In-situ growth of iron-based metal-organic framework crystal on ordered mesoporous carbon for efficient electrocatalysis of p-nitrotoluene and hydrazine

Shuang Yuan, Xiangjie Bo, Liping Guo[*]

Key Laboratory of Nanobiosensing and Nanobioanalysis at Universities of Jilin Province, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, PR China

HIGHLIGHTS

- Constructing a novel electrocatalyst based on H_2N-Fe-MIL-88B@OMC by in-situ growth method.
- Improved electrocatalytic properties due to the synergy between H_2N-Fe-MIL-88B and OMC.
- Efficient electrocatalysis of p-nitrotoluene reduction and hydrazine oxidation.
- The wide linear range for detecting p-nitrotoluene.
- The detection limit of hydrazine reaching nanomolar level with high sensitivity.

GRAPHICAL ABSTRACT
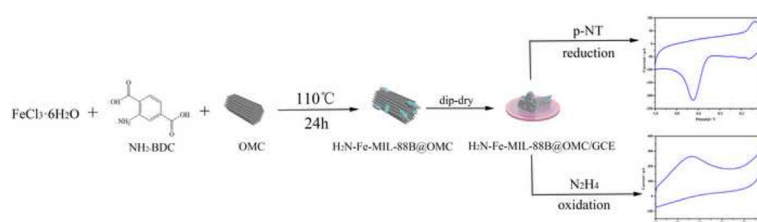
ABSTRACT

In this paper, H_2N-Fe-MIL-88B@OMC composites were fabricated by the simple hydrothermal method through in-situ growth iron-based metal-organic frameworks (H_2N-Fe-MIL-88B) on ordered mesoporous carbon (OMC). Compared with pure H_2N-Fe-MIL-88B crystals, the introduction of OMC can shrink the size of H_2N-Fe-MIL-88B, increase the specific surface area, decrease the electron transfer resistance and drastically improve the electrochemical performance of H_2N-Fe-MIL-88B@OMC. The composite exhibits remarkable electrocatalytic activity for p-nitrotoluene (p-NT) reduction and hydrazine (N_2H_4) oxidation. Therefore, a novel electrochemical sensor based on H_2N-Fe-MIL-88B@OMC was constructed for the efficient detection of these two environmental pollutants, respectively. Under the optimal experimental conditions, the proposed sensor displays a wide linearity range for p-NT that is composed by two line segments (20–225 μM and 225–2600 μM) and the limit of detection (LOD) is 8 μM (S/N = 3). Meanwhile, the sensor also shows a linear response to N_2H_4 in the range of 0.006–0.061 μM and 0.061–611.111 μM with a high sensitivity of 20.1 μA/μM·cm^2 in low concentration range as well as a very low LOD as 5.3 nM (S/N = 3). And the response time of the sensor for N_2H_4 detection is about 1 s. In addition, the proposed sensor shows satisfactory electrochemical stability, reproducibility, selectivity and practicability. H_2N-Fe-MIL-88B@OMC may be a splendid candidate for developing electrochemical sensors to detect environmental pollutants.

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1. Introduction

With the rapid development of science and technology, more and more chemical reagents have been used in a lot of fields from industry to agriculture [1,2]. However, chemical reagents also cause many great negative impacts [3], of which environmental pollution is one of the most conspicuous issues [4,5]. It is well known that *p*-nitrotoluene (*p*-NT) and hydrazine (N_2H_4) are commonly used chemicals and play important roles in many practical applications [6–9]. It is noteworthy that *p*-NT is harmful to bioaccumulation even at very low concentration and may cause long-term adverse reactions in the aquatic ecological environment [10,11], which is also detrimental to health [12,13]. Meanwhile, N_2H_4 is considered a carcinogen and environmental pollutant, which can cause serious pollution to water resources [14,15]. Therefore, effective detection of *p*-NT and N_2H_4 is vital to human health and environmental protection.

Nowadays, many techniques have been used to detect environmental pollutants, such as gas chromatography [16,17], liquid chromatography [18,19], fluorescence [20,21], chemiluminescence [22,23], and electrochemical analysis [24,25]. Among them, the electroanalytical methods have drawn much specific attention due to their simple operation, high sensitivity and fast response. However, fluorescence analysis seems to be the main method used to detect *p*-NT right now [26–28]. Electrochemical detection of *p*-NT not only reported rarely, but also their linear ranges need to be improved [29–31]. Thus, it is very important to construct an electrochemical sensor with a wide linearity range for effective detection of *p*-NT. At the same time, a variety of composites have been reported to detect N_2H_4 [32,33], for instance, Omar and co-workers designed a composite of zinc cobaltite intercalated with polyaniline for detecting N_2H_4 [34]. Dai et al. synthesized flower-like Co_3O_4/graphitic carbon nitride nanocomposite to detect N_2H_4 [35]. Gao et al. developed hydroxyapatite/chemically reduced graphene oxide composite for sensing N_2H_4 [36]. Zhang and co-workers reported palladium nanoparticles loaded on cobalt-wrapped nitrogen-doped carbon nanotubes for the detection of N_2H_4 [37]. However, the sensitivity of N_2H_4 detection remains to be improved. Thence, it is necessary to design a novel nanomaterial with a high sensitivity for detecting N_2H_4.

Recently, many people are committed to assembling and developing some of composites with highly active. As a class of crystalline porous materials, metal-organic frameworks (MOFs) are made up of metal ions and multidentate organic linkers by coordination links, having three-dimensional (3D) frameworks, which also have lots of distinct properties, including uniform-structured cavities, large surface area, high specific pore volume and tunable pore size [38]. MOFs have been widely used in supercapacitor [39], catalysis [40], gas absorption [41] and energy [42,43]. In addition, such features also make it possible to install a lot of active sites within the porous framework, which facilitates electrocatalysis [44,45]. In the meantime, applying MOFs as the electrocatalyst is also a relatively new field of study, having unlimited research value. However, there are few studies about electrochemical applications by directly using MOFs due to their intrinsic low electronic conductivity and poor electrochemical stability [46]. Accordingly, using conducting or semiconducting materials as the electric bridges to increase the overall electrical conductivity of the composites may be an effective strategy to improve the electrochemical performance of MOFs [47], such as noble metal nanoparticles [48], multi-walled carbon nanotubes [49], graphene [44,50] and porous carbons [51] have been hybridized with MOFs. Carbon materials have received great attention because of their unexceptionable electric conductivity [52,53]. Particularly, ordered mesoporous carbon (OMC), as a mesoporous carbon material, has numerous excellent

characteristics, such as the number of mesopores, large specific surface area, high conductivity, outstanding stability and simple synthesis [54,55]. Hence, OMC may be a promising material to improve the electrochemical performance of MOFs.

H_2N-Fe-MIL-88B is an iron-based MIL-type (MIL: Materials Institute Lavoisier) MOFs with the advantage of simple synthesis. The 3D pore structure of H_2N-Fe-MIL-88B is made up from trimers of FeO_6 octahedra linked to benzenedicarboxylate anions and consists of tunnels concatenated through bipyramidal cages [56]. Meanwhile, the structure of H_2N-Fe-MIL-88B is very flexible and can be used to adsorb different molecules making it an interesting choice for electrochemical sensors [57]. However, H_2N-Fe-MIL-88B was generally used as a template for the thermal decomposition of electrocatalysts [58–60] and its own electrocatalytic properties have rarely been investigated. Therefore, the composites composed of OMC and H_2N-Fe-MIL-88B may be promising for electrochemical sensor.

In this paper, we report a low budget, facile approach for synthesis of composites (H_2N-Fe-MIL-88B@OMC) *via* in situ growth of H_2N-Fe-MIL-88B crystals on OMC. And the in-situ growth method is conducive to the uniform dispersion and compact combination of H_2N-Fe-MIL-88B and OMC. Meanwhile, the introduction of OMC not only enhances the conductivity and electrochemical stability, but also leads to more active sites, and a lot of mesopores in the composites are conducive to mass transfer. Furthermore, the synergistic effect between OMC and H_2N-Fe-MIL-88B can obviously improve the electrocatalytic performance of composites. Thus, the electrocatalyst based on H_2N-Fe-MIL-88B@OMC exhibits remarkable electrocatalytic activity for the reduction of *p*-NT and the oxidation of N_2H_4. And the proposed electrochemical sensor also can be used for detecting *p*-NT and N_2H_4 in the actual samples. These findings may develop a new pathway for the application of MOFs to electrochemical sensors.

2. Experimental section

2.1. Reagents and materials

Pluronic F-127, Pluronic P123, Tetraethyl orthosilicate (TEOS) and Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Aladin Industrial Co., Ltd. Acetic acid (CH_3COOH) and ethanol (C_2H_5OH) were acquired from Tianjin Guangfu technology development Co., Ltd. 2-aminoterephthalic acid (H_2N-BDC) and *p*-nitrotoluene (*p*-NT) were obtained from Shanghai Macklin Biochemical Co., Ltd. Hydrazine (N_2H_4) was purchased from Sinopharm Chemical Reagent Co., Ltd. Sucrose, sulfuric acid (H_2SO_4) and hydrofluoric acid (HF) were acquired from Beijing Chemical Co., Ltd. The supporting electrolyte was $0.1\ mol\ L^{-1}$ (0.1 M) of phosphate buffer solution (PBS) with different pH, which were made up from sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4). And the electrolyte (0.1 M PBS) used for electrochemical experiment was degassed with nitrogen (N_2) for half an hour or more in order to remove oxygen. All reagents are analytical grade without further processing and ultra-pure water was obtained from a Millipore system. And all instruments were displayed in supporting information.

2.2. Synthesis of ordered mesoporous carbon

Ordered mesoporous carbon (OMC) was synthesized according to the method reported before [61,62]. Typically, the SBA-15 was prepared by using TEOS as silica source and Pluronic P123 as surfactant [63]. Then using SBA-15 as hard template and sucrose as carbon source to synthesis OMC, the carbonization was executed by pyrolysis with continuous heating to 900 °C under nitrogen