li, Z. Facile fabrication of CuO nanowire modified Cu electrode for non-enzymatic glucose detection with enhanced sensitivity. *RSC Adv.* 2014, 4, 28842–28847.

(35) Li, K.; Fan, G.; Yang, L. Novel ultrasensitive non-enzymatic glucose sensors based on controlled flower-like CuO hierarchical films. *Sens. Actuators, B* 2014, 199, 175–182.

(36) Rahman, M. M.; Ahammad, A. J. S.; Jin, J.-H.; Ahn, S. J.; Lee, J.-J. A comprehensive review of glucose biosensors based on nanostructured metal-oxides. *Sensors* 2010, 10, 4855–4886.

(37) Huang, C. L.; Weng, W. L.; Huang, Y. S.; Liao, C. N. Enhanced photolysis stability of Cu$_2$O grown on Cu nanowires with nanoscale twin boundaries. *Nanoscale* 2019, DOI: 10.1039/C9NR01406C.

(38) Chan, T.-C.; Lin, Y.-M.; Tsai, H.-W.; Wang, Z. M.; Liao, C.-N.; Chueh, Y.-L. Growth of large-scale nanotwinned Cu nanowire arrays from anodic aluminum oxide membrane by electrochemical deposition process: controllable nanotwin density and growth orientation with enhanced electrical endurance performance. *Nanoscale* 2014, 6, 7332–7338.