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Morphology-tuned preparation of nanostructured resorcinol-formaldehyde carbonized polymers as highly sensitive electrochemical sensor for amaranth

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ABSTRACT

Three kinds of nanostructured resorcinol-formaldehyde (RF) carbonized polymers were prepared in different acidic solutions such as 0.2 M HCl, 0.2 M H_2SO_4 and 0.2 M HAc. Measurements of scanning electron microscopy and nitrogen adsorption-desorption isotherms indicated that the morphology and surface area of the prepared polymers were heavily dependent on the used reaction medium. The oxidation behaviors of amaranth revealed that the prepared polymers displayed different electrochemical reactivity toward the oxidation of amaranth. On the surface of RF carbonized polymers, the oxidation signals of amaranth enhanced obviously, and the prepared RF-1 carbonized polymer in 0.2 M HCl was more active for the oxidation of amaranth. As a result, a novel electrochemical sensor with high sensitivity was developed for amaranth. It was used in the drink sample analysis, and the detected results consist with the values that obtained by high-performance liquid chromatography.

1. Introduction

In recent years, the abuse of food additives has obtained considerable attention. Synthetic colorants, especially azo dyes, have been considered as the largest group of food additives, and been widely used due to their fascinating properties. However, it is essential to be noted that most synthetic colorants are pathogenic, particularly when they are consumed in large amounts [1–3]. Amaranth, a typical and extensively-applied azo food colourant, has been strictly controlled in foodstuffs [4]. Therefore, it is quite important to study sensitive, rapid and convenient analytic methods for amaranth. Due to the unique properties such as high sensitivity, rapidness, good handling convenience and low cost, electrochemical sensor has obtained more and more attention. Until now, different electrochemical methods have been developed for the determination of amaranth [5–10], however, the detection sensitivity is relatively low.

Nanostructured resorcinol-formaldehyde (RF) polymers, a three-dimensional network polymers, are highly fascinating due to their attractive properties such as large surface areas, high porosities, controllable pore structures, remarkable electrical conductivity and outstanding thermal and mechanical properties [11,12]. Pekala and co-workers [13] appear to have been the first to synthesize RF organic sol-gels according to a hydrolysis-condensation reaction mechanism that is analogous to the sol-gel synthesis of inorganic oxides. After pyrolysis, the resulting RF organic sol-gels were carbonized and RF polymers were prepared. Overall, the preparation of RF polymers undergoes three main stages. The first stage is the preparation of wet gel, which involves preparing the sol mixture and the subsequent gelation and curing of the gel. The second stage is drying the wet gel, and the third stage is the pyrolysis (carbonization) [11]. Until now, RF polymers exhibit significant potential in many applications such as separation [14], catalysis [15] and energy storage [16].

In this work, three kinds of resorcinol-formaldehyde carbonized polymers (RF) were prepared in different acidic solutions, and we found that their morphology and surface area were heavily dependent on the reaction medium. Moreover, the prepared nanostructured polymers exhibited different signal enhancement abilities toward the oxidation of amaranth, and the enhancement mechanism was discussed. Based on the morphology-controlled electrochemical enhancement of RF carbonized polymers, a novel sensing system with high sensitivity was developed for the rapid detection of amaranth.

2. Experimental section

2.1. Reagents

All chemicals were of analytical grade and used as received. 0.01 M standard solution of amaranth (Sigma) was prepared using ultrapure water, and stored at 4 °C. Pluronic P123 ($M_{av} = 5800$, $EO_{20}PO_{70}EO_{20}$) was purchased from Sigma-Aldrich. Resorcinol, formaldehyde (37 wt%), HCl (37 wt%), graphite powder (micrometer size, spectral

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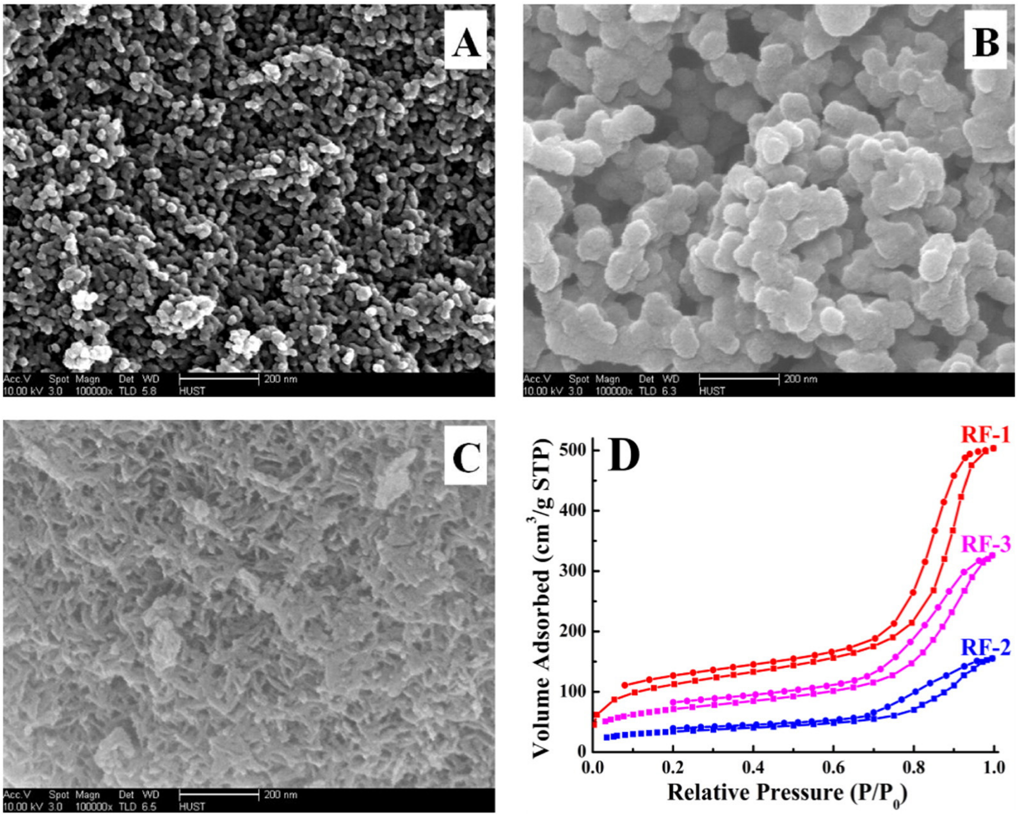

Fig. 1. SEM images (A–C) and nitrogen sorption isotherms (D) of RF-1, RF-2 and RF-3.

reagent) and paraffin oil were purchased from Sinopharm Chemical Reagent Company (Shanghai, 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 660E electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode system. The working electrode was a modified carbon paste electrode (CPE) with diameter of 3 mm, the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum wire. Scanning electron microscopy (SEM) characterization was conducted with a Quanta 200 microscope (FEI Company, Netherlands). Nitrogen adsorption-desorption isotherms were obtained on an ASAP 2020 analyzer.

High-performance liquid chromatography (HPLC) determination of amaranth was carried out with an Agilent 1100, coupled with UV–VIS detector. The C18 analytical column (4.6 mm × 150 mm × 5 μm) was used. The gradient mobile phase was acetate buffer containing of 20 mM ammonium acetate and 1% acetic acid (A) and methanol (B), filtered through 0.45-μm Millipore filter prior to use. The linear gradient elution was programmed as follows: 0–5 min, 20–35% B; 5–12 min, 35–100% B; 12–30 min, 100% B; 30–31 min, 100–20% B; 31–35 min, 20% B. The flow rate was 1 mL min^{-1} while the column temperature was maintained at 30 °C. The sample injection volume was 20 μL, and the detection was performed at a wavelength of 254 nm [17].

2.3. Preparation of carbonized polymers

Firstly, 0.30 mmol of P123 was dissolved in 45.0 mL of 0.2 M HCl to form a clear solution. Subsequently, 70.00 mmol of formaldehyde and 50.00 mmol of resorcinol were added under stirring. After 2-h reaction and washing, the resulting polymer gel phase was dried at 80 °C for 24 h. Finally, the sample was carbonized at 350 °C for 3 h under a N_2 atmosphere, and the produces were indicated as RF-1. For examining the effects of medium, another two carbonized polymers were also prepared according to above procedure using 0.2 M H_2SO_4 (RF-2) and 0.2 M HAC (RF-3).

2.4. Construction of electrochemical sensor

The prepared samples (0.10 g) and graphite powder (0.90 g) were exactly weighed, and then put in a carnelian mortar. The total mass was controlled at 1.0 g and the mass content of carbonized polymer was 10%. After that, 0.20 mL paraffin oil was added into the powder and then mixed homogeneously. Finally, the resulting carbon paste was tightly pressed into the end cavity of electrode body, and the electrode surface was polished on a smooth paper. The unmodified CPE was prepared just using 1.0 g graphite powder and 0.20 mL paraffin oil.

2.5. Analytical procedure

0.1 M phosphate buffer with pH of 6.0 was used as the supporting electrolyte for the detection of amaranth. After 2-min accumulation at 0.4 V, the differential pulse voltammograms were recorded from 0.40 to 1.00 V, and the oxidation peak current at 0.72 V was measured as the analytical signal for amaranth. The pulse amplitude was 50 mV, the pulse width was 40 ms, and the scan rate was 40 mV s^{-1}.

3. Results and discussion

3.1. Characterization of the prepared polymers

The morphology of the prepared carbonized polymers in 0.2 M HCl, 0.2 M H_2SO_4 and 0.2 M HAc were studied using SEM, and results were shown in Fig. 1. It was found that the obtained RF-1 samples in 0.2 M HCl consisted of spherical nanoparticles, and particle size was about 25 nm. For the RF-2 samples that prepared using 0.2 M H_2SO_4, the

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