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Electrochemical enhancement of acetylene black film as sensitive sensing platform for toxic tetrabromobisphenol A

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Abstract

Developing sensitive and simple analytical methods for tetrabromobisphenol A (TBBPA) is very important because TBBPA is widely existed in the environment and the biological toxicity is high. Herein, three kinds of acetylene black (AB) films with different morphology and electrochemical reactivity were prepared, and then used to construct different electrochemical sensors for TBBPA. On the surface of AB films, the direct oxidation signals of TBBPA increase greatly, and moreover, the prepared AB films exhibit different enhancement ability toward TBBPA oxidation. The

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influences of pH value, amount of AB particles and accumulation time were studied on the oxidation signals of TBBPA. As a result, a sensitive electrochemical sensor based on the remarkable enhancement effects of AB film was developed for the rapid detection of TBBPA. The linear range was from 10 to 350 μg L^{-1}, and the detection limit was 6.08 μg L^{-1} (cal. 11 nM). This new sensing system was used for the analysis of TBBPA in water samples, and good recoveries in the range of 99.3 ~ 104.5% were obtained.

Key words: Tetrabromobisphenol A (TBBPA); Electrochemical sensor; Rapid determination; Acetylene black; Signal enhancement

1. Introduction

Tetrabromobisphenol A (TBBPA), the most widely produced brominated flame retardant, has been extensively used in electronic equipments. TBBPA has been regarded as a permanent organic pollutant, and studies have proved its biological toxicities such as immunotoxicity [1], endocrine effects [2], nephrotoxicity [3], developmental toxicity [4] and anti-thyroid hormonal activity [5]. Until now, a number of methods such as high-performance liquid chromatography (HPLC) [6], liquid chromatography-mass spectrometry (LC-MS) [7], gas chromatography-mass spectrometry (GC-MS) [8] and enzyme-linked immunosorbent assay (ELISA) [9] have been reported for the determination of TBBPA.

Compared with chromatographic and immunosensing methods, electrochemical

determination is superior in terms of rapidness, handling convenience, low cost and in-situ monitoring. Although indirect electrochemical methods based on the catalytic effects of $[Fe(CN)_6]^{3-/4-}$ and the signals of $[Fe(CN)_6]^{3-/4-}$-TBBPA complex have been developed for the determination of TBBPA [10], the studies regarding direct electrochemical detection of TBBPA are very limited. Therefore, it is still full of challenge to develop convenient, rapid and sensitive electrochemical platform for the direct determination of TBBPA.

Acetylene black (AB) is a special kind of carbon material with a number of extraordinary properties, including high electric conductivity, regular nanopores, efficient ionic paths, large surface area and good stability [11-14]. These features indicate that AB is an excellent sensing material for construction of high-performance electrochemical sensors. However, the soluble ability of AB particles is very low, and it is very crucial to obtain homogeneous AB sensing film. Herein, AB particles were dispersed into different systems by ultrasonication, including dimethyl formamide (DMF), chitosan (CS) aqueous solution, and the mixture of dihexadecyl hydrogen phosphate (DHP)/water. After that, three kinds of AB films were prepared *via* evaporating solvent, and denoted as AB film, AB-CS film and AB-DHP film. Interestingly, we find that the prepared AB films exhibit different surface morphology and electrochemical reactivity. Moreover, the resulting AB films display different signal enhancement ability toward the oxidation of TBBPA, and the AB film that prepared by AB-DMF suspension is much more active for the oxidation of TBBPA, reflected by the greatly-increased oxidation signals. Based on the remarkable

enhancement effects of AB film, a sensitive, simple and rapid electrochemical method has been successfully developed for the direct determination of TBBPA.

2. Experimental section

2.1. Reagents

All chemicals were of analytical grade and used as received. A stock solution of 2.0 mg mL^{-1} TBBPA (from Lab of Dr. Ehrenstorfer, German) was prepared with ethanol, and stored at 4 ^{o}C. AB particles (purity > 99.99%) were purchased from STREM Chemicals (USA). Dihexadecyl hydrogen phosphate (DHP) was obtained from Sigma (USA). Chitosan (CS) (degree of deacetylation ≥ 90%) and DMF were obtained 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 660A electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode system. The working electrode was an AB film modified glassy carbon electrode (GCE), 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). Particle size analysis was performed with a LB-550 Dynamic Light

Scattering Particle Size Analyzer (HORIBA, Japan). Atomic force microscopy (AFM) was performed with a SPM 9700 microscope (Shimadzu, Japan).

2.3. Preparation of AB films

To prepared different AB suspension solutions, 10.0 mg of AB samples were individually added into 5.0 mL of DMF, 5.0 mL of 0.02 M HAc solution containing 0.02% CS or 5.0 mL of water containing 10.0 mg DHP. After 3-h ultrasonication, three AB suspensions (i.e. AB-DMF, AB-CS and AB-DHP) at a concentration of 2.0 mg mL^{-1} were obtained. After that, a GCE with a diameter of 3.0 mm was polished with 0.05 μm alumina slurry, and ultrasonically washed using ultrapure water to give a clean surface. Finally, 2.0 μL of the AB suspensions was cast onto the surface of GCE, and dried under an infrared lamp in air. The resulting AB films were denoted as AB film, AB-CS film and AB-DHP film.

2.4. Analytical procedure for TBBPA

0.1 M acetate buffer solution with pH of 4.6 was used as the supporting electrolyte for the electrochemical determination of TBBPA. Differential pulse voltammograms were recorded from 0.20 to 0.70 V after 4 min accumulation, and the oxidation peak current at 0.57 V were measured for the analysis of TBBPA. The pulse amplitude was 50 mV, the pulse width was 50 ms, and the scan rate was 40 mV s^{-1}.

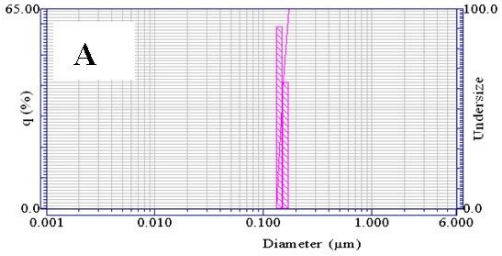
2.5. Sample analysis

Various types of water samples were collected from different lakes in Wuhan City, and filtered using a cellulose acetate filter with a pore size of 0.45 μm. The obtained sample solution was stored at 4 °C before measurement. When determining TBBPA, 5.00 mL of sample solution was added into 5.00 mL, 0.2 M acetate buffer (pH 4.6), and analyzed according to analytical procedure.

3. Results and discussion

3.1. Characterization of different AB films

To compare the properties of different AB suspensions, the particle size distributions were measured. From Fig. 1, we clearly find that the particle size distribution of AB-DMF suspension is much narrower, suggesting that the AB particles that dispersed in DMF is more uniform. In addition, the average particle size was determined to be 148.8, 253.1 and 377.2 nm for the suspension of AB-DMF, AB-DHP and AB-CS suspensions. The smaller average particle size and more uniform distribution manifest that the dispersion ability of AB particles in DMF is superior.



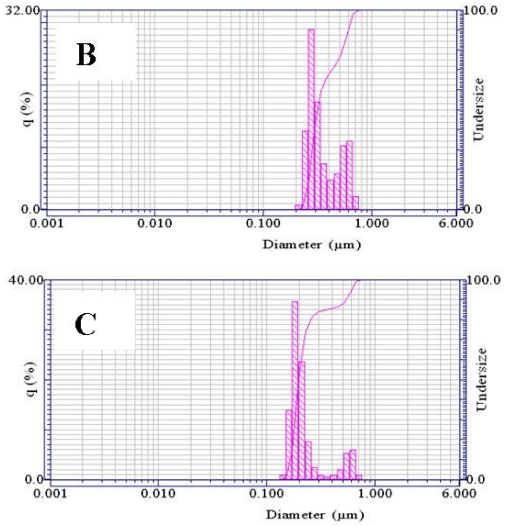


Fig. 1 Particle size distributions of AB-DMF (A), AB-CS (B) and AB-DHP suspensions (C).

The surface morphology of different AB films was characterized by SEM, and the results were shown in Fig. 2. The surface of unmodified GCE is very smooth (A), and a number of spherical particles are clearly observed on GCE surface after modification with AB-DMF suspension (B), AB-CS suspension (C) and AB-DHP suspension (D). Furthermore, AFM was used to further characterize the surface structures on different GCEs. From the comparison that shown in Fig. 3, it is apparent that the modification of AB particles obviously enhances the surface roughness of GCE. Moreover, we clearly find that the surface morphology of the prepared AB films shows great difference. The AB film that prepared using AB-DMF suspension exhibits higher surface roughness and contains more three-dimensional structures, likely providing larger sensing area and higher accumulation efficiency.

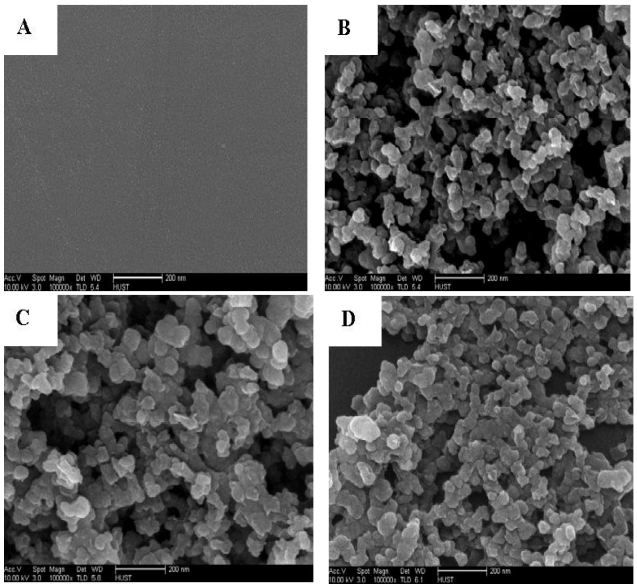


Fig. 2 SEM images of GCE (A) and modified GCEs with AB film (B), AB-CS film (C) and AB-DHP film (D).

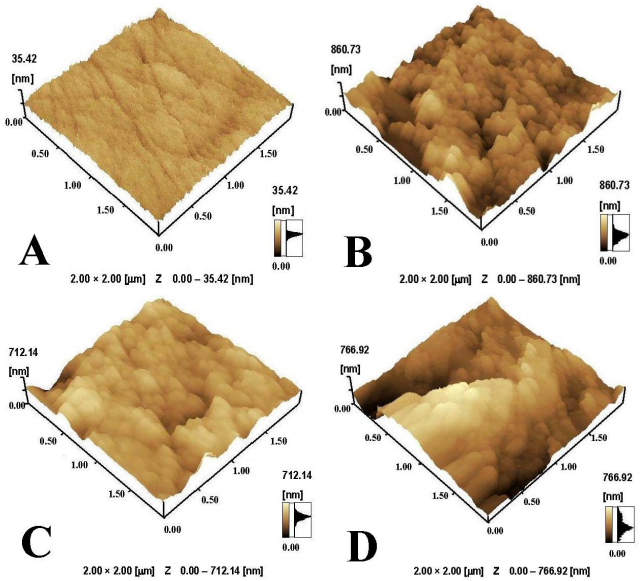


Fig. 3 AFM images of GCE (A) and modified GCEs with AB film (B), AB-CS film (C) and AB-DHP film (D).

The electrochemical sensing areas of different AB films were measured using ferrocene (Fc) as the probe. Fig. 4 shows the cyclic voltammograms (CV) of Fc on the

bare GCE (curve a) and modified GCEs with AB-CS film (AB-CS/GCE, curve b), AB-DHP film (AB-DHP/GCE, curve c) as well as AB film (AB/GCE, curve d). A pair of redox peaks with peak potential separation (ΔE_p) of 75 mV is observed, and the peak currents increase on all the AB film modified GCEs, compared with those of the bare GCE. Moreover, when increasing the scan rate (v) from 0.05 to 0.25 V s^{-1}, the redox peak potentials remain unchanged, but the oxidation peak currents (I_{pa}) increase linearly with the square root of scan rate. Therefore, the electrode reactions of Fc on these electrodes are all nearly reversible and diffusion-controlled processes. So the effective sensing areas (A) for different electrodes can be calculated according to Randles-Sevcik equation. Here, the values of A were calculated to be 0.0479, 0.0553, 0.0592, and 0.0682 cm^2 for GCE, AB-CS/GCE, AB-DHP/GCE and AB/GCE, respectively. The difference of effective sensing areas indicates that the AB films prepared by different methods exhibit different electrochemical reactivity. As indicated in Fig. 2 and Fig. 3, the AB film prepared from the DMF dispersion solution is more uniform and porous, and thus creates an apparently larger electrochemical sensing surface.

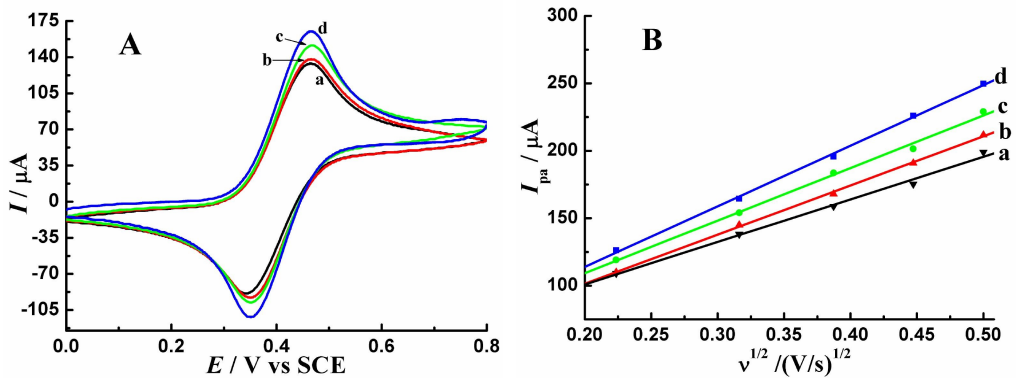


Fig. 4 (A) Cyclic voltammograms of 5 mM Fc in 0.1 M tetrabutylammonium

perchlorate on GCE (a), AB-CS/GCE (b), AB-DHP/GCE (c) and AB/GCE (d), scan rate, 100 mV s^{-1}; (B) Dependence of oxidation peak currents of Fc on the scan rate.

3.2. Signal enhancement effects of AB films

The oxidation behaviors of trace levels of TBBPA on different AB films were compared using differential pulse voltammetry (DPV). Fig. 5A shows the DPV curves of TBBPA on different AB films, and Fig. 5B illustrates the variation of oxidation peak currents of TBBPA. On the surface of bare GCE (curve b), an oxidation peak at 0.60 V is observed for 100 μg L^{-1} TBBPA. The peak height is relatively low, revealing that the oxidation activity of TBBPA on GCE surface is poor. When using AB-CS film (curve d), the oxidation wave of TBBPA increase by 1.5-fold, suggesting that the AB-CS film enhances the oxidation activity of TBBPA. It is necessary to be noticed that the oxidation activities of TBBPA further increase obviously on the surface of AB-DHP/GCE (curve f) and AB/GCE (curve h). Compared with the values on bare GCE, the oxidation peak currents of TBBPA are individually enhanced by 3.5-fold and 6.0-fold on the AB-DHP film and AB film. From Fig. 5B, we clearly find that the oxidation signals of TBBPA on different electrodes consist with the sequence of AB/GCE > AB-DHP/GCE > AB-CS/GCE > GCE. The different electrochemical behaviors of TBBPA on different GCEs may be interpreted with the different electrochemical property and structure of different electrodes. As testify above, the AB film resulted from AB-DMF suspension consists of uniform and smaller particles, and displays larger response area. Undoubtedly, the obtained AB film exhibits higher

electrochemical reactivity toward the oxidation of TBBPA. In addition, the DPV curves on different electrodes in the absence of TBBPA were also recorded. No oxidation peaks appear, suggesting that the oxidation wave is attributed to TBBPA.

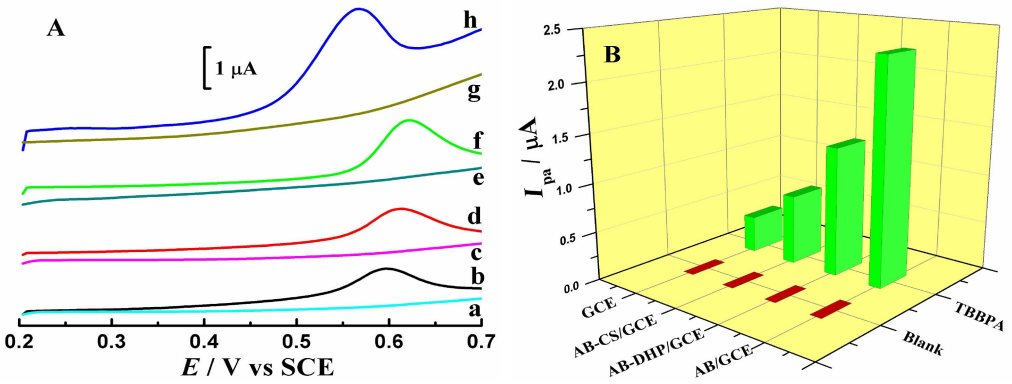


Fig. 5 (A) DPV curves on GCE (a, b), AB-CS/GCE (c, d), AB-DHP/GCE (e, f) and AB/GCE (g, h) in 0.1 M acetate buffer (pH 4.6) (a, c, e, g) and in the presence of 100 μg L^{-1} TBBPA (b, d, f, h); (B) Three-dimensional histogram of oxidation peak currents of TBBPA on different electrodes. Accumulation time: 4 min.

3.3. Electrochemical determination of TBBPA

The electrochemical behaviors of 5.0 mg L^{-1} TBBPA in 0.1 M acetate buffer solutions with different pH values were studied using cyclic voltammetry (CV) to discuss the influences of pH value. During the cyclic sweep from 0.20 to 0.90 V, just an oxidation wave is observed for TBBPA on different GCEs such as GCE, AB-CS/GCE, AB-DHP/GCE and AB/GCE, indicating an irreversible electrode process. When gradually improving pH value from 3.6 to 5.6, the oxidation peaks shift negatively, revealing that protons are involved in the oxidation process. Fig. 6 shows the oxidation peak currents of TBBPA on different GCEs with the variation of

pH values. It is found that the oxidation signals of TBBPA enhance gradually when increasing pH value from 3.6 to 4.6, and then gradually decrease with further improving pH values. For achievement of higher response signals, 0.1 M acetate buffer with pH of 4.6 is used for the detection of TBBPA.

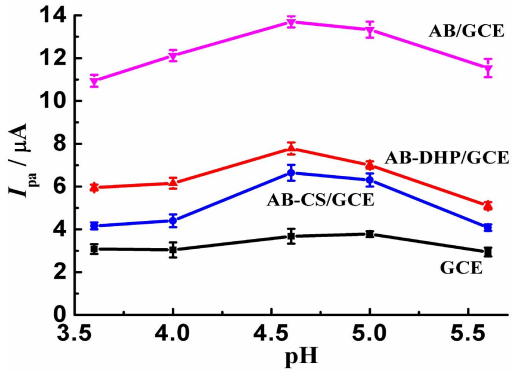


Fig. 6 Variation of oxidation peak currents of 5.0 mg L^{-1} TBBPA with pH values on different GCEs, scan rate: 100 mV s^{-1}.

The influences of accumulation conditions on the oxidation signal of TBBPA were examined. When the accumulation potentials alter from 0 to 0.40 V, the oxidation peak currents of TBBPA hardly change, suggesting the small influence of accumulation potential. However, the influence of accumulation time is apparent (Fig. 7A), i.e., the oxidation peak currents of TBBPA firstly increase with accumulation time in the range of 0 ~ 4 min and tend to be stable thereafter. Considering sensitivity and detection efficiency, an accumulation period of 4 min is employed.

Fig. 7B illustrates the effect of the modifier amount of the AB-DMF suspension on the response of TBBPA. It is found that the oxidation peak currents of TBBPA increase remarkably by enlarging the amount of AB-DMF suspension from 0 to 2.0

μL, and tend to be stable with higher modifier amounts. Therefore, 2.0 μL of AB-DMF suspension is employed for the modification of GCE.

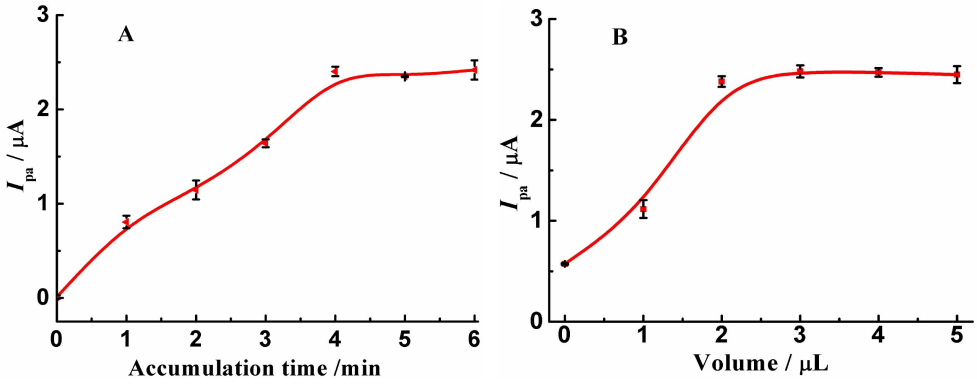


Fig. 7 Influences of accumulation time (A) and amount of AB-DMF suspension (B) on the oxidation peak currents of 100 μg L^{-1} TBBPA. Other conditions were the same as Fig. 5. Error bars represent the standard deviations of three measurements.

Under the optimized working conditions, the linear range and detection limit of AB/GCE for the detection of TBBPA were evaluated by DPV. As shown in Fig. 8, the oxidation peak currents (I_{pa}, μA) increase linearly with the concentration of TBBPA (C, μg L^{-1}) over the range from 10 to 350 μg L^{-1}. The linear regression equation is I_p = 0.02219 C, and the correlation coefficient is 0.998. The detection limit, defined by three signal-to-noise ratios (S/N=3), is calculated to be 6.08 μg L^{-1} (11 nM). The relative standard deviation (RSD) was 4.5% for the parallel detection of TBBPA on ten AB/GCE, indicative of good reproducibility. The influences of potential interferents on the detection of TBBPA were also studied. It is found that 0.2 μM metal ions including Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, 2.0 μM phenols like p-cresol, p-chlorophenol and p-nitrophenol, and 0.2 μM bisphenol A (BPA) have no

interferences on the detection of 100 μg L^{-1} TBBPA (signal change < 10%).

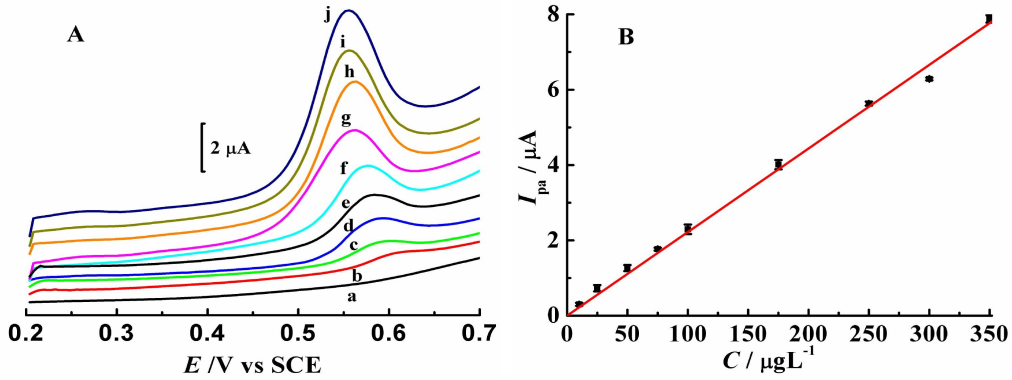


Fig. 8 (A) DPV curves of TBBPA on AB/GCE with concentrations of 0 (a), 10 (b), 25 (c), 50 (d), 75 (e), 100 (f), 175 (g), 250 (h), 300 (i) and 350 μg L^{-1} (j); (B) Calibration curve for TBBPA. Error bars represent the standard deviations of three measurements.

3.4. Practical application

The proposed method was used in different water samples to evaluate its practical application. No TBBPA was detected in the orginal water samples, and TBBPA standards with different concentrations were spiked into the orginal samples, and then analyzed according to analytical procedure. Each sample was determined by three times, and the RSD was lower than 5.2%, revealing good reproducibility. The content was obtained by the standard addition method, and the results were listed in Table 1. The recovery is in the range from 99.3% to 104.5%, suggesting that the developed sensing method is accurate and feasible.

Table 1 Detection of TBBPA in water samples.

No.	Added ($\mu g\ L^{-1}$)	by AB/GCE ($\mu g\ L^{-1}$)	RSD (n = 3)	Recovery
1	100.00	99.27	3.0%	99.3%
2	50.00	52.10	5.2%	104.2%
3	25.00	26.13	3.3%	104.5%

4. Conclusions

AB particles are successfully dispersed in DMF or the aqueous solutions of DHP or CS to form stable suspensions, and subsequently used for constructing different AB film modified GCEs by simple drop casting methods. The produced AB film modified electrodes are found to possess large sensing areas and good electrochemical activity toward the oxidation of TBBPA. Particularly, the AB film modified GCE (AB/GCE) prepared from the dispersion of AB in DMF shows an excellent electrocatalytic response for the oxidation of TBBPA, reflected by the apparently enlarged oxidation peak currents and the obviously reduced oxidation overpotential. Based on this, a simple electrochemical method for the rapid and sensitive detection of TBBPA is established, which possessed a wide linear range from 10 to 350 $\mu g\ L^{-1}$ and a low detection limit of 6.08 $\mu g\ L^{-1}$. The present work thus demonstrates the promising application of AB film modified electrodes in environment analysis.

Acknowledgements

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Sensitive and rapid electrochemical method was developed for TBBPA based on enhancement effects of acetylene black particles.