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Nitrogen-doped hollow carbon spheres wrapped with graphene nanostructure for highly sensitive electrochemical sensing of parachlorophenol

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ABSTRACT

Owing to awfully harmful to the environment and human health, the qualitative and quantitative determination of parachlorophenol (PCP) is of great significance. In this paper, by using silica@polydopamine as template, nitrogen-doped hollow carbon spheres wrapped with reduced graphene oxide (NHCNS@RG) nanostructure was prepared successfully via a self-assembly approach due to the electrostatic interaction, and the obtained NHCNS@RG could exhibit the unique properties of NHCNS and RG: the NHCNS could impede the aggregation tendency of RG and possess high electrocatalytic activity; the RG enlarges the contacting area and offers many area-normalized edge-plane structures and active sites. Scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, X-ray diffraction and electrochemical method were used to characterize the morphology and structure of NHCNS@RG. Then, the NHCNS@RG hybrids were applied for the electrochemical sensing of PCP, under the optimized conditions, the detection limit of PCP obtained in this work is 0.01 μM and the linear range is 0.03–38.00 μM.

1. Introduction

Parachlorophenol (PCP), an environmental pollutant, is extensively applied as preservative agent for paints, wood, vegetable fibers, leather and disinfectants. Moreover, PCP is also widely used as an important intermediate for the synthesis of herbicides, insecticides, fungicides, pharmaceutical and dye production. Because of its tendency to bioaccumulate in the food chain and its toxicity towards the humans and environment, PCP has been listed as one of the priority pollutants by the United States Environmental Protection Agency (Yang et al., 2015; Zhang et al., 2014a). Therefore, the identification and detection of PCP is very important. Due to the low cost, simple operation, time saving, high sensitivity and selectivity, electrochemical techniques currently attracted attention in the determination of PCP (Amine et al., 2016; Wu et al., 2015; Yang et al., 2015). However, the highly sensitive and rapidly electrochemical determination of PCP is still a great challenge.

Up to now, considerable attentions have been paid to hollow nanostructures owing to their fascinating properties (e.g., low density, high surface-to-volume ratio, shell permeability) and promising applications in a wide range of areas (Feng et al., 2014). Among the families experienced impressive advances, hollow carbon nanospheres (HCNS) are very interesting owing to the outstanding advantages such as nontoxic, cheap, good chemical stability and electrical conductivity (Dong et al., 2012; Liu et al., 2015a; Xu et al., 2012), these interesting properties enable HCNS have important potential applications for developing highly sensitive electrochemical sensors. However, presently HCNS were only applied in catalysis (Lee et al., 2014; Liu et al., 2011), lithium-ion battery (Jayaprakash et al., 2011; Liu et al., 2013), oxygen-reduction (Schaefer et al., 2010), supercapacitor (Fang et al., 2014) and water treatment (Cheng et al., 2014; Liu et al., 2014), there is little work focused on the applications of HCNS in electrochemical sensors.

Graphene, a single-atom thick 2D nanostructure, has received considerable attention in sensors due to its large theoretical specific surface area (~2630 m^2/g), good biocompatibility, low production cost and high conductivity (Raccichini et al., 2015; Weaver et al., 2014). Most recently, it was reported that PCP could be abundantly absorbed on graphene surface (Fan et al., 2015; Meng et al., 2015), this make us convince that graphene is a perfect nanomaterial for electrochemically detecting PCP. However, graphene generally tends to form irreversible agglomerates or even restack to form graphite through the π-π interactions and van der Waals force, and the easy aggregation of graphene during the processing could largely reduce its surface area and lessen the

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number of the electrochemically active sites (Chen et al., 2015; Lin et al., 2013), which is not beneficial for sensing PCP by electrochemical method. In fact, for resolving the aggregation of graphene, various protective reagents, such as octadecylamine (Che et al., 2010), surfactants (Li et al., 2008), 1-octyl-3-methylimidazolium ions (Acik et al., 2012) and DNA (Guo et al., 2010; Song et al., 2016), have been used for improving the dispersibility of graphene, whereas the presence of protective reagents may lead to the reduction of the effective surface area and conductivity, this will inevitably decrease the analytical performance of graphene (Li et al., 2015; Shi et al., 2014; Zhu et al., 2016).

Most recently, a new method, novel carbon materials as "spacers" between graphene sheets has been developed to prevent the aggregation of graphene for lithium-sulfur batteries (Zhou et al., 2015a), capacitive deionization (Wang et al., 2014a), catalytic (Zhang et al., 2014b), methanol oxidation (Zhu et al., 2014) and supercapacitor (Liu et al., 2015b), whereas little in electrochemical sensing. These carbon nanomaterials, including carbon spheres, polypyrrole spheres and ordered mesoporous carbons, have many advantages, such as high surface permeability, good conductivity and larger specific surface area (Liu et al., 2015a; Wang et al., 2014b). However, most of these methods are complex, expensive and environmentally harmful. Inspired by these insights, it is convinced that introducing a simple, low cost and green method to prepare novel HCNS/graphene hybrids and using the hybrids for electrochemical sensing of PCP is of great significance.

In 2011, Dai's group (Liu et al., 2011) prepared silica@polydopamine (SiO_2@PDA) via the polymerization of dopamine hydrochloride (DA) on SiO_2 surface, herein, by using SiO_2@PDA (positive charged) and graphene oxide (GO, negative charged) as precursors, a hierarchical nanostructure, nitrogen-doped HCNS-reduced GO (NHCNS@RG) hybrids were fabricated via a simple method (Scheme 1). The NHCNS@RG hybrids were then used to modify electrode for electrochemical sensing of PCP. For detecting PCP, the NHCNS@RG nanocomposites could exhibit the synergetic properties of NHCNS and RG: the NHCNS effectively impede the aggregation tendency, enhance the effective surface area of RG, and have highly electrocatalytic activity toward PCP due to the presence of N (Zhou et al., 2015b); the RG could enlarge the contacting area and offer many area-normalized edge-plane structures and active sites, these are very beneficial for achieving highly sensitive electrochemical sensing of PCP. Under the optimized conditions, the highly sensitive and rapid electrochemical sensing of PCP was successfully achieved, and the limit of detection (LOD) is 0.01 μM with a wide linear range from 0.03 to 38.00 μM. The obtained LOD is much lower than those reported in previous literatures.

2. Experimental section

2.1. Reagents and apparatus

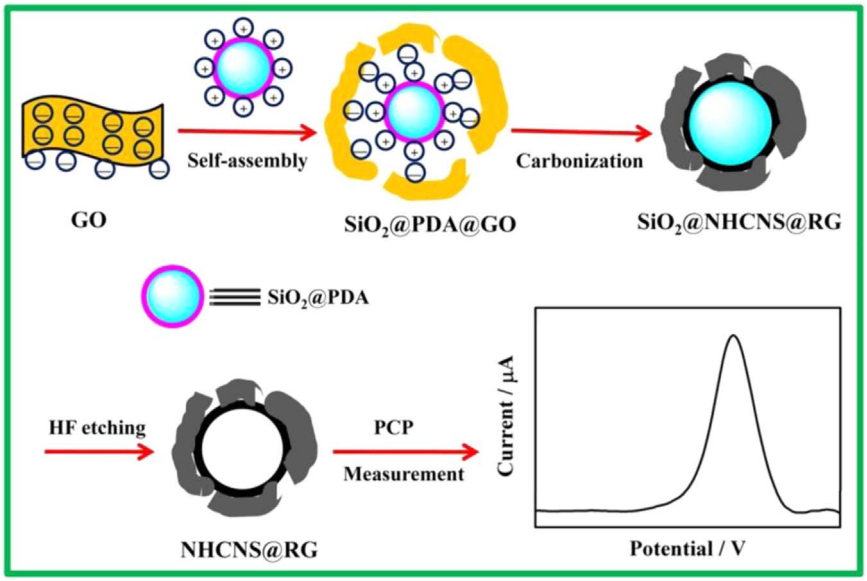
PCP, dopamine and SiO_2 particles (diameter, ~360 nm) were purchased from Alfa Aesar (USA). GO were prepared according to the Hummers method. All other chemicals were of analytical grade and used directly without further purification. The supporting electrolyte was 0.1 M phosphate buffer solution (PBS) prepared with Na_2HPO_4 and NaH_2PO_4. Aqueous solutions used throughout were prepared with ultra-pure water (> 18 MΩ cm) obtained from a Millipore system.

All electrochemical measurements were performed on a CHI 660E Electrochemical Workstation (Chenhua Instrument Company of Shanghai, China). A conventional three-electrode cell was used with a glassy carbon electrode (GCE, with a diameter of 3 mm) as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode (saturated KCl) electrode as the reference electrode. Except the specific statement, the electrochemical measurements were carried out in 0.1 M PBS (pH 6.0) at room temperature (25 ± 2 °C). All the potentials in this paper were referred to Ag/AgCl electrode (saturated KCl).

2.2. Synthesis of NHCNS@RG hybrids

The SiO_2@PDA was prepared firstly according to the previous report (Liu et al., 2011) with some modifications (Scheme S1). In brief, SiO_2 particles were washed with tris(hydroxymethyl)aminomethane (TRIS) buffer and mixed with TRIS buffer containing DA for 24 h by vigorous stirring, the SiO_2@PDA nanocomposites were obtained by centrifugation and drying in vacuum at 60 °C overnight.

For preparing NHCNS@RG hybrids (Scheme 1), 100 mL GO suspension (0.5 mg mL^{-1}) was mixed with 100 mL SiO2@PDA suspension (2 mg mL^{-1}) and the mixture were stirred for 24 h to



Scheme 1. The procedure for preparing NHCNS@RG hybrids.