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In-situ synthesis of graphitic carbon nitride/iron oxide–copper composites and their application in the electrochemical detection of glucose

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ABSTRACT

A simple method was proposed for the synthesis of graphitic carbon nitride (g-C_3N_4)/iron oxide-copper nanostructures through a one-step pyrolysis of Cu_3 $[Fe(CN)_6]_2$ and melamine. The iron oxide and copper nanostructures, derived from Cu_3 $[Fe(CN)_6]_2$, were decorated onto g-C_3N_4 nanosheets, which can effectively protect the resultant graphitic carbon nitride nanosheets from restacking. The derived Fe_2O_3 and Cu nanostructures greatly enhance the electro-catalytic property of as-prepared composites. Three components including g-C_3N_4 nanosheets, Fe_2O_3 and Cu cooperatively enhance the electrochemical performance of non-enzymatic glucose detection. Modified electrodes based on g-C_3N_4/Fe_2O_3-Cu composites could detect glucose in the range of 0.6 μM–2.0 mM with a detection limit of 0.3 μM. The as-fabricated modified electrodes also demonstrated good stability and anti-interference performance.

1. Introduction

Graphitic carbon nitride (g-C_3N_4), as a two-dimensional material, has attracted a great deal of attention due to its excellent physical and chemical properties such as unique optoelectronic characteristics, thermal and chemical stability [1–3]. Owing to its special visible-light absorption property, g-C_3N_4 has been widely applied in the field of catalysis [1–5]. However, the pristine g-C_3N_4 presents low specific surface area, poor conductivity and chemical inertness, which restricts applications of g-C_3N_4 in many fields [3]. Therefore, a growing number of research works have been dedicated to functionalization of g-C_3N_4 including texture and property modification. The texture modification is usually carried out by using liquid solvent to exfoliate pristine g-C_3N_4 into thin layers. However, this kind of liquid solvent-exfoliation strategy requires appropriate solvents and long sonication time [6]. Apart from this, two kinds of methods including chemical oxidation and protonation have been also proposed to functionalize the pristine g-C_3N_4 [7–9]. They both can achieve good-quality and effective post-functionalization of g-C_3N_4. However, the big problem is that the yield of the final product is not high. In order to achieve effective and efficient functionalization of g-C_3N_4, several in-situ methods have been proposed to prepare functionalized g-C_3N_4 such as element doping, copolymerization and incorporation of metal species into g-C_3N_4 matrix [3,10,11]. In addition, in-situ method is also an efficient and effective approach for the synthesis of g-C_3N_4 composites. The modified g-C_3N_4 and its composites, with improved functionality, have broaden their applications in fields of electronics, bio-imaging, energy storage and sensors [12–17].

Diabetes mellitus has been regarded as one of most serious diseases in the contemporary world. In order to reduce complications, early diagnosis and good self-management is very crucial for diabetics to control their blood glucose level in the normal range. There have been many approaches to glucose detection including colorimetric, fluorescent, thermometric, photo-electrochemical, electrochemiluminescent and electrochemical methods [18–25]. Among these methods, electrochemical methods have been widely used for glucose detection. There have been several electrochemical methods for quantitative determination of glucose, including amperometry, electrochemical impedance spectroscopy, pulse-voltammetry and potentiometry [26–31]. Amperometric

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enzymatic method has been commonly used and regarded as a simple and efficient way to achieve glucose detection with good selectivity and high sensitivity. However, due to the involvement of enzymes, the accuracy and stability of enzymatic methods can easily be affected by some environmental conditions such as temperature, pH value, humidity, and toxic chemicals [32]. Therefore, it is not reliable enough to use enzymatic assay to detect glucose in harsh operational conditions. The non-enzymatic methods are preferred for use, compared with other methods, because of remarkable sensitivity, stability and fast detection speed [33]. However, non-enzymatic methods usually suffer from weak selectivity. Therefore, it would be of great significance for non-enzymatic glucose detection to achieve good selectivity. Electrode materials can play a key role in the detection of glucose. Various nanomaterials have been developed as electrode materials for non-enzymatic detection of glucose, especially some enzyme mimicking materials like transition metal oxides. Iron oxide has been known for its peroxidase-like activity. The redox couple of Fe^{3+}/Fe^{2+} can facilitate the final heterogeneous chemical oxidation or reduction of target substrates [34]. It is also worth to note that g-C_3N_4 has also proved to possess intrinsic peroxidase-like activity [35]. In addition, various metallic nanostructures have been developed and used as electrode materials for the detection of glucose because of their good electro-catalytic properties [26,36,37]. Among these metallic nanostructures, copper nanostructures have been widely used for the electro-catalytic oxidation of glucose [26,38–40]. However, the sole use of copper nanostructures is difficult to achieve good stability for electroanalysis due to their easy oxidization and aggregation in air and solution [41]. The combination of copper nanostructures with other nanomaterials can effectively enhance the electrochemical performance of non-enzymatic glucose assay, due to the increased electro-catalytic active area and the promoted electron transfer for glucose oxidation [42,43]. Furthermore, copper nanoparticles functionalized with capping molecules, or organic or inorganic coatings, can prevent the dissolution of the copper oxide and increase the stability of the electrode [44,45]. g-C_3N_4 can be a good material and frequently used as the support with other metal species to form heterojunctions. It can be ascribed to the surface uncondensed N-containing functional groups that can provide reducing and stabilizing sites for metal nanocrystals and their precursors [3,46].

In this work, graphitic carbon nitride/copper-iron oxide nanostructures were prepared through a simple pyrolysis of $Cu_3[Fe(CN)_6]_2$ and melamine. The copper and iron oxide nanostructures were decorated onto the surface of thin layers of g-C_3N_4. Three components including Cu, Fe_2O_3 and g-C_3N_4 show a synergistic effect on achieving cooperatively enhanced electro-catalytic performance towards oxidation of glucose. The electrodes modified by g-C_3N_4/Fe_2O_3-Cu composites could detect glucose in the range of 0.6 μM–2.0 mM with a detection limit of 0.3 μM. The electrode based on g-C_3N_4/Fe_2O_3-Cu composites also demonstrated good stability and anti-interference performance for glucose detection.

2. Experimental section

2.1. Materials synthesis

Typically, $Cu_3[Fe(CN)_6]_2$ was synthesized based on a previous report [47], mixing 0.03 M $CuCl_2$ with 0.02 M $K_3[Fe(CN)_6]$. The as-prepared solution was stored at room temperature and aged for one week. The precipitate was further collected by centrifugation and washed several times with absolute ethanol and de-ionised water. The resultant $Cu_3[Fe(CN)_6]_2$ was then vacuum dried at temperature of 60 °C. For synthesis of graphitic carbon nitride, melamine was treated with HCl solution before it is used for preparation of graphitic carbon nitride. Two grams of HCl-treated melamine and 1 g $Cu_3[Fe(CN)_6]_2$ were firstly ground and then added into 50 mL absolute ethanol, followed by stirring for 2 h. The mixture was further heated in an electric oven at a temperature of 60 °C to evaporating ethanol. The resultant solid was then ground and transferred to a crucible, followed by pyrolysis in a tube furnace at a temperature of 550 °C for 4 h. The pyrolysis was under the atmosphere of nitrogen, with the heating and cooling rate of 2 °C/min. The as-synthesized product was firstly grounded, and then washed several times with absolute ethanol and de-ionised water. The product was collected by centrifugation and vacuum dried at a temperature of 60 °C. The g-C_3N_4/Fe_2O_3-Cu composites were finally obtained for fabricating electrodes in the following experiment.

2.2. Materials characterization

The morphologies of the g-C_3N_4/Fe_2O_3-Cu composites were characterized by scanning electron microscopy (Zeiss Supra 55 VP field emission scanning electron microscope), transmission electron microscopy (TEM: Tecnai-12, accelerating voltage: 120 kV) and high resolution transmission electron microscopy (HRTEM: Tecnai-G2 F30 S-Twin, accelerating voltage: 300 kV). The Brunauer-Emmett-Teller (BET) surface area was obtained by nitrogen adsorption/desorption isotherm measurements at 77 K on a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2020 system, and the corresponding pore diameter distributions were calculated using the BJH (Barrett–Joyner–Halenda) method. The phase information of the samples was measured by a BRUKER D8 Discovery X-ray diffractometer with Cu/Kα radiation (1.5406 Å). The X-ray photoelectron spectroscopy (XPS) analysis was conducted on an EASY ESCA spectrometer (VG ESCA LAB MKII).

2.3. Electrochemical measurements

The GCEs based on g-C_3N_4/Fe_2O_3-Cu composites were used as working electrode with a conventional three-electrode system. Platinum foil ($1 \times 1\ cm^2$, 0.5 mm) was employed as a counter electrode and a saturated calomel electrode was used as the reference electrode. Cyclic voltammetry and amperometry were carried out with the three-electrode system using a CHI 660C electrochemical workstation. Cyclic voltammograms were measured in the voltage range of −0.2-0.7 V at a scan rate of 100 mV s^{-1}. The amperometric curves were examined at the applied potential of 0.5 V under gently stirring.

3. Results and discussion

3.1. Morphology and composition analysis of the composites

The morphology and microstructure of g-C_3N_4/Fe_2O_3-Cu composites were studied by SEM, TEM and HRTEM analysis. The results are shown in Fig. 1. As shown in Fig. 1 (A–B), Fe_2O_3 and Cu nanostructures are randomly distributed onto g-C_3N_4 nanosheets. The element composition of the resultant composites were characterized by EDS spectrum. As can be seen in Fig. 1(C), the EDS spectrum indicates that there are six elements in as-prepared composites including C, K, N, O, Cu and Fe. The TEM images in Fig. 1(D–E) confirm the as-prepared composites with a porous structure, and Fe_2O_3 and Cu nanostructures are randomly dispersed on thin-layered g-C_3N_4. The HRTEM image of the as-prepared composites is shown in Fig. 1(F). From Fig. 1(F), The clear lattice fringes demonstrate two d-spacings of 0.21 and 0.27 nm, which corresponds to the (111) facet of Cu(0) and the (104) facet of the Fe_2O_3. It can further confirm the formation of Fe_2O_3 and copper