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Short communication

Nonenzymatic glucose detection at ordered mesoporous carbon modified electrode

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ABSTRACT

This work reports on a novel nonenzymatic amperometric glucose sensor based on the ordered mesoporous carbon (OMC). Amperometric method was used to evaluate the electrocatalytic activity of the OMC modified electrode toward nonenzymatic glucose in alkaline media in presence and absence of chloride ions. The results indicated that OMC showed electrocatalytic activity for the oxidation of glucose in alkaline solution. The resulting biosensor exhibited excellent performance for glucose determination with high sensitivity of 10.81 μA/mM and a low detection limit of 0.02 mM. The OMC modified electrode is also to resistant the interference from common interfering substances such as ascorbic acid, dopamine and uric acid.

1. Introduction

The most serious problem of the enzymatic glucose sensor is their lack of stability due to the intrinsic nature of enzyme. To resolve this problem, previous studies had shown attempts where the glucose concentration can be determined without using enzymes [1–9]. Different substrates such as platinum [10,11], gold [12,13], Hg adatom modified electrode [14] were explored to develop effective nonenzymatic glucose sensors. However, poisoning by adsorbed intermediates [15], low sensitivity and poor selectivity are main drawbacks of these electrodes. The Pt–Pb alloy electrode [8] had shown good selectivity, relatively stable and large response. Despite these advantages, surface poisoning by chloride ions remained a serious problem. It has been reported that mesoporous platinum with large roughness [16] can overcome this drawback.

Carbon nanotubes (CNTs) electrode showed also reproducible sensitivity in the presence of high concentration of chloride ion [17]. Recently, there has been significant interest in the development of novel carbon materials, ordered mesoporous carbons (OMC), owing to their considerable properties, such as uniform and tailored pore structure, high specific surface area, large pore volume and chemical inertness [18,19]. Those carbon materials that, sometimes, show a similar electrochemical behavior as carbon nanotubes [20] can be used in the electrochemical determination of some molecules [20,21].

On the basis of this progress made on carbon-based electrocatalysts in nonenzymatic glucose sensing, one of the most important clues brought to our attention is that a high active surface area of the electrode materials plays a key role in the electro-oxidation of glucose [22]. It has recently been reported that, compared to CNTs, OMC exhibits remarkably strong and stable electrocatalytic response toward some compounds [23]. Despite these characteristics of OMC, to the best of our knowledge, no work has been reported on the determination of glucose at OMC modified electrode.

In this communication, we report on enhanced amperometric response to glucose and the performance of nonenzymatic glucose sensor based on the mesoporous carbon. With acceptable sensitivity and good selectivity in the presence of high concentration of chloride ion, OMC is found to be a promising enzyme -free glucose sensor.

2. Experimental

2.1. Reagents

Glucose was purchased from Beijing Chemical Reagent Co. (China). Nafion solution (5 wt.% in 12–20% water/lower aliphatic alcohols) was obtained from Aldrich. All other chemicals were of analytical reagent grade and were used as received. Double distilled water was used to prepare aqueous solutions.

2.2. Synthesis of OMC

The mesoporous SBA-15 was prepared using Pluronic P123 (nonionic triblock copolymer $EO_{20}PO_{70}EO_{20}$) as a surfactant and tetraethoxysilane as a silica source, according to the literature [24]. OMC was synthesized using SBA-15 as a template, sucrose as carbon source following the reported procedure [19].

2.3. Preparation of the modified electrodes

The glassy carbon (GC) electrode was polished before each experiment with 1, 0.3 and 0.05 μm alumina powder, respectively, rinsed

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thoroughly with doubly distilled water between each polishing step. Then it was washed successively with a solution of nitric acid + acetone (V: V = 1:1) and doubly distilled water in ultrasonic bath and dried in air. 10 mg of OMC were added to 9 ml of PBS solution (pH 7.1). After addition of 1 ml of Nafion, the mixture was sonicated for 30 min. The colloid (20 µl) was dropped on the surface of the GC electrode and this was allowed to dry at room temperature. The obtained modified electrode was denoted as OMC electrode. For comparison, the process was repeated without OMC and the electrode is then symbolized by GC/Nafion.

2.4. Electrochemical and other measurements

Electrochemical experiments were carried out using a CHI 830b Electrochemical Analyzer (CH Instruments, Shanghai Chenhua Instrument Corporation, China) in a conventional three-electrode cell. The working electrode used was glassy carbon (GC) electrode or the modified electrode. A platinum electrode was taken as the counter electrode and an Ag/AgCl (in saturated KCl solution) electrode served as the reference electrode. Small angle X-ray diffraction (XRD) patterns were obtained on an X-ray Pmax 2200 PC (Rikagu, Japan) operating at 40 kV and 40 mA and using CuKa radiation. Nitrogen adsorption and desorption isotherms were measured on ASAP2020 (Micromeritics, USA). The pore size distributions (PSD) were calculated by the BJH method. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2010 electron microscope.

3. Results and discussion

In our previous reports [21,25], OMC was characterized. From XRD patterns, three peaks that can be indexed as (100), (110), (200) diffractions are associated with p6mm hexagonal symmetry in OMC, indicating the hexagonal order of OMC. From the TEM image, the long-range ordering has been observed and in agreement with the XRD results. Also, the sample exhibited an adsorption–desorption hysteresis loop indicative of the occurrence of pores. Thus with its narrow size distribution centered at 4.5 nm, OMC is mostly mesoporous and the BET surface area was found to be 1520 $m^2\ g^{-1}$. From the physicochemical characteristics above, it is clear that the sample synthesized is a mesoporous carbon with its ordered mesostructure.

The voltammetric response of OMC electrode in the presence of 5 mM glucose was investigated using linear sweep voltammetry and the results are shown in Fig. 1. In comparison with the blank solution (curve a), it has been observed that the oxidation process starts at

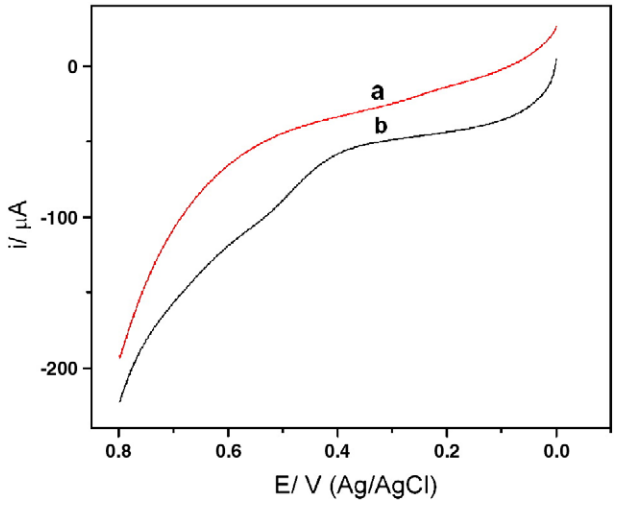

Fig. 1. Linear sweep voltammograms of OMC electrode to 0 mM glucose (a) and to 5 mM glucose in 0.1 M KOH. The scan rate was 50 mV/s.

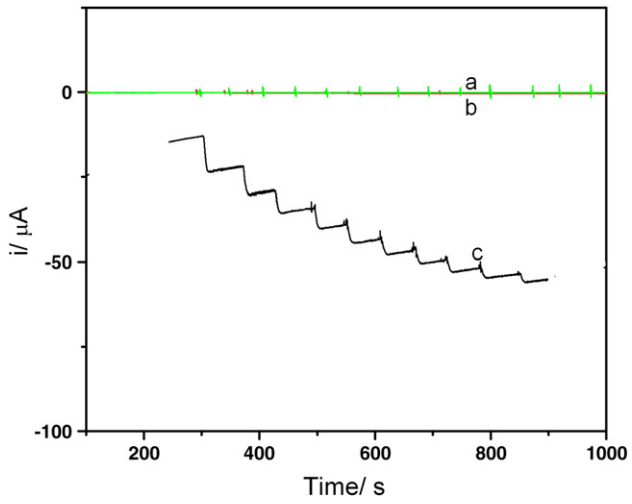

Fig. 2. Current–time response curves of GC (a) GC/Nafion (b) and OMC (c) electrodes upon successive additions of 0.5 mM glucose in 0.1 M KOH at applied potential of 0.45 V.

almost 0.4 V (curve b). It is also interesting to note that the current response remained wit the same magnitude when the solution was bubbled with nitrogen gas. It has been reported that CNTs can be used to detect glucose [17] and some properties of these carbon-based materials are sometimes improved with ordered mesoporous carbons [20,23]. This indicates that, like CNTs, OMC has electrocatalytic activity towards glucose. We think that the mesoporous structure of the OMC, especially the high surface area that can favour the oxidation of glucose, is responsible of that electrocatalytic ability.

However, it has been noted that the peak currents were not very obvious and this is maybe due to the adsorption of intermediates [15]. This phenomenon can be limited with the amperometric method where the solution is stirred [26]. Amperometry under stirred conditions was then adopted to determine glucose at OMC electrode and the results are presented in Fig. 2. Upon successive additions of 0.5 mM glucose, the GC (a), and GC/Nafion (b) electrodes are not responsive. In contrast, OMC electrode (c) responds to the changes in glucose concentration, producing steady-state signals. As it has been said above, the high active surface area of OMC and its ordered

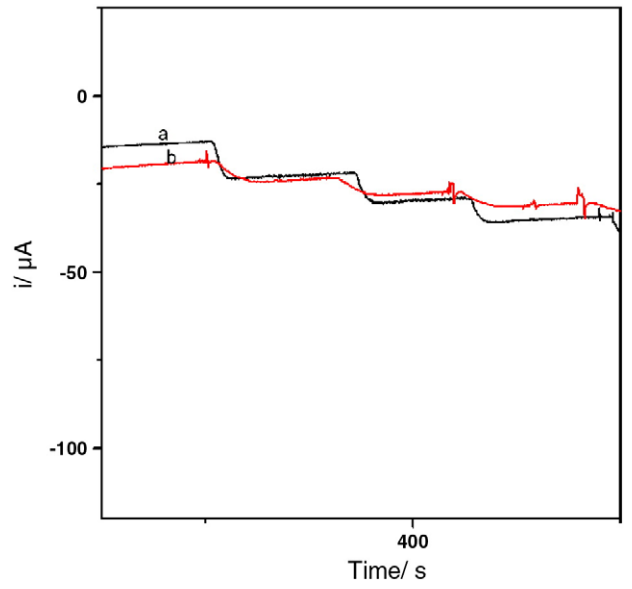

Fig. 3. Current–time response curves of OMC electrodes upon successive addition of 0.5 mM glucose in 0.1 M KOH (a) and 0.1 M KOH + 0.2 M KCl at applied potential of 0.45 V.

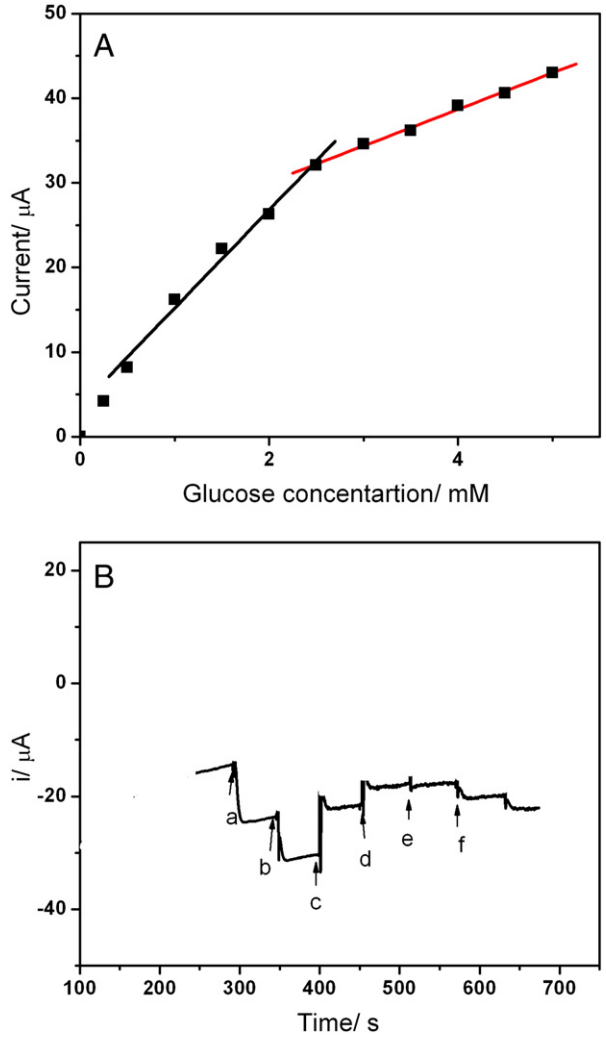

Fig. 4. (A) Dependence of the current response versus the glucose concentration at OMC electrode in KOH. Applied potential 0.45 V. (B) Current–time response curves of OMC electrode in KOH with successive addition of 0.5 mM glucose (a), 0.5 mM glucose (b), 2 mM AA (c), 2 mM DA (d), 2 mM UA (e), 0.5 mM glucose (f). Applied potential 0.45 V.

mesostructure [16,22] are the possible reasons of this high electrocatalytic activity towards glucose. It is also known that the solubilization of OMC by Nafion results in a stable and efficient sensor for the detection of some substances [27].

The poisoning of chloride ions has been investigated and the results are shown in Fig. 3. After addition of high concentration of KCl (0.2 M), the response of OMC electrode is not very affected as shown with curve a and curve b. However, the stability is a little influenced by the high concentration of chloride ions. The glucose response of the initial activity remained 78% after 190 min of stirring glucose solution containing the chloride ions whereas in the absence of these ions, it remained 83%. The electrode is a little less stable than the previously reported one [22] but it can be used with the accepted detection limit compared to the recent report [29].

The analytical performance of glucose at OMC electrode in 0.1 M KOH with the applied potential of 0.45 V is shown in Fig. 4A. There are two linear regions of glucose concentration, respectively in 0.5–2.5 mM (correlation coefficient; 0.989) and in 2.5–5 mM (correlation coefficient; 0.997). The two linear regions of glucose concentration have been also reported by Rong et al. [28]. Here this phenomenon of the two linear regions is due to the adsorption of intermediates. At the beginning, in the region 0.5–2.5 mM, the response increases rapidly with the concentration of glucose. However, although the solution is stirred, the adsorption of intermediates can occur after a certain time. Therefore, in the region 2.5–5 mM, the current increases slowly and this is due to the adsorption of intermediates.

A high sensitivity of 10.81 μA/mM and calculated detection limit of 0.02 mM ($S/N = 3$) agree with the recently reported work [29]. The biosensor showed 96% of the initial performance after 10 days, indicating an acceptable stability.

Amperometric response of the OMC electrode was examined in the presence of some electroactive interfering substances such as Ascorbic acid (AA), Dopamine (DA), and Uric acid (UA) at higher levels. Fig. 4B presents the selectivity testing results in KOH. Although AA and DA perturb the amperometry curve, no oxidation of these substances can occur at 0.45 V. It can be observed that UA has no influence on the determination of glucose. Moreover, it is interesting to note that after additions of those substances in high levels the OMC electrode still is responsive to the glucose with a small decrease in sensitivity of 5%. The selectivity is higher than that of the overoxidized polypyrrole nanofiber electrode modified with cobalt (II) phthalocyanine tetrasulfonate [29] and the carbone nanotube modified electrode [17].

4. Conclusion

Ordered mesoporous carbon showed another attractive feature in electrocatalytic applications. It can be used as a working electrode for the determination of glucose without using the enzyme with high sensitivity and good selectivity. In view of the physiological level of glucose [30] and that of the interfering agent [31], OMC electrode appears to be good enough for clinical application without enzyme. The very interesting performance of that glucose sensor is the suppression of the interference from common interfering substances such as ascorbic acid, dopamine and uric acid. Further investigation on the mechanism of the glucose oxidation at OMC electrode is in progress.

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