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Research paper

Template-based synthesis of uniform bimetallic nickel-tin oxide hollow nanospheres as a new sensing platform for detection of erythrosine in food products

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ABSTRACT

In this work, for the first time, uniform nickel and tin bimetallic oxide was synthesized by calcining the carbon nanospheres (CNSs) templates. This novel synthesized bimetallic oxide was used to fabricate a modified carbon paste electrode (Ni-Sn-oxide NSs/CPE). This electrode was used as a high sensitive sensor for voltammetric determination of erythrosine (Er) in 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 5.9). The synthesized bimetallic NSs were characterized by different techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and the X-ray diffraction (XRD). The hollow spherical nature of these Ni-Sn-oxide NSs was clearly revealed by the morphology studies. The dependence of oxidation peak current on pH of the solution, amount of modifier, scan rate, accumulation time and potential, interference effect and concentration of analyte were studied to optimize the experimental conditions. The experimental results suggested that the modified electrode have promoted electron transfer reaction for the oxidation of Er. The modified electrode exhibited effective surface area, more reactive sites and excellent electrocatalytic activity toward the oxidation of Er in two linear calibration ranges of 0.1–1 and 1–100 μmol L^{-1} with detection limit of 2.1 nmol L^{-1}. The novel proposed voltammetric method was successfully applied in the determination of Er in food products. The results indicated that the proposed method is sensitive, selective, fast and simple for determination of Er.

1. Introduction

Semiconductor metal oxides have attracted considerable attentions due to their distinctive and fascinating properties. Researches are being carried out to improve their efficiency to the maximum possible extent [1]. Principally two strategies were adopted: changes in preparation methods and/or adds another dopant. Mixed oxides of transition metals are capable of mutual interactions, leading to the formation of complex structure. It has been reported that the catalytic activity of mixed oxides is usually higher than that of their individual oxides [2–5]. Key to this success is the ability to obtain high surface to volume ratio and to control the electronic structure of these mixed oxides in contrast to conventional individual oxides, allowing their efficiency to be increased, or their optical and electronic properties to be changed.

Among metal oxides nanomaterials, NiO and SnO/SnO_2 and related materials have been a subject of intense research due to their unique characteristics and their potential applications in many areas that include electronics, photonics, magnetic, mechanics, and sensing [6–13]. Till now, several strategies have been proposed to improve the electrical properties of NiO and SnO_2 nanoparticles. Some of researchers believe that can change electroactivity of NiO and SnO_2 by changing their morphology. In this regard, researches in this field show that the various synthesis approaches provide versatile tools to control the size, shape, and compositional of the oxides nanoparticles [14]. In the other words, select the suitable synthesis method can produce NiO and SnO_2 nanostructures with high surface area such as nanoflowers [15], nanoplates [16], nanoparticles [17], nanorods [18], nanotubes [19], hollow spheres [20], nanoribbons, nanosheets, nano box-beams, and mesoporous structures [21]. The significantly higher electrical activity has been reported for the aforementioned structures [22]. Some of scientists believe that pasting NiO and particles with some conductive additive materials such as carbon nanotubes [23], graphene, graphene oxide [24] and ionic liquids [25] can also help to improve their electrochemical performance by accelerating the electron transformation among active materials. Recently, some other of researchers have found improved properties and

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multi-function for the Ni and Sn oxide nanomaterials through the fabrication of multi-components such as core/shell, heterostructure or intermetallic, alloyed and bimetallic structures [26–28].

Among the multi-components nanostructures, bimetallic oxides have received more attention due to their exotic properties arising from the synergistic effects between two metals and wide applications in many fields such as energy storage, catalysts, optical detection, biomedical applications, magnetic sensors, biosensors and electrochemical sensors. For example, Wu et al. have demonstrated that the CuO-ZnO nanocomposite increased the sensitivity of an electrochemical sensor for on-line carbon monoxide detection at high temperature [29]. Wang et al. prepared a series of nanosized coupled ZnO/SnO_2 photocatalysts and reported the excellent sensitivity of them in the degradation of methyl orange [30]. Uozumi et al. reported that a heterocontact of n- and p-type semiconducting metal oxides could show unique sensing properties [31]. They showed that CuO-infiltrated ZnO composite could enhance the access of gas molecules to individual electrocatalyst and hence promote gas sensitivity. Recently, great efforts have been devoted for improving the new physical and chemical properties derived from the bimetallic nickel-tin oxides. Compared with NiO and SnO_2, bimetallic nickel-tin oxides have been endowed with rich redox reactions and improved electric conductivity which are beneficial to broad electrochemical applications ranging from sensing sensors, catalyst, energy saving, battery and etc [32].

Considering that electrochemical efficiency of the materials strongly depend on their morphologies, a large number of studies in bimetallic nickel-tin oxides fields have been allocated to suggestion of novel morphologies of these bimetallic oxides. Up to now, various structures were reported for them such as hollow nanofibers, nanofibers, porous microcages, nanohelixes, spheres, hollow squares, nanorods [33]. Until now, among these nanostructures have not been reported hollow nanospheres for bimetallic nickel-tin oxides. The hollow nanostructures possessing high specific surface areas can offer abundant active sites for electrocatalysis, easy transport channels for electrolyte ions, and continuous passageways for charge carrier transport. For this reason, this kind of nanostructures fabrication is one of great scientific and technological interest. Over the past decades, many efforts have been made in the development of different methods for designing and fabrication of hollow nanospheres, such as chemical vapor deposition or epitaxy [34], layer by-layer technique [35], microemulsion [36], polymer/surfactant micellar templating [23], incorporating the metal cations into the shell of carbon spheres during the hydrothermal carbonization step [37], sacrificed templated or templated engaged replacement reaction [38], including hard ones such as monodispersed silica [39], or polymer latex spheres [40], reducing metal nanoparticles [41] and CNSs [42], as well as soft ones, for example, emulsion droplets/micelles [43] and even gas bubbles [44]. Structures prepared from these routes usually suffer from disadvantages related to high cost, tedious synthetic procedures and a low yield of hollow nanospheres with very thin walls which may prevent them from being used in large-scale applications. Therefore, it is desirable to develop a facile synthetic pathway to fabricate semiconductor hollow nanospheres of various compositions. Nevertheless, the control of the size, dimension, and composition of the building blocks of the hollow nanostructures in an expected manner is still a great challenge. In the present study, we demonstrate that highly uniform nickel-tin oxides hollow nanospheres can be synthesized successfully on a large scale by a controlled precipitation route (instead of adsorption) using urea as the precipitating agent in the presence of CNSs templates.

Until now, many electrochemical sensors derived from bimetallic oxides hollow nanospheres have been developed and utilized for the detection of different materials. But, among these nano structures no reports treated of bimetallic Ni-Sn oxides NSs as a sensor for determination of food colorants material.

Nowadays, determinations of food colorants have been become a hot topic because of the relationship between food, nutrition, and health. Food colorants are used for maintenance and improvement of color appearance in foods. Erythrosine (Er), is a synthetic colorant used in cherries, canned fruits, custard mix, sweets, bakery and snack foods. Excessive intake of Er can cause allergies, vomiting, bronchial, asthma, behavior disturbances, hyperactivity, central nervous system disturbances, renal or thyroid disorder, and hemolytic disorders [45]. Therefore, accurate determination of Er is very important. Presently, the analytical methods such as high performance liquid chromatography [46], capillary electrophoresis [47], thin layer chromatography [48], micellar electrokinetic chromatography [49], spectrophotometry [50] and electrochemical [51] methods have been reported for the detection of Er. Most of the methods listed are time consuming, expensive, need complicated and tedious preconcentration and the requirements for highly skilled personnel. Compared to these methods, the electrochemical techniques are attractive owing to their high sensitivity, reproducibility, inherent simplicity, ease of miniaturization, low cost and relatively short analysis time [52].

For the first time, we could synthesis a novel bimetallic oxides hollow nanospheres by a simple and cheap synthesis method and those were used to fabricate a modified carbon paste electrode (Ni-Sn-oxide NSs/CPE). This electrode was used as a high sensitive sensor for determination of Er in food samples. Up to now, no other works in the literatures have been reported on the preparation of a modified electrode by bimetallic Ni-Sn oxide on CPE.

2. Experimental

2.1. Reagents and solutions

All chemicals including, glucose (analytical grade), erythrosine (MW = 879.86 g mol^{-1}), ethanol (99.999% purity), sodium hydrogen phosphate, sodium dihydrogen phosphate, graphite powder (99.999% purity, −200 meshes), $NiCl_2{\cdot}6H_2O$ (MW = 237.71 g mol^{-1}), $SnCl_2{\cdot}2H_2O$ (MW = 225.63 g mol^{-1}), urea (MW = 60.06 g mol^{-1}), paraffin oil (density = 0.88 kg dm^{-3}), with the highest purity available were purchased from Merck (Darmstadt, Germany) and were used without further purification. All the solutions were prepared using double-distilled water. Phosphate buffer solution (PBS) in the range of pH 5–8 was prepared by mixing appropriate volumes of 0.1 mol L^{-1} $Na_2HPO_4{\cdot}12H_2O$ and 0.1 mol L^{-1} $NaH_2PO_4.H_2O$. A stock solution of 0.01 mol L^{-1} Er was prepared with double-distilled water and stored in under cover of darkness, which was diluted with double-distilled water to the desired concentration before use.

2.2. Apparatus

The electrochemical measurements, including cyclic voltammetry (CV), and differential pulse voltammetry (DPV) were carried out using a PalmSens analyzer at 25 ± 1 °C. A conventional three electrode cell was employed, incorporating a saturated Ag/AgCl electrode, a platinum wire and a modified CPE, which were used as the reference, auxiliary and working electrodes, respectively. DPV experiments were performed using the pulse amplitude of 0.025 V, pulse interval time of 0.05 s, and scan rate of 0.01 V s^{-1} over the potential range of 0.5–1.1 V *vs.* Ag/AgCl. All the pH values were measured with a Metrohm pH meter (model 827, Swiss made). Scanning electron microscope (SEM) images were obtained with Electroanalyzer Sama 500 and a model CM10 transmission electron microscope (TEM; Philips) was used to characterize the morphol-

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