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Highly-sensitive electrochemical sensing platforms for food colourants based on the property-tuning of porous carbon

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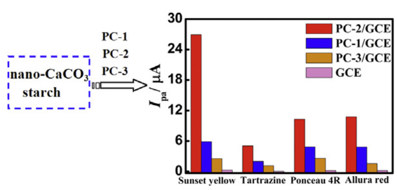
HIGHLIGHTS

- PC samples with different morphology and electrochemical activities were prepared.
- Highly sensitive electrochemical sensing platform was developed for food colourants.
- The accuracy and practicability was testified to be good by HPLC.

GRAPHICAL ABSTRACT



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ABSTRACT

It is very challenging to develop highly-sensitive analytical platforms for toxic synthetic colourants that widely added in food samples. Herein, a series of porous carbon (PC) was prepared using $CaCO_3$ nanoparticles (nano-$CaCO_3$) as the hard template and starch as the carbon precursor. Characterizations of scanning electron microscopy and transmission electron microscopy indicated that the morphology and porous structure were controlled by the weight ratio of starch and nano-$CaCO_3$. The electrochemical behaviours of four kinds of widely-used food colourants, Sunset yellow, Tartrazine, Ponceau 4R and Allura red, were studied. On the surface of PC samples, the oxidation signals of colourants enhanced obviously, and more importantly, the signal enhancement abilities of PC were also dependent on the starch/nano-$CaCO_3$ weight ratio. The greatly-increased electron transfer ability and accumulation efficiency were the main reason for the enhanced signals of colourants, as confirmed by electrochemical impedance spectroscopy and chronocoulometry. The prepared PC-2 sample by 1:1 starch/nano-$CaCO_3$ weight ratio was more active for the oxidation of food colourtants, and increased the signals by 89.4-fold, 79.3-fold, 47.3-fold and 50.7-fold for Sunset yellow, Tartrazine, Ponceau 4R and Allura red. As a result, a highly-sensitive electrochemical sensing platform was developed, and the detection limits were 1.4, 3.5, 2.1 and 1.7 $\mu g\ L^{-1}$ for Sunset yellow, Tartrazine, Ponceau 4R and Allura red. The practical application of this new sensing platform was demonstrated using drink samples, and the detected results consisted with the values that obtained by high-performance liquid chromatography.

1. Introduction

Synthetic colourants have been widely added in foodstuffs thanks to their fascinating properties such as excellent colour uniformity, good water solubility, low production cost and high stability. However, most synthetic colourants are pathogenic, particularly if they are excessively consumed [1–4]. Therefore, it is

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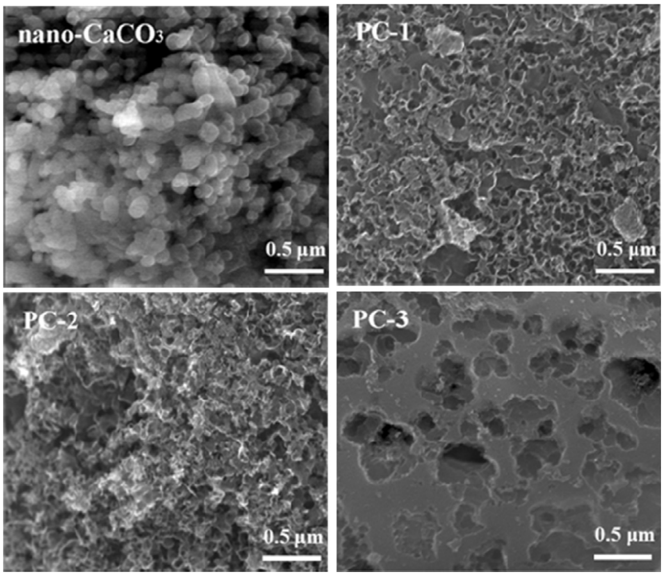

Fig. 1. SEM images of nano-$CaCO_3$, PC-1, PC-2 and PC-3.

worthwhile and important to develop sensitive, rapid and simple detection platforms for toxic synthetic colourants, for guaranteeing the food quality and the consumers' safety.

Until now, various techniques have been developed for the detection of synthetic colourants, including spectrophotometry [5], high-performance liquid chromatography with ultra violet/diode array detector (HPLC-UV/DAD) [6], ultra performance liquid chromatography with photo diode array detector (UPLC-PDA) [7], and HPLC with tandem mass detectors (HPLC-MS/MS) [8]. Recently, electrochemical detection has obtained more and more application in the field of food safety analysis due to following advantages such as good handling convenience, speediness, high sensitivity, automatics and in situ monitoring. From the molecular structures, we clearly found that most synthetic colourants are electrochemical active because they contain –N=N– and phenolic hydroxy groups. So, a number of electrodes have been developed for the electrochemical determination of food colourants. For example, hanging mercury drop electrode (HMDE) was used for the detection of Tartrazine and Sunset yellow based on the reduction of –N=N– group [9]. Besides, alumina microfibers modified-carbon paste electrode (CPE) was reported for the determination of Sunset yellow [10]. Based on the signal enhancement of multi-walled carbon nanotubes (MWCNT)-modified glassy carbon electrode (GCE), sensitive electrochemical methods were also developed for the determination of Ponceau 4R and Allura Red [11]. Using graphene-phosphotungstic acid hybrid (GN-PTA) film-modified GCE, Sunset yellow and Tartrazine were successfully detected [12]. In addition, a modified GCE by ionic liquid, graphene oxides and MWCNT (IL-GO-MWCNT/GCE) were also developed for the simultaneous determination of Ponceau 4R, Allura Red and Tartrazine [13].

Porous carbon (PC) has attracted tremendous attention because of a large variety of remarkable properties including large surface area, tunable pore size over a wide range, strong accumulation ability and high stability. Until now, they exhibit significant potential in many applications, including catalysis [14,15], absorbents [16], energy storage [17,18] and sensing [19–25]. Among various preparation methods, nanocasting strategy using hard template or soft template has been proven to be the most efficient way to prepare PC with high specific surface area and uniform pores. Herein, a series of PC samples were prepared using $CaCO_3$ nanoparticles (nano-$CaCO_3$) as the template and starch as the carbon precursor. Interestingly, we found that the morphology and porous structure of PC samples were easily tuned by changing the weight ratio of starch and nano-$CaCO_3$. More importantly, the signal enhancement abilities of PC samples toward the oxidation of food colourants were also controlled by the starch/nano-$CaCO_3$ weight ratio. On the surface of different PC samples, the electron transfer rate and accumulation abilities of food colourants showed great difference, resulting in different oxidation signals. As a result, a novel PC sensing material with higher electrochemical reactivity and stronger signal enhancement effects was achieved. Toward the oxidation of Sunset yellow, Tartrazine, Ponceau 4R and Allura red, the resulting PC sample enhanced their oxidation signals by 89.4-fold, 79.3-fold, 47.3-fold and 50.7-fold. These encouraging results manifest that the prepared porous carbon is totally qualified for constructing a highly-sensitive analytical platforms for these widely-used synthetic food colourants.

2. Experimental section

2.1. Reagents

All chemicals were of analytical grade and used directly. 1.0 mg mL^{-1} stock solutions of Sunset yellow, Tartrazine, Ponceau 4R and Allura red (Sigma, USA) were individually prepared using ultrapure water, and stored at 4 °C. Starch and DMF were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). $CaCO_3$ nanoparticles with diameter of 100 nm were provided by Shanxi Xintai NanoMater. Co., Ltd. (Shanxi, China). Ultrapure water (18.2 MΩ) was obtained from a Milli-Q water purification system and used throughout.

2.2. Instruments

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode system. The working electrode was a PC-modified GCE, the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum wire. Scanning electron microscopy (SEM) was performed

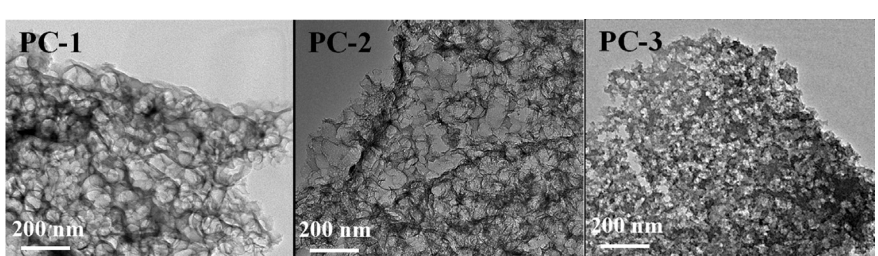

Fig. 2. TEM images of PC-1, PC-2 and PC-3.