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One Pot Synthesis of Cuprous Oxide Nanoparticles on Multi-Walled Carbon Nanotubes for Nonenzymatic Glucose Sensors

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In this paper, a nonenzymatic sensor for the detection of glucose was developed on the basis of multi-walled carbon nanotubes decorated by Cu_2O nanoparticles (Cu_2O@MWNT) as electrocatalysts. The nanocomposites (Cu_2O@MWNT) were successfully fabricated by a facile and effective polyvinyl pyrrolidone (PVP)-assisted hydrothermal reduction method. The resulting morphology and microstructure were characterized by TEM, XRD and XPS. The results confirm the high dispersion of Cu_2O nanoparticles were successfully anchored on MWNTs. Moreover, Cu_2O@MWNT which modified glassy carbon electrode (GCE) exhibits better nonenzymatic electrocatalytic responses to glucose in alkaline media. And the resulting sensor displays fast response (within 3s), wide linear range (from 2μM to 1.35 mM), the detection limit is 0.72μM (at signal/noise = 3) and high sensitivity and selectivity. The Cu_2O@MWNT nanohybrid films represent promising sensor materials for nonenzymatic glucose sensing in electrochemical analyses and other electrocatalytic applications.

Keywords: Synthesis; Nonenzymatic sensors; Cuprous oxide (Cu_2O) nanoparticles; Electrocatalysis

1. INTRODUCTION

In recent years, the nonenzymatic sensors of metal oxide nanomaterials have been widely concerned because of its high catalytic activity, low cost, non-toxicity, and good stability. Cu_2O is a well-known p-type semiconductor with a bulk band gap of 2.2 eV [1, 2]. Cu_2O nanostructures can be potentially applied in many fields such as: solar energy conversion, [3] lithium-ion batteries, [4] gas sensing, [5] nonenzymatic biosensors [6] high-efficiency photocatalysis, [7] surface enhanced Raman spectroscopy platform, [8] etc. At present, various morphologies of Cu_2O nanoparticles including nanorods, [9] nanocubes, [10] nanospheres, [11] nanowires [12] and polyhedrons [13] have been synthesized and studied in order to achieve the desired applications. As the copper element in Cu_2O is an intermediate valence state, the variable valence state makes Cu_2O have a unique catalytic activity, so the Cu_2O nanomaterials have been developed for the electrochemical detection of electroactive substances.[14,15] So far, several works involved the determination of H_2O_2 and glucose employing Cu_2O-based nanocomposites as catalyst [16,17]. However, those sensors show a narrow range of detection and poor selection. Therefore, a new type of Cu_2O-based material should be developed to promote the sensor performance.

The reliable, accurate and fast detection of glucose is important in clinical diagnostics of blood glucose, regulation of metabolism, and biochemical analyses [18, 19]. Hence, a great deal of work has been focused on the development of highly sensitive, rapid and accurate methods to monitor blood glucose levels, especially the electrochemical techniques. There are various enzymatic and non-enzymatic glucose sensors constructed [20]. Generally, enzymatic biosensor has the inevitable instability and sensitivity to temperature, pH value and humidity. However, the non-enzymatic glucose sensors are promising because of their better stability and higher durability against external conditions and high reliability, sensitivity and selectivity, low detection limit [19, 20].

Herein, Cu_2O@MWNT composites were synthesized through a simple hydrothermal reduction method using polyvinyl pyrrolidone (PVP) as stabilizer and dispersant. The results confirm that the uniform size distribution of Cu_2O nanoparticles on the surface of MWNTs without agglomerates, moreover the Cu_2O@MWNT hybrids exhibit high electrochemical activity for constructing nonenzymatic glucose sensors.

2. EXPERIMENTAL

2.1 Synthesis of Cu_2O@MWNT composites

MWNTs with the lengths of 0.1-10 μm were purchased from Nanjing XFNano Technology Co., Ltd. (China), and were purified according to literature [21] prior to use. Ascorbic acid (AA), dopamine (DA), uric acid (UA), glucose, sodium citrate (SC), NaCl, KCl and NaH_2PO_4 were bought from Aladdin reagent Co., Ltd. (China). The solutions were prepared with ultrapure water (>18MΩ). In a typical procedure, a 100mg purified MWNTs and 50mg PVP were mixed into 200 mL deionized water in a 500 ml round bottom flask under stirring at 50 ^{o}C for 6 hr, followed by addition of 40 mg $CuCl_2$. After another 1h of stirring, the resulting mixture was transferred to a Teflon-lined stainless steel autoclave and loaded into an oven preheated to 160 ^{o}C for 1 hr. Subsequently, the reaction system was cooled to 30°C, the suspension was filtered with a Millopore filter (pore diameter, 0.45μm) and the obtained product was washed with DI water and absolute ethanol. The black precipitates were eventually collected was dried at 80 ^{o}C for 24 hr under vacuum.

2.2 Characterization

TEM images were obtained from JEM-2100 (Japan) with a 200 kV accelerating voltage. The structure of the samples was examined by X-ray powder diffractometer (XRD, Shimadzu, X-6000, Cu

Kα radiation (λ= 0.154 nm)). X-ray photo-electron spectroscopy (XPS, Kα) analyses were carried out using a Thermo Fisher X-ray photoelectron spectrometer equipped with Al radiation as the probe.

2.3 Electrochemical experiment

The electrochemical experiments were performed on a CHI 660E electrochemical workstation (CH Instrument, Shanghai) using a standard three-electrode system at room temperature. 2.0 mg Cu_2O@MWNT powder was dispersed in 0.5mL DMF. 3μL Cu_2O@MWNT suspension was cast on a well-polished glassy carbon electrode (GCE, φ= 3 mm) twice. After the film was dried, Nafion solution (1.5% in ethanol) was pipetted on the catalyst surface for protection. A platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively.

3. RESULT AND DISCUSSION

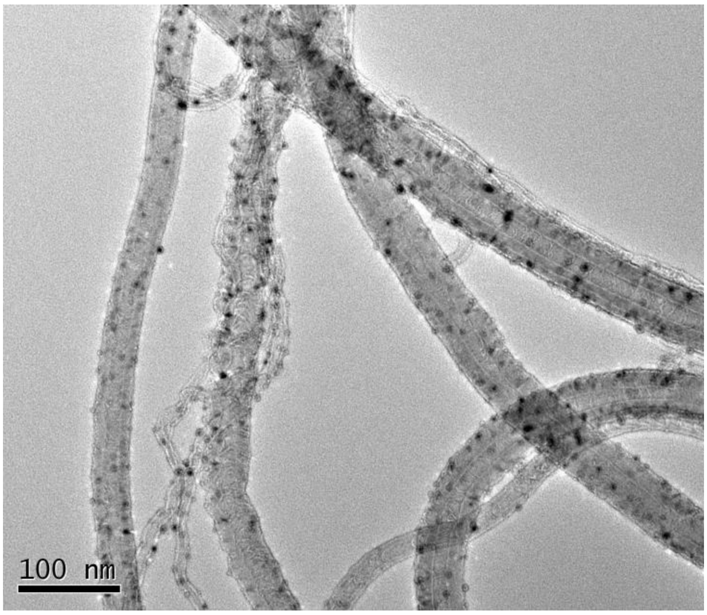


Figure 1. TEM images of as-prepared Cu_2O@MWNT composites

Figure 1 is the typical TEM image of as-prepared Cu_2O@MWNT nanocomposite. Highly dispersed Cu_2O nanoparticles were successfully anchored on the surface of MWNTs, which can provide large available surface and enhance the electrocatalytic activity. PVP used here is the reducing and stabilizing reagent to synthesize the composites. Such protuberant structure enables more electrochemically active surface area of Cu_2O to be accessed by the electrolyte, promoting the surface redox reaction and improving electrochemical activity.

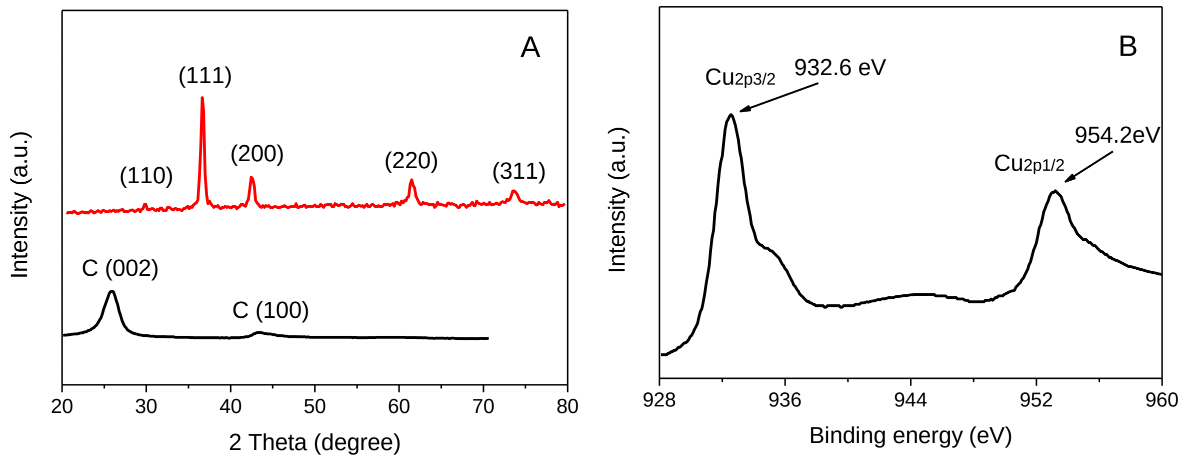
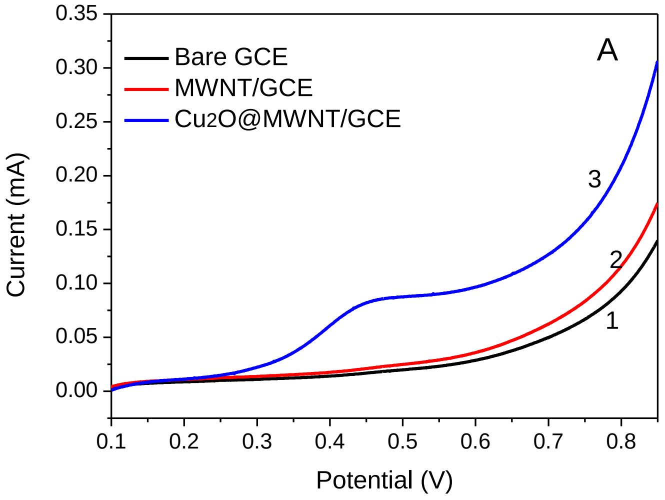


Figure 2. (A) XRD patterns of the MWNTs and Cu_2O@MWNT, (B) High-resolution XPS spectra of Cu2p.

Figure 2A shows the X-ray diffraction patterns of the MWNTs (black curve) and Cu_2O@MWNT composite (red curve). The broad diffraction peak at around 25.8° was assigned the (002) diffraction of graphite from the MWNT, The diffraction peak at around 43° was associated with the (100) plane of the hexagonal structure of carbon. The red curve shows XRD spectrum of Cu_2O@MWNT composite. Five characteristic diffraction peaks positioned at about 29.8°, 36.7°, 42.5°, 61.6°and 73.5°could be corresponding to the (110), (111), (200), (220) and (311) crystalline planes of the cubic phase Cu_2O with cubic phase (JPCDS 78–2076), respectively. In addition, no peaks of impurities are detected, which indicates that the Cu_2O nanostructures are pure and well-crystallined. To further confirm it is Cu_2O nanoparticles loaded on the MWNTs, we undertook the XPS measurement on the composites. Figure 2B presents high-resolution XPS spectra of Cu2p. It can be clearly observed that two peaks assigned to Cu2p3/2 and Cu 2p1/2 centered at binding energies (BEs) of 932.6 and 954.2 eV, respectively, A spin-energy separation of 21.6 eV was observed between the two peaks, which is in good agreement with the published data for Cu $2p_{3/2}$ and Cu $2p_{1/2}$ in Cu_2O [22-24]. This result was also consistent with XRD analysis.



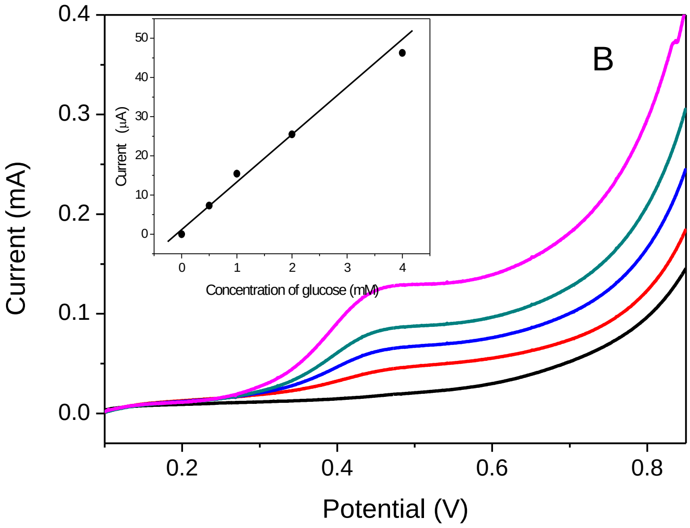


Figure 3. (A) Linear sweep voltammetry (LSV) of different modified electrodes in N_2-saturated 0.1M KOH solution containing 2mM glucose: (A1) bare GCE, (A2) MWNT modified GCE, (A3) Cu_2O@MWNT composite modified GCE. (B) LSVs of the Cu_2O@MWNT modified GCE in 0.1M KOH solution containing different concentration of glucose (0, 0.5, 1.0, 2.0, 4.0mM) at a scan rate of 50 mV/s.

To estimate the electrochemical properties and sensing application of the Cu_2O@MWNT composites in glucose detection, a non-enzymatic glucose sensor was constructed by the composites modified GCE surface. Figure 3A displays LSV of different modified electrodes in N_2-saturated 0.1M KOH solution containing 2mM glucose at 50 mV/s. From the current response, the Cu_2O@MWNT modified GCE exhibits typical current response for the catalytic oxidation of glucose (A3). However, no significant oxidation peak for glucose can be found at the MWNTs modified GCE (A2) and bare GCE (A1). Such excellent electrocatalytic activity of the Cu_2O@MWNT composites may be attributed to high catalytic active sites for the glucose oxidation provided by the Cu_2O particles and the introduction of the MWNTs play an important role in the improvement of the effective electroactive surface area and providing the conductive bridges for accelerating the electron-transfer between electrode and electrolyte.

Figure 3B shows the LSV responses obtained at the Cu_2O@MWNT modified electrode in 0.1M KOH solution containing different concentrations of glucose at 50 mV/s. Obviously, No oxidation peak appears in the absence of glucose. Notable enhancement of anodic peak current with addition of glucose from 0 to 4mM at about +0.45 V, the amperometric current response of Cu_2O@MWNT exhibits a good linear dependence on glucose concentration as shown in Figure 3B. These results demonstrate that the as-obtained composites can act as a promoter to enhance the electrochemical oxidation of glucose.

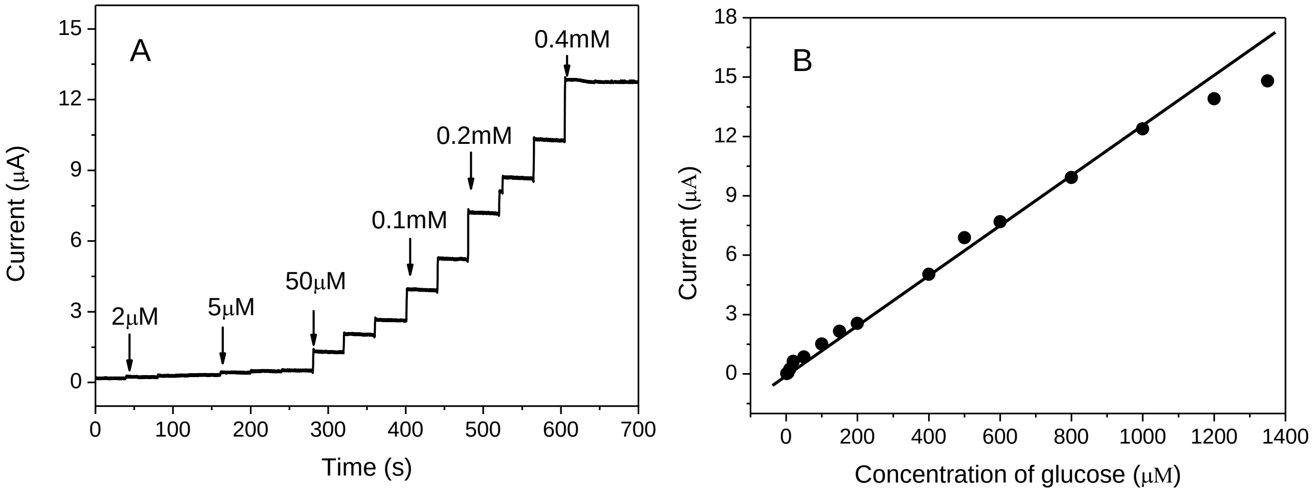


Figure 4. (A) Amperometric responses of the Cu_2O@MWNTs modified electrode after successive addition of glucose in 0.1M KOH solution at 0.5V. (B) Plot of the corresponding current vs. glucose concentration.

Electrocatalysts are usually evaluated via by measuring current response at a fixed potential after successive addition of the analyte for sensing application. Figure 4A shows the current responses at the composites modified GCE for a successive addition of glucose at optimal potential of 0.5 V in 0.1M KOH. The current responds quickly to reach the steady state current within 3 s after the addition of glucose, which suggests a fast and sensitive response to glucose oxidation. This phenomenon is attributed to the highly electroconductivity and surface area of MWNTs and large active sites of Cu_2O nanoparticles.

The corresponding i-t curve also reveals that the catalytic currents gradually increase upon successive addition of glucose. Figure 4B shows that the resulting non-enzymatic glucose sensor displays a wide linear relationship with the concentration of glucose from 2μM to 1.35 mM, and the detection limit is 0.72μM (at signal/noise = 3)

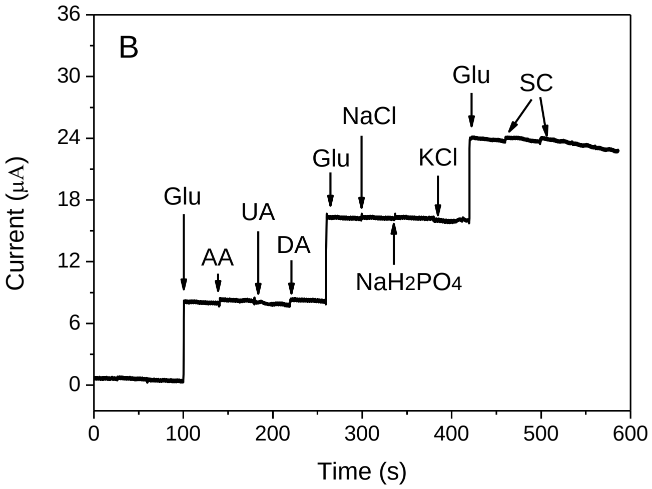


Figure 5. Interference measurement of the Cu_2O@MWNTs modified electrode in 0.1M KOH at 0.5 V, 0.5 mM glucose and 0.1 mM other interferents (ascorbic acid (AA), dopamine (DA), uric acid (UA) and sodium citrate (SC)).

It is well known that AA, DA and UA are seen as crucial small biomolecules for physiological processes in human metabolism. In addition, several electroactive compounds (such as NaCl, NaH_2PO_4 and sodium citrate) normally coexist with glucose in human blood. To estimate the selectivity of the sensor towards enzyme-free glucose detection, some possible interfering small molecules (AA, DA, UA, NaCl, KCl, NaH_2PO_4 and SC) were examined, which normally coexist with glucose in human blood serum. The well-defined glucose responses were obtained, whereas very small responses which can be neglected compared to glucose were observed for interfering species as shown in Figure 5. These results indicate high selectivity of Cu_2O@MWNT modified GCE toward glucose oxidation, which can be a promising candidate used in clinical analysis of glucose in vitro.

Although the previously reported Cu-based non-enzymatic glucose sensors exhibited excellent performance as shown in Table 1, they often suffered some disadvantages such as: cumbersome fabrication processes, easy exfoliation of active component and so on. It can be seen that glucose detection on the Cu_2O@MWNT modified GCE could achieve wider linear range and lower detection limit. These data further indicated that Cu_2O@MWNT composites exhibit a significant improvement of electrochemical performance towards glucose.

Table 1. Comparison of the analytical performance of other Cu-based non-enzymatic glucose sensors.

Modified electrode	Linear range	LOD	References
CuO NFs	6.0 μM –2.5 mM	0.8 μM	[25]
CuO NWs	15 μM M–3 mM	2.0 μM	[26]
Cu/Cu_2O HMs	0.22mM–10.89 mM	0.05 μM	[27]
Cu/Au/CNT	0.1μM–5 mM	0.03 μM	[28]
RGO wrapped Cu_2O	0.3mM–3.3 mM	3.3 μM	[29]
Cu_2O HNCs	1μM–1.7 mM	0.87μM	[30]
Cu_2O/carbon Vulcan XC-72	Up to 1mM	2.4 μM	[31]
Cu2O@MWNT	2μM – 1.35 mM	0.72μM	This work

ABBREVIATIONS:

NF: nanofiber, NW: nanowire, HMs: hollow microspheres, HNCs: hollow nanocubes

4. CONCLUSIONS

In summary, we have developed a simple and effective procedure to synthesize Cu_2O@MWNT composites by using PVP as stabilizer and dispersing agent. The as-prepared Cu_2O@MWNT exhibits excellent non-enzymatic electrocatalytic activity towards glucose oxidation in alkaline media. And the resulting sensor displays fast response (within 3s), wide linear range (from 2μM to 1.35 mM), the detection limit is 0.72μM (at signal/noise = 3) and high sensitivity and selectivity. We believe that such a simple and low-cost preparation method will provide a new way for the large-scale production of high performance composite materials for electrochemical sensing and other detection devices of glucose.

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