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Short Communication

Preparation of Copper/Carbon Sphere Composites with Excellent Electrocatalytic Activity Toward Glucose

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Cu/carbon sphere composites were synthesized by a facile and effective polymer-assisted chemical reduction method. The synthetic Cu/carbon sphere composites have a uniform surface distribution and large coverage of Cu nanoparticles onto graphene oxide, which were characterized with scanning electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction. Electro-oxidation of glucose on Cu/carbon sphere catalysts was investigated by cyclic voltammetry measurement. The composites showed good non-enzymatic electrocatalytic responses to glucose in alkaline media, and can be used for the development of enzyme-free glucose sensors.

Keywords: X-ray techniques; Composite materials; Carbon sphere

1. INTRODUCTION

Because of the importance of reliable and fast methods of monitoring the level of blood sugar for the treatment and control of diabetes as well as food industries, the development for glucose sensors with high sensitivity, high reliability, fast response, excellent selectivity, and low cost has been a subject of concern for decades [1,2]. Amperometric glucose biosensors are one such promising methodology. Most previous studies on this subject involved the use of the enzyme glucose oxidase (GODx) [3], which catalyzes the oxidation of glucose to gluconolactone. Whereas, owing to the nature of enzymes, the most common and serious problem with enzymatic glucose sensors lies in their lack of long-term stability. For instance, the activity of GODx can be easily affected by temperature, pH value, humidity, and toxic chemicals [4]. To solve this problem, many nonenzymatic glucose sensors have also been explored in the hope of improving the electrocatalytic activity and selectivity towards the oxidation of glucose, such as noble metal-based (containing Pt [5] and Au [6], and alloys-based (containing Pt, Ru, Pb, Au, and Cu [7-12]) amperometric glucose sensors.

Carbon spheres (CSs) have attracted a great deal of attention from many researchers in different areas owing to their excellent physical and chemical properties. On the other hand, surface modification and/or coating of CSs have been of considerable interest recently. Coating the CSs with metal or alloy nanoparticles, oxide nanoparticles, or semiconductor nanoparticles could improve the functionality, compatibility and reactivity of the surface, further endow the spheres with specific catalytic, magnetic, electronic, optical, or optoelectronic properties and greatly widen their utility in the fields of electronics, magnetism, optics, catalysis, and bioscience [13-15].

Cu nanoparticles (NPs) have attracted considerable attention for their applications as catalysts for oxidation of small compounds including glucose and hydrogen peroxide. In the application as electro-catalysts, the Cu NPs are required to be finely discrete states, where the size and the shape are critical parameters to be controlled. Therefore, Cu NPs have been prepared in the deposited form on various supports, such as carbon nanofibers [16], mesoporous silica [17], carbon nanotubes [18], by chemical reduction using $NaBH_4$ as reductants. To our knowledge, there are no reports concerning the fabrication of the one-dimensional Cu/carbon sphere hybrid materials.

In this letter, we employed a facile and effective in situ synthesis approach to load copper nanoparticles on the surface of carbon sphere. Carbon sphere surfaces were noncovalently functionalized with polyelectrolyte and then the polyelectrolyte coat on carbon sphere was employed as a template to deposit copper nanoparticles. The electrocatalytic activity of the composites modified electrodes towards glucose oxidation was then investigated by cyclic voltammetry (CV).

2. EXPERIMENTAL

2.1. Materials, chemicals, and synthesis

In a typical experiment, an appropriate amount of glucose (4.0 g) and H_2O (50 ml) was added into a stainless steel autoclave of 60 ml capacity, and mixed into a homogeneous aqueous glucose solution with a glass rod. The reaction furnace was maintained at 180 °C for 4 h, and then cooled to room temperature naturally. A dark precipitate was collected and washed with absolute ethanol. The obtained sample was then dried in a vacuum at 60 °C for 4 h.

Carbon sphere (30 mg), poly(sodium 4-styrenesulfonate) (PSS, M_W 70,000, 30 mg) , and DI water(200 mL) were mixed in a 500 mL three-necked flask under stirring at 90 °C for 5 h, followed by addition $CuCl_2$ (18 mg), the mixture was ultrasonicated at low energy for 1 h. $NaBH_4$ (10 mL, 1 %) was then added slowly, and the reaction mixture was stirred at room temperature for 24 h. After being cooled, the resulting hybrids were collected by centrifugation and were dried at 100 °C under vacuum to give Cu/carbon sphere composites.

2.2. Characterization

The morphology and microstructure of the composites were characterized using scanning electron microscopy (SEM, FEI Sirion200) and high-resolution transmission electron microscopy (HRTEM, Hitachi 9000). The crystallographic structures of the materials were determined by a powder X-ray diffraction system (XRD, TTR-III) equipped with Cu Kα radiation.

2.3. Electrochemical measurements

The electrochemical tests were carried out with a CHI 660C station (CH Instruments, Inc., USA). Pt wire and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. 1mg of Cu/carbon sphere composites was fully dispersed in 1mL of deionized water, the working electrodes were prepared by applying the above catalyst ink onto pre-polished glass carbon(GC) disk electrodes. All experimental solutions were deoxygenated by high-purity nitrogen for 10 min, maintained under nitrogen atmosphere during the measurements.

3. RESULTS AND DISCUSSION

The as-synthesized carbon spheres are examined with SEM. In typical SEM images (Fig. 1a), it is found that the carbon spheres with the diameter around 90 nm are obtained in large scale. The surfaces of these carbon spheres are very smooth without any cracks. The image reveals that most of the carbon spheres are in perfect spherical morphology and some of them are inclined to form chain-like aggregates. Through b shows SEM images with increasing magnifications of the Cu NPs deposited on the carbon spheres surface. Cu NPs can clearly be observed highly and uniformly decorating the surface of the carbon spheres (Fig. 1B). The SEM images show further that the Cu structure possesses a high surface roughness. A closer look reveals that Cu assemble in a very regular fashion over the carbon spheres recalling the broccoli or cauliflower-like heads.

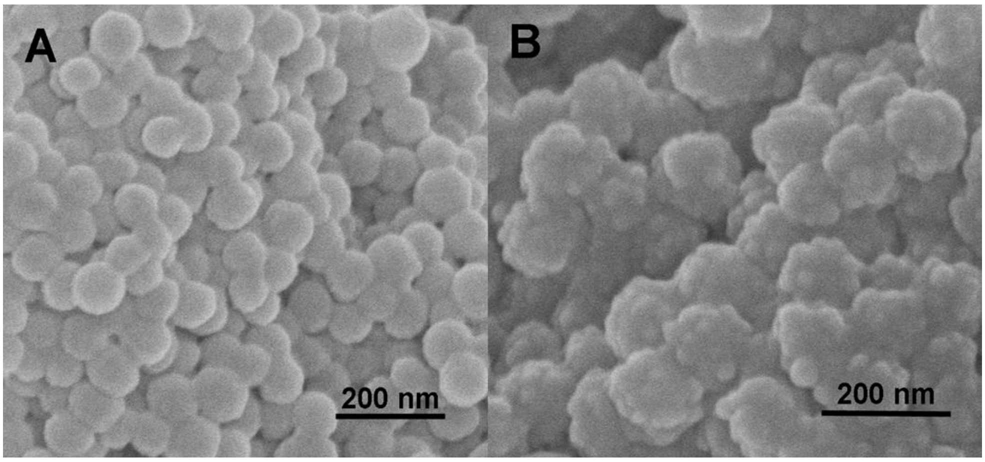

Figure 1. SEM images of (A) as-synthesized carbon spheres (B) Cu/carbon sphere composites.

The graphitization degree of the carbon spheres can be determined Raman spectra. Fig. 2(A) shows the Raman spectrum of the as-produced carbon spheres. Two significant peaks lying at about 1330 and 1590 cm^{-1} correspond to the D-band and the G-band, respectively. The D-band is explained by defects, dislocations, and lattice distortions in the carbon structures. The G-band is attributed to the ordered graphite structure. Generally, the D band to G-band intensity ratio is used to evaluate the defects of carbon materials [19, 20]. The peak intensity ($I_G/I_D \approx 1.3$) indicates that the graphitic layers in carbon spheres are not well ordered and that there are many defects in the sample.

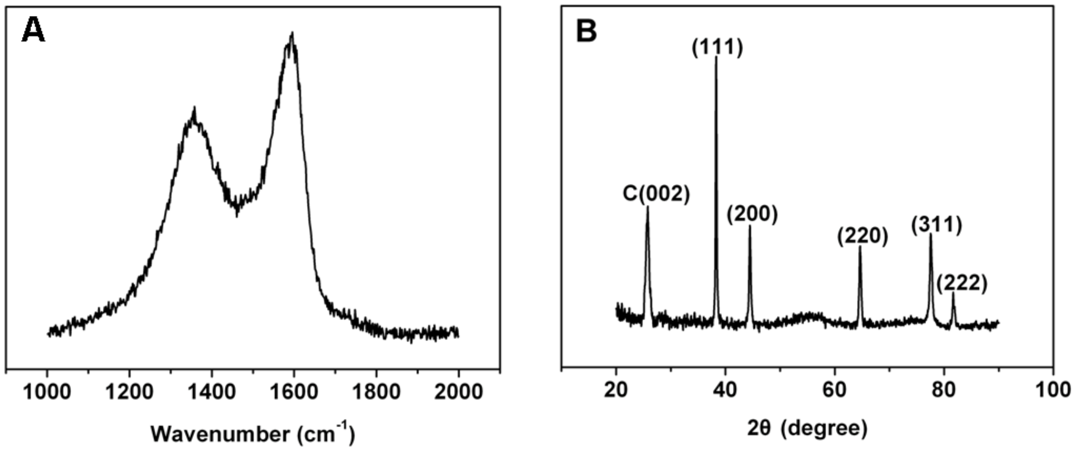

Figure 2. Raman spectra of carbon sphere and typical XRD patterns of Cu/carbon sphere composites.

The chemical structure of Cu/carbon sphere composites were characterized using a power XRD pattern (Fig. 2B). The peaks at about 26° can be assigned to the (0 0 2) crystal planes of graphite structure [21].

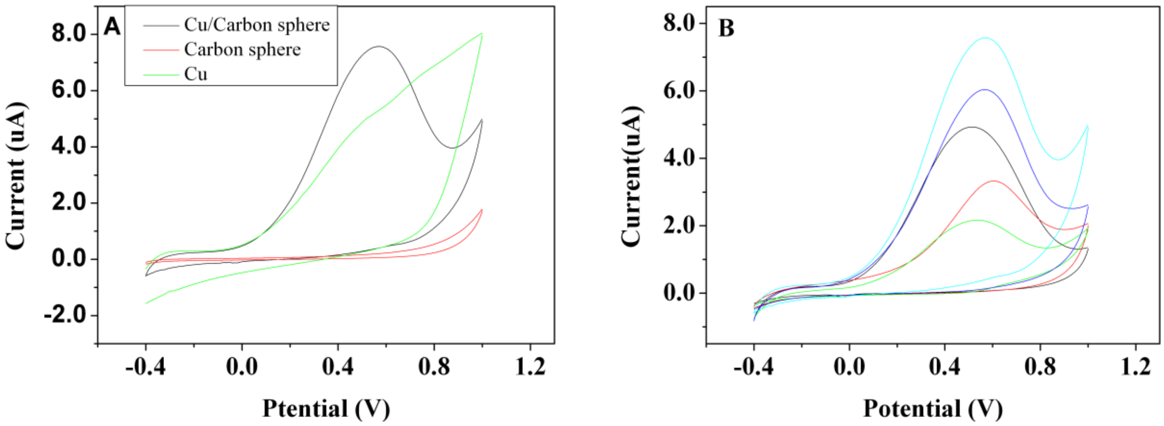

Figure 3. CVs of (A) Cu, carbon sphere and Cu/carbon sphere electrode presence of 1.0 mM glucose in 0.02 M NaOH solution (B) Cu/carbon sphere electrode in 0.02 M NaOH solution containing 0.2, 0.4, 0.6, 0.8, 1.0 mM glucose (a–e) at 50 mV s^{-1}.

The sharp peaks that are attributed to Cu nanoparticles appear. These new diffraction peaks are located at 2θ = 44.3°, 64.4°, 77.4° and 82°, which can be indexed to the (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of the face centered cubic structure of copper. These results indicate that Cu nanoparticles have been combined with carbon sphere. Besides the peaks arising from Cu, a new peak corresponding to the (1 1 1) crystal plane of cubic Cu_2O (JCPDS card no. 65-3288) appears at 2θ = 36.4◦, indicating that Cu_2O phase was formed on the surface of Cu NPs [22].

The electrocatalytic performance of the bare Cu and Cu/carbon spheres electrodes toward the oxidation of glucose was investigated by cyclic voltammetry. Fig. 3A shows the CV behaviors of the bare Cu and Cu/carbon spheres electrode in the presence of 1.0 mM glucose in 0.02 M NaOH solution recorded at 50 mV s^{-1}.

As shown in Fig. 3A, only a small current for glucose oxidation was observed at the Cu electrode. When the Cu/carbon spheres electrode was used, a substantial dramatic increased of current signal was observed. The oxidation process of glucose at the Cu/carbon spheres electrode (Fig. 3A) peaks at + 0.60 V. The above results indicate that the modification of Cu on the surface of carbon sphere significantly improved the electrocatalytic activity towards the oxidation of glucose. Cu on carbon spheres takes advantages of the electrocatalytic activity and high surface area of both Cu and carbon sphere [23]. The character of facilitated electron transfer at carbon sphere can further improve the electrocatalytic effect of the Cu/carbon spheres electrode. The CVs of the Cu/carbon spheres electrode in different concentrations of glucose were also measured, as indicated in Fig. 3B. The currents of the electrocatalytic peaks at +0.60 V increased with increasing the concentration of glucose in 0.02 M NaOH solution. Obviously, the Cu/carbon spheres electrode shows good response to various concentrations of glucose.

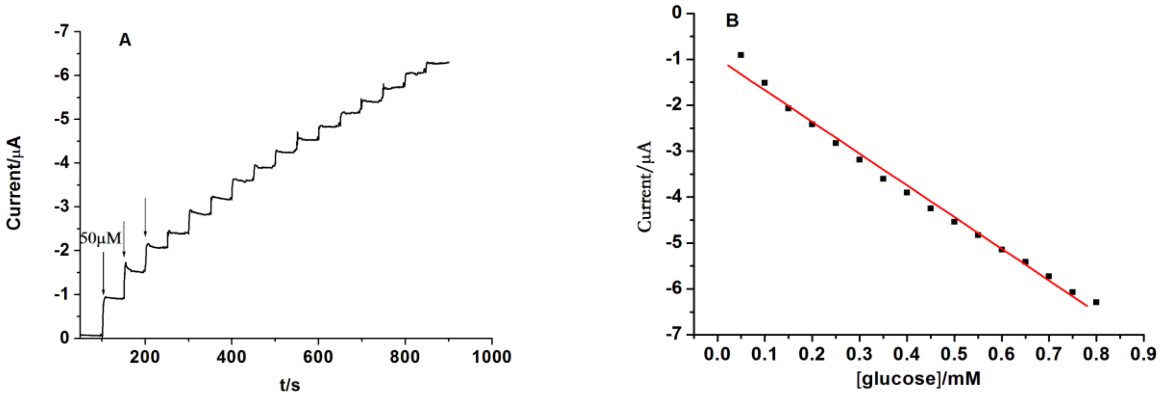

Figure 4. (A) Amperometric i-t response obtained to successive increasing of the 50 uM glucose with Cu/carbon sphere electrode in the 0.02 M NaOH solution at 0.60 V. (B)The linear relationships between the catalytic current and the glucose concentration.

Fig. 4A displays the amperometric responses of a Cu/carbon spheres modified electrode to the successive addition of glucose at an applied potential of 0.60 V under stirring. The supporting electrolyte is 0.02 M NaOH. The Cu/carbon spheres modified electrode exhibits a fast response to the addition of glucose, where a steady-state signal could be reached within 2s. The linear relationship between the current and the glucose concentration is shown in Fig. 4B. A linear response range from 50 uM to 0.8 mM (*R*=0.994), with the sensitivity of 7.32 uA/mM, can be identified there. The detection limit is calculated to be 1.9 uM. This theoretical detection limit is considerably improved comparing with those recently reported glucose sensors such as noble metals and NPs as electrodes. The above experimental results illustrate that the electrochemical sensor based on Cu/carbon spheres electrode has a high sensitivity, low detection limit, and a fast response time.

4. CONCLUSIONS

In summary, we have synthesized electrochemically active Cu/carbon sphere composites via polymer-assisted chemical reduction method. Extensive characterizations by a variety of microscopy and spectroscopic techniques revealed that the Cu-nanoparticles were well distributed on the surface of carbon sphere with uniform size. The electrochemical studies reveal that the composites modified electrodes exhibit good electrocatalytic responses to glucose in alkaline media with a number of attractive features such as high sensitivity and stability, good reproducibility and selectivity, and fast response.

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