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In situ synthesis of ceria nanoparticles in the ordered mesoporous carbon as a novel electrochemical sensor for the determination of hydrazine

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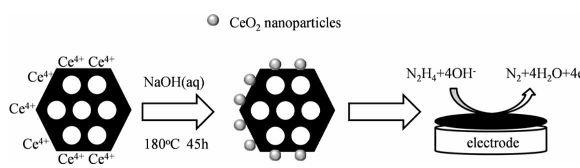
HIGHLIGHTS

- CeO_2–OMC composites were prepared via a hydrothermal method.
- CeO_2–OMC had electrocatalytic ability to oxidation of hydrazine.
- The sensor had high sensitivity, excellent stability and reproducibility.
- The sensor was successfully employed to detect hydrazine in real water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel ceria (CeO_2)–ordered mesoporous carbon (OMC) modified electrode for the sensitive amperometric determination of hydrazine was reported. CeO_2–OMC composites were synthesized via a hydrothermal method at a relatively low temperature (180 °C) and characterized by scanning electron microscopy (SEM), transmission electron microcopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The CeO_2–OMC modified glassy carbon electrode was characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) and indicated good electrocatalytic effect to the oxidation of hydrazine. Under the optimized conditions, the present sensor could be used to measure hydrazine in wide linear range from 40 nM to 192 μM (R^2 = 0.999) with a low detection limit of 12 nM (S/N = 3). Additionally, the sensor has been successfully applied to detect hydrazine in real water samples and the recoveries were between 98.2% and 105.6%. Eventually, the sensor exhibited an excellent stability and reproducibility as a promising method for determination of hydrazine.

1. Introduction

Ordered mesoporous carbon (OMC) is a kind of 3-D nanostructured porous materials which has attracted enormous interest since it was first synthesized by Ryoo et al. [1]. Compared to multiwall carbon nanotubes [2] and graphene [3], OMC has better electrocatalytic and electrochemical properties because of its unique structure such as ordered pore structure, well-defined pore size, high specific surface area and excellent conductivity. Due to these advantages, it could be widely used in energy storage, catalysis, batteries, supercapacitor and sensors [4–8]. Moreover, many metal and metallic oxides like Au [9], Ag [10], Pt [11], CuO [12], MnO_2 [13], NiO [14] was embedded into the surface and pores of OMC, which improved the specificity catalysis of OMC and extended the applications. Ceria (CeO_2), as a low-cost and efficiently catalytic Lanthanide rare earth oxide, was applied widely

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in fuel cell, catalyst and batteries [15–18]. A few sensors based on CeO_2 nanoparticles have been reported in recent years [19–22]. However, the CeO_2 nanoparticles often aggregate and easily break off from the electrode surface [22], resulting in weakening the electrocatalytic ability and stability of the electrodes. What's more, CeO_2 has poor conductivity, which also limits its application in electrochemistry. To solve these problems, OMC can be used as a substrate to disperse and immobilize CeO_2 due to its high surface area and excellent electrical conductivity. The CeO_2–OMC composites are expected to be a potential candidate as electrode material owing to the combination of the catalytic properties of CeO_2 and the fast electron transfer ability of OMC.

Hydrazine (N_2H_4) is an important chemical compound which has been widely used in chemical industry, fuel cell, rocket fuel, agriculture [23–25] attributed to its strong reducibility, strong alkalinity and hygroscopicity. However, hydrazine is harmful to the environment and human health as a kind of highly toxic material as well. It was reported that hydrazine could cause some diseases such as headache, liver and kidney damage, even DNA damage [26,27]. Hence, it is essential to provide a reliable and sensitive method for rapid detection of hydrazine. Up to date, flow injection analysis (FIA) [28], ion chromatography [29], spectrophotometry [30,31] and chemiluminescence (CL) [32,33] have been reported for the determination of hydrazine. However, these methods are complicated, laborious and unable to fulfill the real-time determination. By comparison, chemical modified electrodes (CMEs) can play as an important role to detect hydrazine rapidly based on their easy, economical, and labor-free operation. Many CMEs have been reported such as Au–SH–SiO_2@Cu–MOF [34], CoHCF–MWCNT/GE [35], CeHCF–OMC/GCE [36] and ZnO–MWCNT/GCE [37] and some of them were used for the determination of hydrazine. The previous work had some limitations in cost, linear range, stability, sensitivity and other characteristics. Thus, it is necessary to develop a novel and low-cost material for hydrazine determination.

In this work, CeO_2–OMC composites were prepared at a relatively low temperature (180 °C) via a hydrothermal method, which could avoid damaging the structure of OMC. Simultaneously, the CeO_2–OMC modified electrode was also prepared to serve as an amperometric sensor of hydrazine for the first time. The CeO_2 nanoparticles were well dispersed in OMC, and the hybrid composites increased the electron transfer rate and showed excellent electrocatalytic effect to the oxidation of hydrazine and showed excellent stability and reproducibility.

2. Experimental

2.1. Materials

Ordered mesoporous carbon (OMC, 3–5 nm of pore size) was purchased from XF NANO (Nanjing, China). Nafion solution (5 wt% in 15–20% water/lower aliphatic alcohols) was obtained from Alfa Asear. Ceric ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$), hydrous hydrazine ($N_2H_4 \cdot H_2O$, 80%) and sodium hydroxide (NaOH) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). The phosphate buffer solution (PBS, 0.1 M) was prepared by Na_2HPO_4 and NaH_2PO_4 and the pH value was adjusted by H_3PO_4 or NaOH. All the chemicals were at least analytical grade and used without further treatment.

Pure water was prepared from a UP water purification system (>18 MΩ cm). All the solutions were prepared daily and purged with nitrogen.

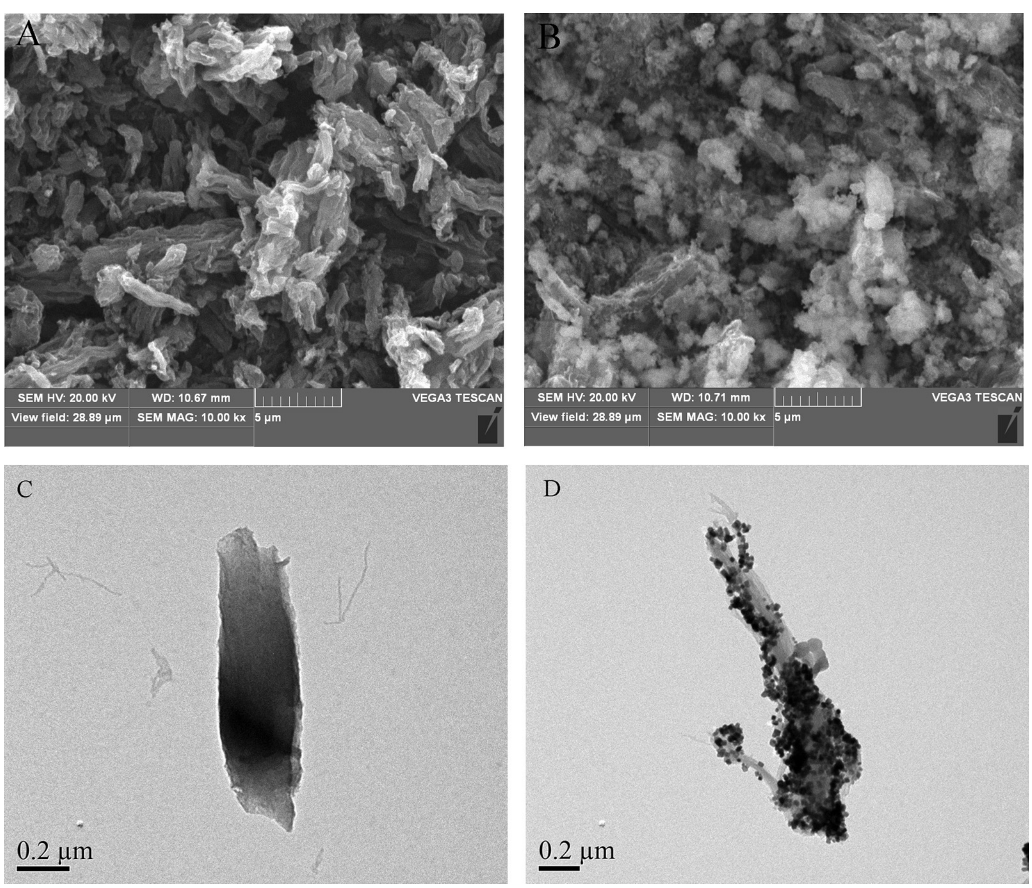

Fig. 1. SEM images of (A) OMC, (B) CeO_2–OMC; TEM images of (C) OMC and (D) CeO_2–OMC.