Materials Research Bulletin 104 (2018) 15–19

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Nitrogen-doped hollow carbon nanospheres for highly sensitive electrochemical sensing of nitrobenzene

Mengjun Liu, Tongrui Zhang, Haoxuan Ren, Lei Wang, Tianjiao Meng, Jincan Zhao, Huan Wang*, Yufan Zhang*

Key Laboratory of Analytical Science and Technology of Hebei Province, College of Chemistry and Environmental Science, Key Laboratory of Medicinal Chemistry and Molecular Diagnosis, Ministry of Education, Hebei University, 071002 Baoding, PR China

ARTICLE INFO

Keywords:
Nitrogen–dopant
Hollow carbon nanospheres
Electrochemical sensor
Nitrobenzene

ABSTRACT

Following hard template method, nitrogen–doped hollow carbon nanospheres (NHCPs) were successfully prepared by using monodisperse silica microspheres as a template and dopamine as carbon and nitrogen precursor. A series of NHCPs-x samples with different pyrolysis temperatures were reported. The composite material formation was characterized by detailed methods (e.g., X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy). Results indicated that NHCPs treated at 750 °C with highest amounts of pyrindinic N showed improved electro-catalytic activity for nitrobenzene (NB) in neutral solution. NHCPs-750 can be developed as an effective sensing platform for the detection of NB, which showed high activity and superior analytical performance, such as a wide linear range of 5–2610 μM, a high sensitivity of 436 μAmM^{-1}, and a low limit of detection of 2.29 μM.

1. Introduction

Nitrobenzene (NB) is a huge industrial importance compound, which utilizes in leather goods, explosive industries, dyes and agricultural chemicals [1]. It mainly exits in industrial effluents and sediments, and is released into the environment [2]. Because its high toxicity with mutagenic, carcinogenic and teratogenic effects on the human health even in low concentration, it has been classified a priority pollutant [3–5]. Therefore, it is of great significance of the fast and accurate detection of NB. Electrochemical technique has been confirmed the truth of being an cheap and effective method due to its intrinsic simplicity, high sensitivity and selectivity. With the even increasing demand for electrochemical sensors, the development of high efficient electro-catalysts has been attracting increasingly attention [6–16].

Carbon materials with various microtextures and wide availabilities represent very attractive materials for electro-catalysts. Among them, hollow carbon nanospheres have been received considerable attention, because of their large surface areas, superior electrical conductivities, simple functionalities, excellent thermal and chemical stabilities [17,18]. Especially, the hollow structure provides large controllable inner pore volume and short diffusion paths for both ions and electrons. In addition, N-doped carbon is the most popular strategy that could improve the electronic conductivity of carbon and reactivity by causing extrinsic defects. Furthermore, the carbon substrates with N doping are able to effectively enhance the catalytic performance since the strong electron donor nature of N can supply negative charges to delocalized π bond of sp^2 hybridized carbon skeleton [19–23].

Herein, we proposed the synthesis of N-doped hollow carbon nanospheres (NHCPs) by a template-based method employing as-prepared monodisperse silica microspheres (MSM) as a template and dopamine as carbon and nitrogen precursor. The N heteroatoms were introduced into the carbon to create reactive sites for fast charge transfer and enhance electro-catalytic activity. The NHCPs have a specific carbon shell and hollow space, providing internal space and path way for ions transport and electrolyte diffuse as electrode materials, which exhibited a good electro-analytical properties for NB.

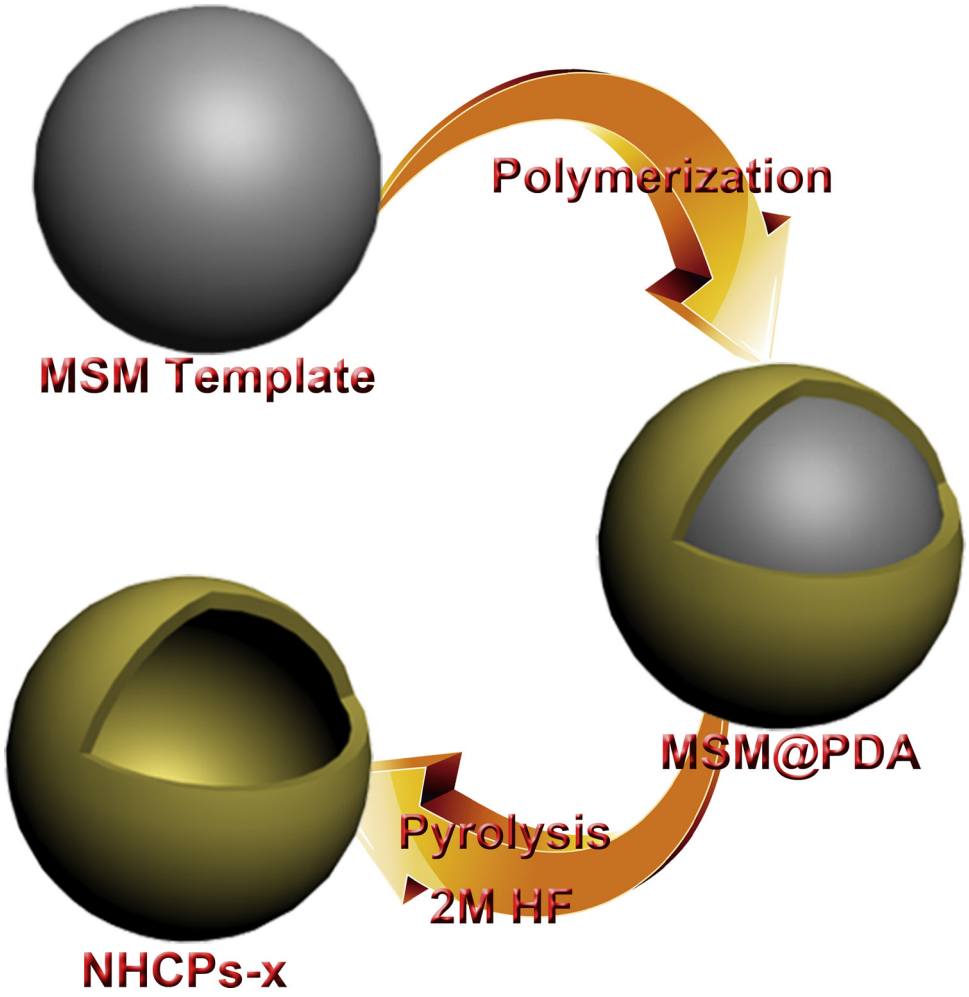
2. Experimental

2.1. Chemical reagents

NB, tris(hydroxymethyl)aminomethane, ethylene oxide/propylene oxide block copolymer (F127), and dopamine hydrochloride were purchased from MACKLIN Reagent. The electrolyte utilized for all experiments were the 0.1 M phosphate buffer solution (PBS pH 7.0). All other chemicals reagents were used as received.

* Corresponding authors.
E-mail addresses: huanwang@hbu.edu.cn (H. Wang), zyf@hbu.edu.cn (Y. Zhang).

https://doi.org/10.1016/j.materresbull.2018.04.005
Received 14 December 2017; Received in revised form 9 March 2018; Accepted 3 April 2018
Available online 04 April 2018
0025-5408/



Scheme 1. Illustration of the preparation of NHCPs.

2.2. Physical characterizations

The morphology of NHCPs was recorded by transmission electron microscopy (TEM) that operated at 200 kV (FEI TECNAL G2, USA). Scanning electron microscope (SEM) were carried out by JSM-7500F JEOL (Japan). Fourier transform infrared (FT-IR) spectroscopy of the sample was recorded with Nicolet Magna 560 FT-IR spectrometer in KBr disk. X-ray photoelectron spectroscopy (XPS) analysis were performed with a thermo ESCA LAB spectrometer (USA). All the electrochemical experiments were performed with an Autolab Electrochemistry Workstation (PGSTAT 302N, Metrohm, Switzerland) with a traditional three-electrode system. Electrochemical impedance spectroscopy (EIS) was conducted using the Autolab electrochemical analyzer in a 0.1 M KCl solution containing 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$, from 0.1 Hz to 10.0 kHz.

2.3. Synthesis of NHCPs materials

The MSM template was prepared by the typical Stöber's method [24]. 150 mg of MSM template, 80 mg of F127 and 50 mg of tris(hydroxymethyl)aminomethane were dispersed in 40 mL of deionized water. Subsequently, 150 mg of dopamine hydrochloride was put into the mixed solution and the system was kept stirring for 24 h at room temperature. The dopamine could be self-polymerized on the outer shell of silica microspheres. The resulting MSM@PDA was collected by centrifugation, followed by rinsed in ethanol before drying at 60 °C. The obtained powder precursors were transferred into the center of a tube furnace, and carbonized by heating the product to typically 550, 650, 750, and 850 °C for 3 h, under a flow of pure N_2. After being cooled down to room temperature, the carbonized product was treated with HF solution (10 wt%) to remove the silica spheres template and generate NHCPs. An illustration of the preparation of NHCPs is presented in Scheme 1.

2.4. Electrochemical measurements

A conventional cell was used containing a three-electrode; the glassy carbon electrode (GCE) or modified electrode served as a working electrode; the counter electrode whereas an Ag/AgCl (3 M KCl) electrode and platinum electrode were reference and counter electrode. In this paper, all potentials were referred and reported versus Ag/AgCl.

Before the GCE (model CHI104, 3 mm diameter) was modified, which was firstly polished seriously to obtain a mirror-like surface with 1, 0.3 and 0.05 μm alumina slurry, and then ultrasonicated in HNO_3 (1:1), absolute ethanol and distilled water for 30 s, respectively. Finally, the electrode was allowed to clean with distilled water and dry with nitrogen gas blowing. 2 mg of electro-catalysts were dispersed into 1 mL of DMF and sonicated to form a homogeneous suspension for 30 min. After dropping 5 μL of the suspension onto the GCE, NHCPs modified electrodes (NHCPs-GCE) were finally formed and dried in air at laboratory temperature.