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Preparation of graphene oxide-wrapped carbon sphere@silver spheres for high performance chlorinated phenols sensor

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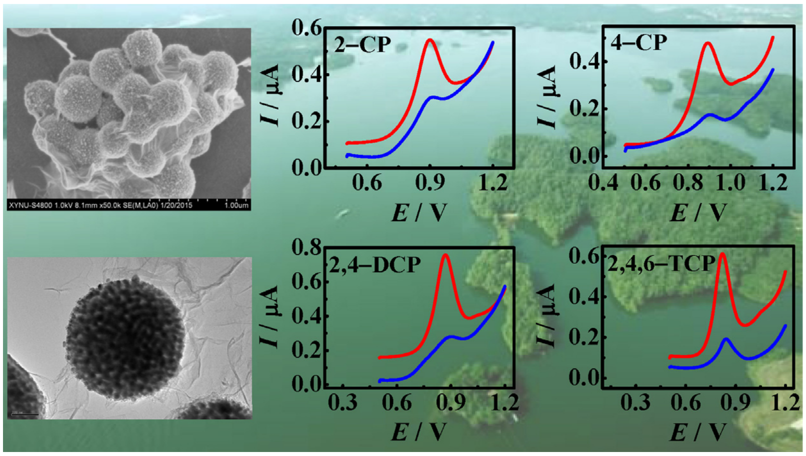
HIGHLIGHTS

- Hierarchical CS@Ag@GO composite was obtained by a simple solution route.
- Signal amplification is achieved for sensitive detection of chlorinated phenols.
- The low-cost method exhibits wide concentration range and acceptable accuracy.
- The method can be successfully applied to detect chlorinated phenols in waters.

GRAPHICAL ABSTRACT



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ABSTRACT

A template-activated strategy was developed to construct core/shell structured carbon sphere@silver composite based on one-pot hydrothermal treatment. The CS@Ag possessed a uniform three-dimensional interconnected microstructure with an enlarged surface area and catalytic activity, which was further mechanically protected by graphene oxide (GO) nanolayers to fabricate intriguing configuration, which was beneficial for efficiently preventing the aggregation and oxidation of AgNPs and improving the electrical conductivity through intimate contact. By immobilizing this special material on electrode surface, the CS@Ag@GO was further used for sensitive determination of chlorinated phenols including 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. The tailored structure, fast electron transfer ability and facile preparation of CS@Ag@GO made it a promising electrode material for practical applications in phenols sensing.

1. Introduction

Recently, the design of architectures with metal-coated core/shell composite microspheres is an interesting and challeng-

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ing task owing to the conjunction of functionalities and properties from cores and metallic shells, and also increasing applications in various fields [1,2]. The preparation of core/shell composite microspheres with noble metallic shells such as Ag and Au has been made great deals of efforts because they show novel electrocatalytic properties. Many physical and chemical routes such as thermal evaporation, ultrasound irradiation, hydrothermal method, self-assembly, electroless plating and solvent-assisted deposition [3–8] have been developed.

For common cores, it is difficult to produce compatibility between the core surface and shell particles, thus it becomes necessary to modify or functionalize the core with specific characteristics or functional groups in order to improve the microenvironment for the subsequent seed growth [9]. Against the disadvantages in the previous procedures like complex surface modifications and seeds impurity, Wright et al. put forward the combined reverse micelle nanoreactor approach and hard-template route, but the seeding step was also needed before the shell coating [10]. We recently reported a facile encapsulation approach to produce $Fe@Fe_3C—C$ core–shell nanostructure using glucose as the reducing agent and carbon source [11]. However, one drawback of this procedure is the requirement of suitable surface chemistry for the pre-synthesized core. Up to now, the prior surface modification or functionalization on the core templates is still the necessary way to coat uniform and complete metal shell in present synthesis of metal-coated core/shell composite. In this regard, carbon sphere (CS) colloidal microspheres present some major advantages, such as their monodispersity, excellent conductivity, controlled size and shape [12]. Most importantly, various hydroxyl groups exist on the surface of CS, which can be broken or form ionized sites (—O— groups) in certain alkaline conditions [13]. And these ionized sites can function as activated sites for the anchor of noble metallic shell, where surface functionalization, seeding, and the subsequent shell growth steps can be simplified into one-pot hydrothermal reaction.

On the other hand, the noble metal nanoparticles inevitably suffer from the problems of aggregation and oxidation in practical applications owing to their relative higher surface energy and small size [14]. Therefore, the well dispersion of noble metal-based composite into a nanosheet-assembled shell, is expected to have excellent conductive and catalytic properties due to their appressed and hierarchical surface. Many groups have intensively reported that graphene oxide (GO), an atomic-layer-thick and two-dimensional structure which bears lots of oxygen-containing functional groups [15], enhanced the electrochemical properties of metal [16], metal oxide [17], polymer [18] and quantum dots [19]. Researchers have demonstrated that embedding noble metal composite in flexible GO nanosheets significantly improved the stability via hybridization, and promoted catalytic activity due to an increase in charge transfer [20,21]. With this in mind, it is expected that hybridizing GO with noble metal-coated core/shell composite will lead to unique electronic and catalytic properties.

The presence of mutagenic and carcinogenic compounds in industrial and domestic wastewater has raised a global issue of environmental concern in the last decades [22]. These compounds, even at very low concentrations, may cause public health hazards. Among them, chlorinated phenols find application as wood preservatives, transformer oils, vegetable fibers, pesticides, repellents and disinfectants [23,24], accompanied by their emissions into the sea water, rivers and even in drinking water. Due to the presence of chlorine atom and aryl structure, chlorinated phenols are exceptionally recalcitrant toward biodegradation and they are of great concern because of their toxicity and carcinogenicity [25,26]. Furthermore, the toxicity of chlorinated phenols tends to increase with increase in their degree of chlorination [27]. Therefore, it is important to develop efficient and cost-effective methods to determine chlorinated phenols in natural water bodies. Chlorinated phenols have been determined using exploiting separation techniques [28–30]. However, electrochemical method is one of the alternatives since its high sensitivity, convenience, good selectivity, low cost and time saving [31–38]. Moreover, electrochemical method provides a reduction of sample and organic solvent consumption, which leads to reduction of waste production. A tyrosinase biosensor based on a graphitized ordered mesoporous carbon was developed by Wang et al. for the rapid detection of phenolic pollutants [39], where the carbon material showed enlarged accumulation ability. Zhu et al. synthesized Ag nanoparticles (AgNPs) for the electrochemical detection of chlorophenol with high electrocatalytic activity [40]. Pop et al. prepared expanded graphite–Ag–zeolite–epoxy composite electrode for the sensitive determination of chlorophenol [41]. These studies implied the superiority of carbon materials and AgNPs in the fabrication of chlorinated phenols electrochemical sensors. However, the application of GO in this area is rare, even though Arriagada et al. have testified the improved adsorption of chlorophenol on GO compared with pristine graphene [42].

Here in our report, we designed a template-activated strategy to realize one-step coating of colloid carbon microspheres with dense AgNPs, and then synthesized well-tailored GO nanosheets-wrapped CS@Ag microspheres. This material, which was defined as CS@Ag@GO, showed a uniform three-dimensional (3D) interconnected structure with closely integrated interface and high surface area, hence, leading to fast electron transfer kinetics, along with high accumulation efficiency of the CS@Ag@GO-modified electrode, which were favorable to the fabrication of highly sensitive electrochemical sensor. The convenient and facile preparation of CS@Ag@GO and excellent performance of the proposed sensor provided new insight for the assay of chlorinated phenols in water samples.

2. Experimental

2.1. Reagents and apparatus

$AgNO_3$, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were purchased from Sigma–Aldrich. Graphite, glucose, 3-aminopropyltrimethoxysilane (APTES) and poly(vinyl pyrrolidone) (PVP, K30) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The reagents were of analytical grade and used as received.

All electrochemical measurements were performed with a CHI 660D electrochemical workstation (CH Instrument Company, Shanghai, China) in a three-electrode cell configuration consisting of a CS@Ag@GO-modified glassy carbon electrode (GCE, diameter of 3 mm) as the working electrode. A platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Measurement of voltammetric analyses were calculated as the average of six measurements.

Fourier transform infrared spectroscopy (FTIR) spectra ($400–4000\,cm^{-1}$) were measured using a PerkinElmer FTIR spectrophotometer with pure KBr as the background. The samples were mixed with KBr with the mass ratio of 1:200 and the mixture was dried and compressed into a transparent tablet for measurement. Powder X-ray diffraction patterns (XRD) of samples were recorded on a Rigaku D/Max-rC powder diffractometer using Cu K_a radiation (40 kV and 100 mA). The diffractograms were recorded in the 2θ range of 5–80 °C with a 2θ step size of 0.01° and step time of 2 s. Energy-dispersive X-ray spectroscopy (EDX) was obtained using a TECNAI G2 20 S-TWIN microscope (FEI Company, Holland). Scanning electron microscope (SEM) analyses were conducted on Hitachi S-4800 instrument operating at 20 kV. Transmission elec-