



The synthesis of carbon/cerium oxide composites clusters with the assistance of the glucaminium-based surfactant and their electrochemical performance in the glucose monitoring



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ABSTRACT

The carbon/cerium oxide (CeO_2) composites clusters were prepared by a facile solvothermal method with the assistance of a glucaminium-based surfactant (*N*-decyl-*N*-methyl-*D*-glucaminium chloride). The CeO_2 has been regarded as an efficient artificial enzyme. The carbon, derived from the glucose-based surfactant, can effectively improve the stability and property of the CeO_2 , and provide surface defects. The C/CeO_2 composites present good electro-catalytic activity towards glucose oxidation. The resultant composites were further used to fabricate modified electrode for the non-enzymatic glucose detection. The electrode, modified by the C/CeO_2 composites, can detect glucose in the range of 2.0 μM –1.8 mM with a detection limit of 0.8 μM . The as-fabricated electrodes also demonstrate good stability and anti-interference performance. The C/CeO_2 composites have great potential in electrochemical sensors.

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1. Introduction

Cerium oxide has been widely applied in the field of catalysis [1], fuel cells [2], supercapacitors, biomedicine [3] and sensors [4,5]. Cerium oxide, exhibits good catalytic property, enzyme mimetic property and oxygen storage capacity property. These properties are originated from its two valence states (Ce^{3+} and Ce^{4+}). However, the above-mentioned properties of CeO_2 have great relationship with the structure and morphology of CeO_2 . Therefore, the design and synthesis of CeO_2 plays a key role in broadening its applications in different fields. There have been some approaches to prepare CeO_2 , such as hydrothermal synthesis [6], precipitation [7], combustion [8], sol-gel [9,10] and electrochemical methods [11,12]. Compared with the above-mentioned methods, solvothermal method can be used for rational controlling the synthesis of CeO_2 with the assistance of surfactants.

In the process of solvothermal treatment, surfactant plays a crucial role in controlling the morphologies and sizes of CeO_2 . There have been some studies on the synthesis of CeO_2 with different morphologies in the presence of surfactants [13–17]. It can be concluded that the CeO_2 , with different morphologies, can be

prepared in the assistance of surfactants. Furthermore, the properties of the as-prepared CeO_2 have a great relationship with the surfactants that are used in the solvothermal synthesis. The glucose-based surfactants have been rarely used to control morphologies of CeO_2 . Glucose-based surfactants have rich oxygen-containing functional groups. These groups can provide a lot of anchoring sites for metal ions. These metal ions can firstly interact with these functional groups, followed by a solvothermal treatment. Metal oxides, with different shapes and morphologies, can be finally prepared. The enzyme-mimicking activity enables CeO_2 to broaden its applications in the field of sensors. The enzyme-mimicking property can be originated from the auto-regenerative cycle of $\text{Ce}^{3+}/\text{Ce}^{4+}$ and oxygen vacancies on the surface of CeO_2 [18]. There have been some sensors based on the CeO_2 , such as humidity sensors [19], gas sensors [5,20] and biosensors [21–24]. With the improvement of the living standard and the change of the dietetic habit of people, diabetes mellitus has been one of the most serious diseases in the world. During the past decades, a significant amount of scientific efforts had been devoted to developing faster and more accurate methods for detecting glucose. There have been several reports about the CeO_2 in applications of glucose detection [21,23–32]. However, these studies focus on the colorimetric and enzymatic detection of glucose. The non-enzymatic detection of glucose is regarded as an important research part of glucose sensors. There is rare study on the application of CeO_2 in the non-

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enzymatic detection of glucose. Owing to the intrinsic enzyme-mimicking property, CeO₂ can be as a good electrocatalyst in the electro-oxidation of glucose.

In this paper, a glucaminium-based surfactant (*N*-decyl-*N*-methyl-*D*-glucaminium chloride) was used for the surfactant-assisted synthesis of the C/CeO₂ composites. The glucaminium-based surfactant, with adjacent hydroxyl groups and quaternary ammonium, are efficient in controlling the synthesis of C/CeO₂ clusters. The as-prepared CeO₂ clusters were further used to fabricate modified electrodes for non-enzymatic detecting glucose. Owing to the excellent electro-catalytic property of CeO₂, the modified electrode based on the C/CeO₂ clusters could detect glucose in the wide range of 2.0 μM–1.8 mM. The detection limit was 0.8 μM.

2. Experimental section

2.1. Materials and apparatus

Cerium nitrate (Ce(NO₃)₃·6H₂O) was analytical reagent grade and used for precursor of CeO₂. Chitosan (CHT, M.W. 100,000–300,000, deacetylation degree ≥95%) were purchased from Sigma-Aldrich Chemical Reagent Company (Shanghai, China). Absolute ethanol serving as solvent was AR grade. All the other reagents were of analytical reagent grade, and used without further purification. Double distilled water was used throughout in this experiment.

Electrochemical experiments were performed on Electrochemical analyzer CHI 660a (CH Instrumental Co. USA) with a three-electrode system. A glassy carbon electrode [GCE, 3 mm diameter] and the electrode modified by the resultant CeO₂ composites serves as the working electrode, a saturated calomel electrode (with 2.0 mol/L KNO₃ salt bridge) as the reference electrode and platinum wire as the counter electrode, respectively. Powder X-ray diffraction (XRD) studies of the C/CeO₂ clusters were recorded on a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu/Kα radiation (1.5406 Å). Scanning electron microscope (SEM) measurements were conducted on a Zeiss Supra 55 VP field emission scanning electron microscope equipped with an energy dispersive spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) technology was used to study the bonding states of the elements on an EASY ESCA spectrometer (VG ESCA LAB MKII). All experiments were carried out in KOH (0.02 M) at room temperature (25 °C).

2.2. Synthesis of the C/CeO₂ composites

The C/CeO₂ composites were synthesized via a solvothermal method with the assistance of a glucaminium-based surfactant. The glucaminium-based surfactant (*N*-decyl-*N*-methyl-*D*-glucaminium chloride) was prepared according to the previous report [33]. *N*-decyl-*N*-methyl-*D*-glucamine was synthesized by combining two moles of *N*-methyl-*D*-glucamine with one mole of 1-bromodecane and 0.5 mol of sodium carbonate in 150 mL methanol. *N*-decyl-*N*-methyl-*D*-glucamine bromide was prepared using one mole of *N*-decyl-*N*-methyl-*D*-glucamine and one mole of 1-bromodecane. *N*-decyl-*N*-methyl-*D*-glucaminium bromide further reacted with hydrochloric acid to prepare *N*-decyl-*N*-methyl-*D*-glucaminium chloride. The nuclear magnetic resonance (NMR) analysis of the as-prepared *N*-decyl-*N*-methyl-*D*-glucaminium chloride was provided in the [Supplementary Material](#).

Three millimoles of Ce(NO₃)₃·6H₂O were added into the solution that mixed with 15 mL absolute ethanol and 15 mL di-stilled water and stirred for 1 h. 0.3 mmol as-prepared surfactant (*N*-decyl-*N*-methyl-*D*-glucaminium chloride) was then added into the above mixed solution and stirred for 1 h. The as-obtained mixed

solution was then transferred to autoclave and put in the oven at the temperature of 140 °C for 24 h. After the solvothermal treatment, the as-obtained precipitate was collected by centrifugation, followed by washing with absolute ethanol and deionized water several times. The as-obtained product was then vacuum dried at temperature of 60 °C. Finally, the product was collected and ready for the following experiments.

2.3. Fabrication modified electrode and electrochemical measurements

Firstly, the glassy carbon electrodes (GCEs) were respectively polished with 0.05, 0.3 and 1 μm α-alumina powders. They were rinsed thoroughly with deionized water after each polishing step. They were then successively sonicated in 1:1 nitric acid, acetone and deionized water. Finally, these GCEs were dried at room temperature.

The C/CeO₂ composites were attached onto the GCE surface via using the biopolymer chitosan (CHT) as an immobilization matrix. 3 mg of the C/CeO₂ composites were suspended in 10 mL CHT (0.3 wt % prepared in 1% (v/v) acetic acid). 10 μL of the as-obtained suspension was dropped onto the electrode surface and allowed to vacuum dry in room temperature.

The electrochemical measurement was carried out with a convention three-electrode system. The C/CeO₂ clusters modified electrode as a working electrode, the platinum plate counter electrode and the saturated calomel (with 2.0 mol L⁻¹ KNO₃ salt bridge) reference electrode (SCE) were immersed in 50 mL of 0.02 mol L⁻¹ KOH solution containing glucose which was stirred by a magnetic stirrer. Cyclic voltammetry (CV) and amperometry were carried out with a three-electrode system using an electrochemical workstation in 0.02 mol L⁻¹ KOH solution. The measurements of cyclic voltammetry were performed in a potential range from -0.1 to 0.8 V at the scan rate of 100 mV s⁻¹. The amperometry was performed at the applied potential of 0.50 V.

3. Results and discussion

3.1. Morphology, structure and composition analysis

The phase information of the obtained sample was analyzed by the XRD. The result is presented in Fig. 1. As shown in Fig. 1(A), the XRD pattern of the as-synthesized sample shows sharp diffraction peaks at around 28.588, 33.129, 47.555, 56.429, 59.181, 69.527, 76.829 and 79.210, which can correspond to the crystal planes of (111), (200), (220), (311), (222), (400), (331) and (420) of CeO₂ (JCPDS 65-5923). The EDS spectrum of the sample is shown in Fig. 1(B). As shown in Fig. 1(B), there are three main elements in the C/CeO₂ composites. The morphology of the as-obtained C/CeO₂ composites was measured by the SEM and TEM techniques. The results are displayed in Fig. 1(C–D). As can be seen in Fig. 1(C–D), the C/CeO₂ composites demonstrate cluster-shape architecture. The nanostructured CeO₂ particles have been aggregated as clusters. The mechanism of formation of C/CeO₂ clusters, in the presence of the glucaminium-based surfactant, can be explained as follows: In the process of solvothermal treatment, the hydroxyls in *N*-decyl-*N*-methyl-*D*-glucaminium chloride can be as good sites for absorbing Ce³⁺ ions. After solvothermal treatment, there would be still some residual hydroxyls in the surface of the as-obtained CeO₂ nanoparticles. According to the previous report [34], these as-obtained CeO₂ nanoparticles were then aggregated because of the attraction from the elimination of surface hydroxyls on the adjacent particles via a condensation reaction dehydration between two surfaces, as follows: Ce–OH + HO–Ce=Ce–O–Ce + H₂O.

XPS technology was further used for the analysis of the

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