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Formation of Fe_2O_3 microboxes/ macroporous carbon hybrids from Prussian blue template for electrochemical applications

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ABSTRACT

Iron oxide (Fe_2O_3) material is considered as a promising catalyst for electrochemical applications. This study reports a design of magnetically Fe_2O_3 microboxes loaded on macroporous carbon (MPC) hybrids for high-performance electrocatalysts. The obtained Fe_2O_3 microboxes were converted by decomposition of Prussian blue microcubes ($Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$) at a moderate temperature of 350 °C in air. MPC materials with excellent conductivity can offer a platform for the incorporation of Fe_2O_3 microboxes to form novel hybrid nanostructures with synergetic effects. Because of the unique structural properties and synergetic catalytic effect, a sensitive electrochemical sensor for nitrobenzene was developed based on Fe_2O_3/MPC, which showed a wide linear range, low detection limit, high sensitivity, and good stability.

1. Introduction

Nitrobenzene (NB) is a compound of immense industrial importance utilized in agricultural chemicals, leather goods, dyes and explosive industries [1]. It is released into the environment mostly from industrial effluents and mainly exits in water and sediments [2]. It has been listed as a priority pollutant due to its high toxicity with teratogenic, carcinogenic and mutagenic effects on the human health even in low concentration [3–5]. Therefore, the rapid and accurate detection of NB is of great significance. Electrochemical technique has been proven to be an inexpensive and effective way 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 [6–9].

Transition metal oxides have been extensively studied for decades due to its low cost, non-toxicity, ease of production, high specific capacitances, and ease of storage [10–24]. The Fe-rich catalysts have been attracting significant attention owing to their promising electrocatalytic activity among various transition metal oxides [25–28]. Prussian blue (PB), a typical porous multifunctional material composed of iron centers bridged by hexacyanoferrate, with the chemical formula $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$, have gained increasing attention in recent years [29–31]. PB has a highly defined 3D network structure at molecular level. Given its unique properties and structure, PB is demonstrated as suitable precursors to synthesize hierarchical Fe_2O_3 microboxes. When evaluated as an electrode material for electrocatalysis, the as-synthesized Fe_2O_3 microboxes manifested high specific electrochemical performance. However, single phased Fe_2O_3 still have insufficient performance because of their intrinsic weaker material properties of electronic conductivity, mechanical stability, and electrocatalytic ability [32].

3D macroporous carbon (MPC) is one of the most promising sources for electrochemical applications among the various types of carbon materials [33–39]. The MPC exhibits uniform tailored and unique macroporous structure, high specific surface area, large pore volume, excellent conductivity, good thermal stability and chemical inertness, which make them suitable for applications in catalysis, sensing, and energy storage. Additionally, the high density of edge plane-like defective sites on MPC may provide many favorable sites for electron transfer to electroactive molecules, which makes MPC potential novel materials for investigating the electrochemical behavior of the substances. In particular, MPC

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materials as unique host matrices can offer a platform for the incorporation of other nano-entities to form novel hybrid nanostructures with synergetic effects.

Synthesis of materials with complex nanostructures can provide more opportunities to tune the physical and chemical properties of the material, which has been proposed as a promising way to improve their performances in electrochemical applications. In view of the advantages of magnetic Fe_2O_3 microboxes and MPC, our group demonstrates the major objective of this work is to present the synthesis of Fe_2O_3/MPC composite materials and their electrochemical applications.

In this work, Fe_2O_3 microboxes loaded MPC nanocomposite, which are synthesized derived from PB/MPC hybrid materials via an easy annealing treatment in air. NB was selected as marking molecule to evaluate the electrochemical activity of the Fe_2O_3/MPC. The electrochemical results showed that Fe_2O_3/MPC exhibited significant electrocatalytic activity towards NB, indicating that this composite may hold great promise for the design of electrochemical environmental sensors.

2. Experimental

2.1. Chemical reagents

$K_4Fe(CN)_6 \cdot 3H_2O$, poly(vinylpyrrolidone) (PVP), *N,N′*-dimethylformamide (DMF) and NB were purchased from MACKLIN Reagent Co. Ltd. The 0.1 M phosphate buffer solution (PBS pH 7.0), which was made up from NaH_2PO_4, Na_2HPO_4, and H_3PO_4, was employed as a supporting electrolyte. All other reagents were of analytical grade, and all solutions were prepared using double distilled water.

2.2. Instrumentation

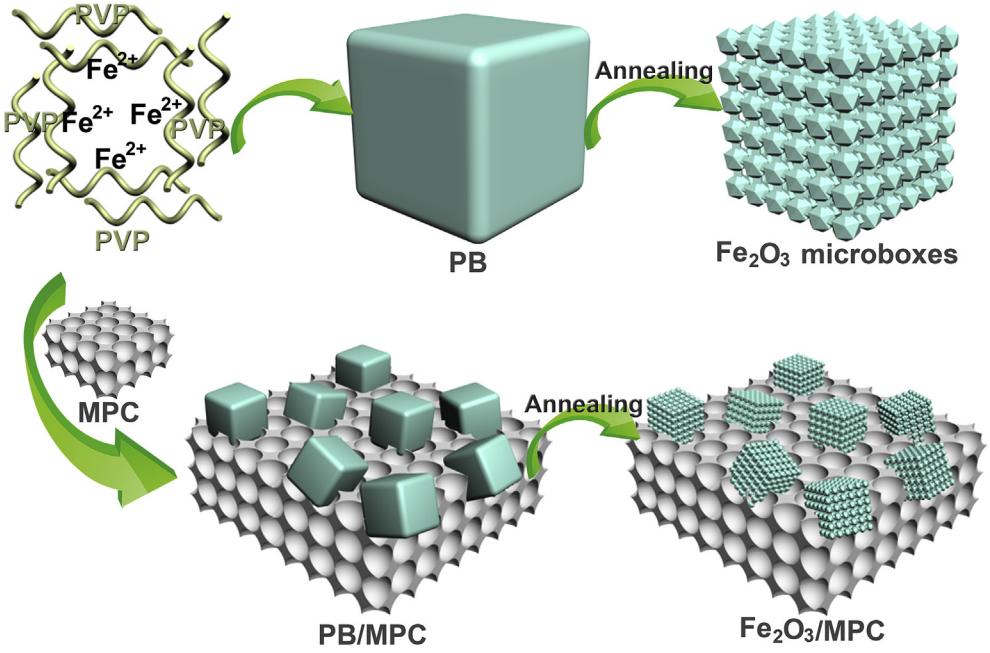
All the electrochemical experiments were performed with an Autolab Electrochemistry Workstation (PGSTAT 302 N, Metrohm, Switzerland). Electrochemical impedance spectroscopy (EIS) was conducted using the Autolab electrochemical analyzer in a 0.1 M KCl solution containing 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$, from 0.1 Hz to 10.0 kHz. Fourier transform infrared (FT-IR) spectroscopy of the sample was recorded with Nicolet Magna 560 FT-IR spectrometer. X-Ray diffraction (XRD) patterns were obtained on a X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu Kα radiation ($k = 0.15406$ nm). Scanning electron microscopy (SEM) images were determined with a PhilipsXL-30 ESEM, operating at 3.0 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with a thermo ESCA LAB spectrometer (USA). A conventional three electrode cell was used; the working electrode was glassy carbon electrode (GCE) or the modified electrode; a platinum electrode was used as the counter electrode whereas an Ag/AgCl (in saturated KCl solution) electrode served as a reference electrode. All potentials in this work were measured and reported versus Ag/AgCl. It is worth mentioning that in this study, all the solutions were purged with purified nitrogen for 20 min to remove oxygen prior to the beginning of a series of experiments and all experiments were carried out at 25 °C.

2.3. Synthesis of PB microcubes

The PB microcubes were prepared as reported previously by Lou's group [31]. In a typical procedure, PVP (4.0 g) and $K_4Fe(CN)_6 \cdot 3H_2O$ (0.20 g) were added to a HCl solution (0.1 M, 60 mL) under magnetic stirring. After stirring for 15 min, a clear solution was obtained. The solution was filled in a 100 mL Teflon liner, placed in an autoclave, and heated to 80 °C for 24 h. The obtained blue product was recovered by filtration, and then washed with distilled water and absolute ethanol. Thereafter, the PB microcubes power was obtained by vacuum drying at 25 °C.

2.4. Synthesis of Fe_2O_3 microboxes

To convert the PB microcubes into Fe_2O_3 microboxes, the as-synthesized PB product was heated at 350 °C for 4 h in air with a temperate ramp of 1 °Cmin^{-1}.



Scheme 1. Illustration of the preparation of Fe_2O_3 microboxes and Fe_2O_3/MPC.