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Novel attapulgite/polyaniline/phosphomolybdic acid-based modified electrode for the electrochemical determination of iodate

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ABSTRACT

A novel attapulgite/polyaniline/phosphomolybdic acid-based amperometric sensing platform was constructed for the determination of iodate. Nanostructured attapulgite was utilized for reducing agglomeration of polyaniline particles, and the as prepared attapulgite/polyaniline composite was used to immobilize phosphomolybdic acid. Excellent electrocatalytic performance was obtained due to the synergistic effect of nanostructured attapulgite, polyaniline and phosphomolybdic acid. The electrochemical responses of as prepared modified electrode were investigated by cyclic voltammetry and chronoamperometry. The modified electrode exhibited linear amperometric response for iodate in the concentration range of 2.0×10^{-6} M–5.2×10^{-4} M ($R = 0.999$). The detection limit was calculated as 5.3×10^{-7} M. Good reproducibility, high stability, fast amperometric response, and possibility of rapid preparation were also great advantages of this modified electrode. Based on this work, the attapulgite/polyaniline/phosphomolybdic acid modified electrode was successfully applied to determine iodate in a commercial table salt sample.

1. Introduction

The table salt is iodized with potassium iodate or iodine in most countries, which is recognized as the most successful strategy for the prevention of iodide deficiency disorders. Deficiency of iodine can result in some disorders, such as goiter, hypothyroidism and mental retardation. However, excess of iodine ingestion can cause goiter and hyperthyroidism [1,2]. Nowadays, some analytical methods for the determination of trace iodate have been proposed, including spectrometry [3], ion chromatography [4], mass spectrometry [5], capillary [6], chemiluminescence [7] and so on. Generally speaking, the above techniques are complicated, time-consuming and/or usually require specialized instruments. Electroanalytical method is comparatively cheap, simple and rapid for the determination of electroactive species. However, low sensitivity, slow kinetics and high overpotential are some limitations of unmodified electrodes [8]. Nowadays, considerable efforts have been devoted to modifying electrode surfaces with electron transfer mediators aiming to overcome these limitations, e.g., iridium oxide nanoparticles modified GCE [9], multi-walled carbon nanotubes/iron(III)/porphyrin films modified GCE [10], gold nanoparticles/poly(3-methylthiophene) composites coated GCE [11], tungsten oxide films coated GCE [12] and so on.

In the field of electrochemistry, polyoxometalates, especially phosphomolybdic acid (PMo_{12}), can be used for the construction of chemically modified electrodes, acting as a mediator in multiple and consecutive electron transfer reactions [13]. It was reported that the attachment of polyoxometalates to electrode surfaces can be achieved by electrodeposition, adsorption, entrapment as dopants into polymers, layer-by-layer self-assembly, sol–gel method and other strategies [14–17]. However, the use of polyoxometalates as electrocatalyst has been hampered by the poor conductivity and considerable leakage [18]. It seems imperative to explore and develop a simple and reliable method to immobilize polyoxometalates with conducting matrix in order to obtain electrocatalyst with expected properties.

As a member of electro-conductive polymers, polyaniline (PANI) is a promising candidate for use as a binding matrix to immobilize polyoxometalates owing to its inherent redox based catalytic activity, excellent electrical conductivity and good chemical stability [19]. However, it should be noted that agglomeration of PANI is an essential problem to be addressed, because relatively low surface area of agglomerates hinder the fast diffusion of target molecules [20].

Attapulgite, a kind of natural nanostructured materials, is a crystalline hydrated magnesium aluminum silicate with fibrous

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morphology. The zeolite-like channels of the mineral result in high adsorption and penetrability due to its regular structure and large specific surface area. Nowadays, attapulgite has attracted increasing attention and been widely used in different fields such as adsorption [21], hydrogen storage [22] and cyclohexene hydrogenation [23].

Herein, we presented a novel attapulgite/PANI/PMo_{12} based amperometric sensing platform for the determination of iodate. In our work, attapulgite played the role of "template-like" due to the high adsorption and penetrability to reduce the serious agglomeration of PANI, leading to higher effective surface area and shorter penetration depth for target molecules in biosensor applications [24]. Compared to other templates, attapulgite had an obvious advantage that it could perform excellent template effect with negligible cost. The assembly of attapulgite/PANI on electrode was achieved by linking attapulgite/PANI composite with the negatively charged PMo_{12} film via bridges of positively charged PANI. Then attapulgite/PANI and PMo_{12} were mutually stabilized by strong interactions of PMo_{12} anions with amine groups of PANI chains [25–27]. Due to the synergistic effect, as prepared attapulgite/PANI/PMo_{12} modified electrode exhibited linear amperometric responses towards iodate in the concentration range of 2.0×10^{-6} M–5.2×10^{-4} M ($R = 0.999$) and the detection limit was down to 5.3×10^{-7} M.

2. Experimental

2.1. Chemicals and reagents

Potassium iodate, sodium phosphomolybdate, aniline, ammonium persulfate, ethanol, potassium ferricyanide, sulfuric acid, hydrochloric acid, sodium sulfate and potassium chloride were analytical grade and purchased from Chengdu Chemical Reagent Co., Ltd. (Chengdu, China). Attapulgite clay was obtained from the Mingguang Attapulgite Mine Factory (Anhui, China). Aniline was purified by vacuum distillation prior to use. Doubly distilled water was used throughout the whole experiments.

2.2. Synthesis and characterization of attapulgite/PANI composite

3.0 mg attapulgite was added to 35 mL 1.0 M hydrochloric acid solution contaning 1.0 mL aniline monomer and stirred for 0.5 h at ice bath. Added into the above mixture was 20 mL 1.0 M hydrochloric acid containing 2.52 g ammonium persulfate and the reaction system was kept stirring for 9 h. The as prepared composite was separated by filtration and repetitive washing with distilled water. Finally, the washed precipitate was dried at 60 °C for 12 h. For comparison, PANI was synthesized according to the similar procedure above just in the absence of attapulgite.

The crystallographic structures of attapulgite, PANI and attapulgite/PANI composite were characterized by X-ray diffraction analyzer (XRD, X' Pert PRO, PANalytical BV) with Cu Kα radiation ($\lambda = 0.154060$ nm) and recorded from 3.0° to 40° at a speed of 2.0° per minute. The morphologies of attapulgite, PANI and attapulgite/PANI composite were obtained using a scanning electron microscope (SEM, Ultra 55, Zesis).

2.3. Electrode preparation and electrochemical measurements

GCE was polished up to a mirror finish with 0.50 μm and 0.050 μm alumina powders successively and then washed by sonication in doubly distilled water repeatedly.

5.0 mg attapulgite/PANI composite was dispersed into 1.0 mL 50 mM PMo_{12} solution and blue suspension was obtained by successive sonication. 5.0 μL as prepared suspension was dropped onto GCE and dried in air. Then PMo_{12} was assembled on modified electrode surface via potential cycling for 50 cycles in 0.50 M H_2SO_4 + 50 mM $Mo_{12}Na_3O_{40}P$ solution at scan rate of 50 mV/s in potential range of $-0.20 \sim 0.60$ V. Finally, attapulgite/PANI/PMo_{12}/GCE was prepared successfully. For comparison, Preparation of PANI/PMo_{12}/GCE and PMo_{12}/GCE were similar to that of attapulgite/PANI/PMo_{12}/GCE just using PANI/GCE and bare GCE as matrixs instead of attapulgite/PANI/GCE.

The data of cyclic voltammetry (CV) and chronoamperometry (CA) were recorded with PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA) by introducing a three-electrode test system using platinum electrode as counter electrode, bare or modified GCE as working electrode referred to saturated calomel electrode (SCE).

3. Results and discussion

3.1. XRD characterization of attapulgite/PANI composite

Shown in Fig. 1 were XRD patterns of attapulgite, PANI and attapulgite/PANI composite, respectively. The peaks of attapulgite at 8.0°, 13.6°, 19.7° and 26.6° corresponded to the primary diffraction of (1 1 0), (2 0 0), (0 4 0) and (4 0 0) planes (Fig. 1a) [28]. For PANI, the peaks at 14.9°, 20.3° and 25.0° were attributed to (0 1 1), (0 2 0) and (2 0 0) planes (Fig. 1b) [29]. It was noted that weak peaks at 8.0° and peaks near 20.0° of as prepared attapulgite/PANI composite revealed the perfect combination of attapulgite and PANI (Fig. 1c). The XRD pattern of as prepared attapulgite/PANI composite were similar to those of pure PANI, while the reflection peaks of attapulgite were weak, which could be ascribed to the low diffraction intensity due to the small amount and the shielding effect of PANI [30].

3.2. SEM characterization of attapulgite/PANI composite

Shown in Fig. 2 were SEM images of attapulgite, PANI and attapulgite/PANI composite. It could be found that attapulgite was of average diameter of about 60–130 nm with the morphology of crystal fibers (Fig. 2A). It was revealed that PANI formed rod-like agglomerations during polymerization without attapulgite and agglomerated seriously (Fig. 2B). As for attapulgite/PANI composite, the smaller PANI particles homogeneously coated on the surfaces of attapulgite and presented a rather porous and dispersed morphology (Fig. 2C).

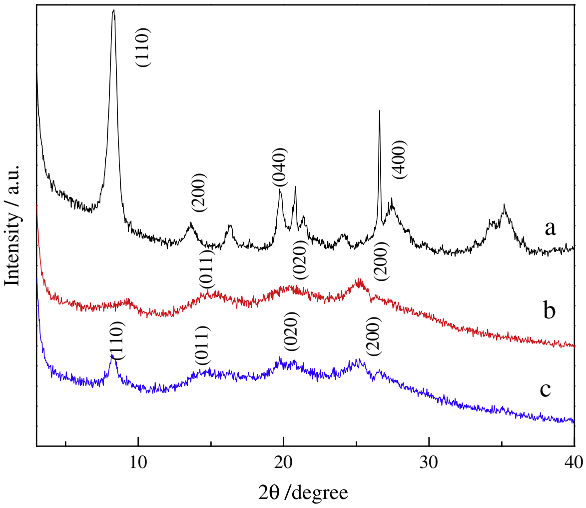

Fig. 1. XRD patterns of attapulgite (a), PANI (b) and attapulgite/PANI composite (c).