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Original article

Preparation of chitosan/N-doped graphene natively grown on hierarchical porous carbon nanocomposite as a sensor platform for determination of tartrazine

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ABSTRACT

In this work, the chitosan and N-doped graphene natively grown on hierarchical porous carbon (N-PC-G/CS) nanocomposite was obtained by ultrasonic method, as a novel sensor platform for determination of tartrazine (TT). The nanocomposite as prepared had well dispersivity in water and excellent conductivity. The N-PC-G/CS nanocomposite was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption, fourier transform infrared (FTIR) and electrochemical impedance spectroscopy (EIS). The application of N-PC-G/CS for determination of tartrazine (TT) was investigated by chronocoulometry (CC), cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Under optimized conditions, the sensor displayed a sensitive response to TT within a wide concentration range of 0.05–15.0 μmol/L, the detection limits is 0.036 μmol/L (S/N = 3). Furthermore, this nanocomposite could be efficiently applied for determination of TT in soft drink samples.

1. Introduction

Tartrazine (TT) has been extensively used in peoples foods and drinks thanks to the excellent performance including brightness in color, inexpensive and free solubility in water, it also make foods more attractive. However, the TT would induce allergic and asthmatic reactions on the premise of intake some kinds of drugs (*e.g.* aspirin, benzoic acid), especially people with poor immunity [1]. More seriously, the studys have been reported that the excess level of TT can be harmful to health and cause diseases such as childhood hyperactivity, neurobehavioural poisonousness, reproductive toxicity and cancer [2–4]. Consequently, the use of TT in food products is strictly controlled by different national legislation. The United Nations Food and Agricultural Organization (FAO) and the World Health Organization (WHO) are identified and evaluated the acceptable daily intakes [5,6]. The use of TT has formulated maximum limit of 0.1 g/kg (GB2760-2014) in China. Thus, it is significantly important to control the content and detect the concentration of TT in foods quickly.

Up to date, many methods have been reported for determination of TT, including visable spectrophotometry [7], fluorescence emission spectrometry [8], high performance liquid chromatography (HPLC) [9] and HPLC with tandem mass detectors (HPLC-MS/MS) [10]. Recently, electrochemical methods have obtained more and more application for determination of TT, owing to the advantages of convenience, speediness, high sensitivity and friendly to environment. Meanwhile, TT has electrochemical activity due to containing nitrogen-nitrogen double bond and phenolic hydroxy groups [11]. For example, Qiu *et al.* used graphene oxide and multi-walled carbon nanotubes nanocomposite to modify glassy carbon electrode (GO/MWCNTs/GCE) for determination of TT [12]. Wang *et al.* used ionic liquid graphene oxides and multi-walled carbon nanotubes to modify GCE (IL-GO-MWCNTs/GCE) for determination of TT was developed too [13]. Song *et al.* used exfoliation of graphite to produce a

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highly-sensitive electrochemical sensor for determination of TT [14]. It was reported that Cheng *et al.* used porous carbon to modify GCE (PC/GCE) for determination of TT [11].

N-Doped graphene natively grown on hierarchical porous carbon (N-PC-G), a novel nitrogen-doped hybrid carbon material, which is composed of hierarchical porous carbon micro blocks interconnected with in-situ grown graphene, has been reported by Liang *et al.* Remarkably, owning to the satisfactory structural properties, including large surface area, accessibility and good conductivity, this metal-free material has been used for electrochemical applications [15]. However, like porous carbon or graphene, N-PC-G is hydrophobic and tends to agglomerate irreversibly which limit its further application [16,17]. Chitosan (CS), has been widely used for constructing sensors not only its dramatic properties including excellent film-forming ability, good adhesion and avirulence, but also its protonated to polycationic material in acid media and facilitates the electron transfer after its swelling in reaction mixture due to its hydrophilic nature [18–20]. In this paper, a kind of functionalized nanocomposite was prepared *via* a simple ultrasonic method of N-PC-G with CS. Furthermore, the prepared nanocomposite (N-PC-G/CS) was used as a novel electrochemical sensor platform for determination of TT and applied to soft drinks samples.

2. Results and discussion

2.1. Characterization of PC N-PC and N-PC-G

The morphology of prepared N-doped porous carbon (N-PC) and N-doped graphene natively rooted on hierarchical porous carbon (N-PC-G) samples were analysed using the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1A shows the SEM images of the N-PC product, it was found that the ordered macropores of N-PC arranged regularly, and the diameter was about 150 nm. The images of the N-PC-G clearly show that typically crumpled and wrinkled of these graphene nanosheets, indicating it grown in-situ in porous carbon successfully (Fig. 1B). For observing further information of the samples microstructure, high resolution TEM measurement was employed, as shown in Fig. 1C. N-PC-G has a large number of mesoporous and microporous which located at the walls of large 3D ordered macropores, the diameter of the macropores measured from TEM images is about 150 nm, which is consistance with the SEM observations.

In order to investigate and compare the status of elements in materials of analyzed by X-ray photoelectron spectroscopy (XPS). The survey sweep shows that primary elements of C1s N1s and O1s in samples Fig. 2A, and the atomic percentages are calculated to be 93.11%, 3.38% and 3.51%, indicating that nitrogen of successfully doped in hybrid carbon materials. The high resolution XPS scans C1s spectrum in Fig. 2B can be deconvoluted into four peaks, the higher peak at 284.7 eV is mainly close to the sp^3 C—C bond in aromatic ring, another peak at 286.6 eV corresponds to C—OH, which is commonly observed on carbon material [21]. The emergence of the peak at 288.9 eV corresponding to C—N—C coordination suggested the bonding formation of doped nitrogen atoms to be sp^3-C atoms, respectively [22]. And the enhancement of the peak at 292.05 eV corresponds to —COOH coordination [23]. The N1s peak can be also deconvoluted into three components (as shown in Fig. 2C), and the fitted peaks at 401.2, 399.5 and 398.2 eV are consistent with pyridinic-N, pyrrolic-N and graphitic-N [23,24].

The porosity of the materials was analyzes by nitrogen adsorption–desorption (Fig. 2D). The isotherm of N-PC-G shows significant hysteresis loop extending from 0.05 to 1.0, which indicate that porous carbon are consisting of mesopores and macropores, the raised adsorption amount at low pressure ($P/P_0 < 0.05$) also suggests the existence of micropores. N-PC-G have a high BET surface area (541.627 m^2/g) and the mesoporous size was calculated by BJH method is approximately 4.1 nm, which is consistance with the TEM observations.

Fourier transform infrared (FTIR) spectrum was taken to illustrate intermolecular interactions between components in the novel nanocomposites. Fig. 3A shows the FT-IR spectra of CS, N-PC-G and N-PC-G/CS. For CS, the spectrum showed the typical characteristic absorption bands, which are bands of peaks around 1045, 1087, 1153 cm^{-1} corresponding to the C—O stretching vibrations (ν(C—O—C)), while 1411 cm^{-1} and 1658 cm^{-1} are the characteristic peaks of CH_3 symmetrical deformation mode and carbonyl group (C=O), and characteristic bands of peaks around 3421 cm^{-1} corresponding to the stretching vibration of N—H [25]. Moreover, the characteristic stretching frequency of N-PC-G was observed which are CH, ν(COOH) and OH at 1217 cm^{-1}, 1666 cm^{-1} and 3437 cm^{-1}, which are consistance with the XPS observations. Especially, FT-IR spectrum of N-PC-G/CS nanocomposites depicted a sharp and strong absorbance at 1638 cm^{-1} (corresponding to amide group), indicating that the —COOH groups of N-PC-G reacted with the $—NH_2$ of CS and converts it to amide (—CONH—) group [26]. This unique band frequency clearly indicates the formation of new bonds between CS and N-PC-G.

Fig. 3B shows the digital photographs that are aqueous dispersions of N-PC-G (a), and CS modified N-PC-G (b) stand 24 h after ultrasonication. It was found that the N-PC-G suspended in water eventually settled down after a period time, but the addition of CS resulted in a black colloidal dispersions without visible precipitation, implying that the colloidal dispersion of N-PC-G/CS have good dispersion and found to be stable for at least months.

2.2. Electrochemical characterization the interface of different modified electrodes

The different electrodes evaluate the conductivity by using electrochemical impedance spectroscopy (EIS). Fig. 3C shows the

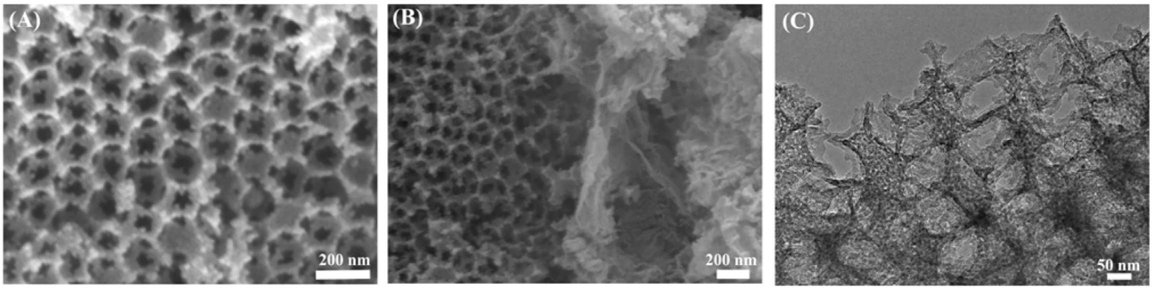

Fig. 1. Typical SEM (scale bar = 200 nm) images of (A) N-PC (B) N-PC-G and (C) TEM (scale bar = 50 nm) images of N-PC-G.