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# Core-shell structured $\text{Co}_3\text{O}_4@\text{PPy}$ composite for electrochemical determination of terbutylhydroquinone†

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TBHQ is a significant synthetic antioxidant, but excessive use of TBHQ is harmful to human health. Therefore, the preparation of a high-efficiency TBHQ electrochemical sensor is of great significance. In this work, a core-shell structured  $\text{Co}_3\text{O}_4@\text{PPy}$  composite is synthesized for TBHQ determination and exhibits remarkable electrochemical properties. The core-shell structure of  $\text{Co}_3\text{O}_4@\text{PPy}$  composite shows the synergistic effects of fast charge transfer, rich active surface area and more active sites. Under optimal conditions, the linear range of the developed sensor is 0.2–600  $\mu\text{M}$ , and the detection limit is 0.05  $\mu\text{M}$  (S/N = 3). In addition, it also has good stability and reproducibility due to the stable protective role of the PPy shell. The proposed sensor can also be applied to practical sample detection.

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## Introduction

Terbutylhydroquinone (TBHQ) is a significant synthetic antioxidant for preventing oxidative degradation of oil and efficiently scavenging free radicals, thus plays a vital role in the food industry.<sup>1,2</sup> Unfortunately, excessive use of TBHQ leads to cell damage and carcinogenesis.<sup>3,4</sup> Many diseases related to the immune system are associated with excessive TBHQ concentration, such as visual impairment, contact dermatitis, and convulsions.<sup>5–8</sup> Therefore, there is a standardized regulation for TBHQ intake of less than 200 mg  $\text{g}^{-1}$  in many countries.<sup>9</sup> Currently, several approaches have been reported for determining TBHQ. Among them, the electrochemical method has been proven to be an ideal technique for monitoring TBHQ due to its high sensitivity, fast detection speed, convenient portability and easy miniaturization.<sup>10,11</sup>

Cobalt tetroxide ( $\text{Co}_3\text{O}_4$ ) is considered to be the most active metal oxide catalyst with certain advantages, such as special chemical stability, large specific surface area and excellent surface redox performance.<sup>12,13</sup> Exposing redox reaction sites

through rational design of the  $\text{Co}_3\text{O}_4$  structure is regarded as a high-efficiency strategy to boost its electrochemical sensing performance. Recently, some studies report a promising strategy on enhancing the electrochemical activity of an electrode by coating with a conducting polymer, which can adapt to the structure change and increase the electrode stability.<sup>14,15</sup> Polypyrrole (PPy) is very suitable for an electrode material, with its high specific surface area, good flexibility and strong conductivity.<sup>16,17</sup> Especially, PPy does not destroy the basic structure of the substrate due to the gentle synthesis process, and can effectively as a shell layer on metal oxides increase electrochemical performance of the electrode materials.<sup>18</sup> Therefore, the combination of PPy and  $\text{Co}_3\text{O}_4$  through a reasonable design is of great significance for TBHQ determination.

In this paper, a  $\text{Co}_3\text{O}_4@\text{PPy}$  composite with core-shell structure is successfully fabricated by a hydrothermal method and chemical oxidation method, which not only shows facilitated electron transfer and enriched reaction sites for a highly efficient determination of TBHQ owing to the synergistic effects of  $\text{Co}_3\text{O}_4$  core and PPy shell. In addition, the PPy shell also increases the stability of the sensor. Considering the excellent properties of the prepared  $\text{Co}_3\text{O}_4@\text{PPy}$  electrochemical sensor, such as wide detection range, high sensitivity, good anti-interference, stability and repeatability, the core-shell structure can be a promising alternative for the determination of TBHQ.

## Experimental

### Reagents and apparatus

Cobalt nitrate ( $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) ( $\geq 98.5\%$ ), pyrrole ( $\geq 98\%$ ), polyvinylpyrrolidone (PVP) ( $M_w$ : 55 000), ammonium persulfate

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(APS), *tert*-butylhydroquinone (TBHQ) ( $\geq 98\%$ ), ethanol ( $C_2H_5OH$ ) ( $\geq 99.7\%$ ), *N,N*-dimethylformamide (DMF) ( $\geq 99.5\%$ ), sodium hydrogen phosphate ( $Na_2HPO_4$ ) ( $\geq 99.0\%$ ), sodium dihydrogen phosphate ( $NaH_2PO_4$ ) ( $\geq 99.0\%$ ), potassium chloride (KCl) ( $\geq 99.0\%$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium *p*-toluenesulfonate ( $C_7H_7SO_3Na$ ) ( $\geq 99.5\%$ ), concentrated sulfuric acid ( $H_2SO_4$ ) ( $\geq 98.0\%$ ) were provided by Damao Chemical Reagent Co. (Tianjin, China). The deionized water was from a Millipore Autopure system (18.20 M $\Omega$ , Millipore Ltd, USA).

The morphology of various materials was observed *via* scanning electron microscopy (SEM, SU8010, Japan) and transmission electron microscopy (TEM, FEI Talos F200X, USA). The crystal phases were characterized by X-ray diffraction (XRD, Bruker Advance, Germany). The FT-IR spectra was obtained with a Fourier transform infrared spectroscopy (FT-IR, Bruker TENSOR 27, Germany). The Raman spectra was analyzed by Raman spectroscopy (Renishaw, U.K.) with a laser excitation of 532 nm. The X-ray photoelectron spectroscopy data were performed by X-ray photoelectron spectroscopy (XPS, Thermo-electricity Instruments, USA). The CHI 630E electrochemical workstation (Shanghai, China) was used to collect all electrochemical data.

### Synthesis of $Co_3O_4$ microcubes

$Co_3O_4$  microcubes was prepared through a method previously reported in the literature. Briefly,  $Co(NO_3)_3 \cdot 6H_2O$  (145.5 mg) was dissolved in 15 mL mixed solution containing deionized (DI) water and ethanol (DI : ethanol = 1 : 1). Subsequently, 100 mg PVP was added into the above solution under stirring continuously for 30 min. Then, the prepared solution was transferred into autoclave and maintained at 180 °C for 12 h. After cooling to room temperature, the product was washed with water and ethanol several times and followed by drying at 60 °C for 12 h to obtain  $Co_3O_4$  microcubes.<sup>19</sup>

### Synthesis of $Co_3O_4@PPy$

$Co_3O_4$  (24 mg) and sodium *p*-toluenesulfonate (33.59 mg) were dispersed in 2 mL ethanol water in a volume ratio of 1 : 1. Sodium *p*-toluenesulfonate was introduced into the PPy chains to increase the conductivity of PPy.<sup>20,21</sup> Afterwards, 12  $\mu$ L of pyrrole monomer was added into the above solution with stirring continuously for 30 minutes. Then, 3 mL of 28.53 mg mL<sup>-1</sup> ammonium persulfate (APS) solution was added slowly under a magnetic stirring. After oxidation induced polymerization, the solution was stirred in ice-water bath for 3 h at low temperature.

Ultimately, the resultant product was centrifuged with ethanol and water for several times and dried in a vacuum at 60 °C to form  $Co_3O_4@PPy$ .<sup>22</sup>

### Preparation of $Co_3O_4@PPy/GCE$

Glassy carbon electrode (GCE) was polished on a chamois with 0.05  $\mu$ m alumina slurry, then was cleaned successively with dilute sulphuric acid, ethanol and double distilled deionized water by sonication. 2 mg of  $Co_3O_4@PPy$  composite was dispersed in 1 mL of DMF to attain homogeneous suspension.

Then, 10  $\mu$ L of the  $Co_3O_4@PPy$  suspension was dropped onto the GCE surface and the solvent was dried under an infrared lamp in order to remove or evaporate the solvent.

### Electrochemical measurement

Cyclic voltammetry (CV) was used to investigate electrochemical properties in 0.1 M PBS solution from -0.4–0.6 V at a scan rate of 100 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was performed in a 5.0 mM  $[Fe(CN)_6]^{3-/4-}$  solution containing 0.1 M KCl. Under the condition of the pulse width was 0.05, the pulse period was 0.5 and the quiet time was 2, differential pulse voltammetry (DPV) with the potential scanning range from -0.4 to 0.6 V was recorded to evaluate electrochemical performance of  $Co_3O_4@PPy$  electrodes.

### Pretreatment of sesame blend oil

Sesame blend oil was purchased from local supermarkets and pretreated for TBHQ determination. In brief, the 5 mL sample of sesame blend oil was mixed with 10 mL ethanol under stirring continuously for half an hour. Then, the mixture was subjected to centrifugation at 8000 rpm for 10 min, and the supernatant was collected and extracted for three time. Finally, the obtained supernatant was stored in a refrigerator.

## Results and discussion

### Characterization of $Co_3O_4@PPy$

The preparation for  $Co_3O_4@PPy$  core shell-structured composite *via* two-steps method is illustrated in Fig. 1a. Firstly,  $Co_3O_4$  is synthesized from cobalt nitrate solution containing PVP at 180 °C by hydrothermal routine, which has an extremely smooth surface and a perfect cubic shape with an average size of 500 nm, as shown in Fig. 1b. Afterwards, the as-synthesized  $Co_3O_4$  microcubes are transferred into different volume of Py monomer solution (6  $\mu$ L, 12  $\mu$ L, 18  $\mu$ L, 24  $\mu$ L) for the surface polymerization.

The structures and morphologies of the as-fabricated  $Co_3O_4@PPy$  composites are respectively presented in Fig. S1a–S1d† and 1c. Their electrochemical properties are also evaluated in Fig. S2.† Apparently, a stable and higher redox couple is observed for  $Co_3O_4@PPy$  with 12  $\mu$ L Py monomer. This may be attributed to the fact that the thickness of PPy has a great influence on the electrochemical properties of  $Co_3O_4@PPy$  composites. When a small amount of Py monomer is polymerized on the surface of  $Co_3O_4$ ,  $Co_3O_4$  could not be completely covered by PPy film. As the volume of Py increases, more PPy film with large specific surface area is polymerized on the surface of  $Co_3O_4$ , which can effectively improve the catalytic activity for the electro-oxidation of TBHQ. However, with the further increase of Py monomer volume, the excessively thicker PPy films on  $Co_3O_4$  surface would not further increased effective surface area, but reduce the electron transfer efficiency and hinder the electro-oxidation of TBHQ.<sup>23</sup>

Fig. 1c shows the SEM morphology of the optimized  $Co_3O_4@PPy$  (12  $\mu$ L), and its high-resolution SEM image shows  $Co_3O_4$  is evenly wrapped by the PPy film with a size of about



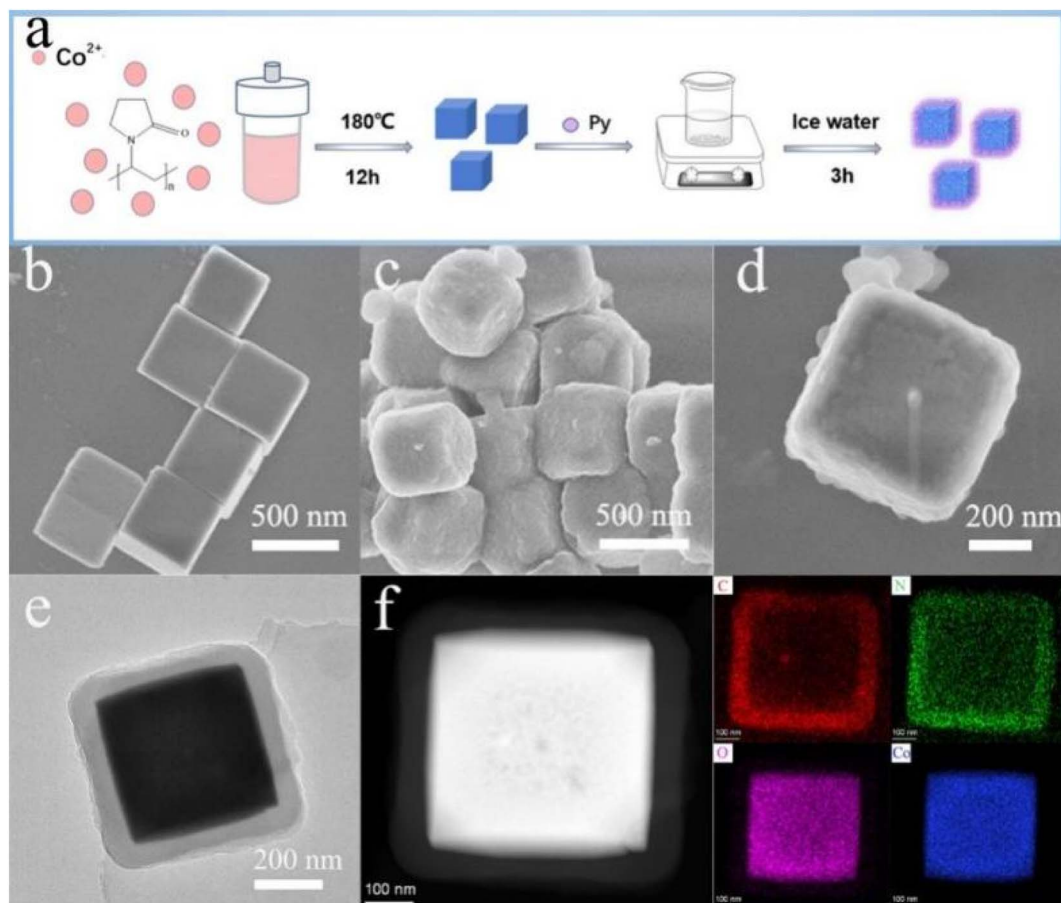


Fig. 1 (a) Schematic illustration of the formation of core-shell Co<sub>3</sub>O<sub>4</sub>@PPy. SEM images of (b) Co<sub>3</sub>O<sub>4</sub> and (c) Co<sub>3</sub>O<sub>4</sub>@PPy. (d) High-resolution SEM image of Co<sub>3</sub>O<sub>4</sub>@PPy. (e) TEM images of Co<sub>3</sub>O<sub>4</sub>@PPy. (f) EDS-TEM elemental mapping of C, N, O, Co for Co<sub>3</sub>O<sub>4</sub>@PPy.

600 nm (Fig. 1d). The transmission electron microscopy (TEM) presents the internal structured morphology of Co<sub>3</sub>O<sub>4</sub>@PPy composite, and the thickness of PPy film is estimated to be about 50 nm (Fig. 1e). Energy dispersive X-ray spectroscopy (EDS) elemental mapping is conducted (Fig. 1f) to reveal the structure of the composites with the outer layer of PPy and the inner core of Co<sub>3</sub>O<sub>4</sub>, and confirm the formation of core-shell structured Co<sub>3</sub>O<sub>4</sub>@PPy.

The crystallographic structure of Co<sub>3</sub>O<sub>4</sub> is shown in Fig. 2a, and the diffraction peaks are consistent with standard spinel Co<sub>3</sub>O<sub>4</sub> (PDF#43-1003). After surface polymerization, a prominent intense peak at 23° is observed at the Co<sub>3</sub>O<sub>4</sub>@PPy composite, which is assigned to the presence of PPy.<sup>24</sup> Raman analysis is also employed to characterize the structure of the Co<sub>3</sub>O<sub>4</sub>@PPy (Fig. 2b). The peak at about 1583 cm<sup>-1</sup> is assigned to symmetrical stretching vibration of aromatic C=C ring; the characteristic peaks at 1370 cm<sup>-1</sup> and 1335 cm<sup>-1</sup> are attributed to the ring stretching mode of PPy; the peak located at 1045 cm<sup>-1</sup> is related to C-H in plane deformation. Notably, the peaks at 691 cm<sup>-1</sup>, 523 cm<sup>-1</sup> and 482 cm<sup>-1</sup> belonging to Co<sub>3</sub>O<sub>4</sub> (ref. 25–27) are greatly reduced after polymerization with PPy, which indicates the excellent encapsulation of PPy outside Co<sub>3</sub>O<sub>4</sub>, resulting in extremely weak peaks of Co<sub>3</sub>O<sub>4</sub> that almost disappear. Fig. S3† displays FT-IR spectrum of as-prepared

Co<sub>3</sub>O<sub>4</sub>@PPy, PPy and Co<sub>3</sub>O<sub>4</sub>, and the attribution of all peaks in FT-IR spectrum is listed in Table S1.†<sup>28–34</sup> It can be observed that the characteristic peaks of Co<sub>3</sub>O<sub>4</sub> and PPy appear on the Co<sub>3</sub>O<sub>4</sub>@PPy composite, indicating the preparation of composite materials. All those characteristic results of XRD, Raman and FT-IR indicate that core-shell structured Co<sub>3</sub>O<sub>4</sub>@PPy is successfully prepared.

X-ray electron spectroscopy (XPS) is scrutinized to characterize the chemical composition and valence states of PPy, Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>@PPy. Fig. S4† shows XPS survey spectrum of Co<sub>3</sub>O<sub>4</sub>@PPy, in which the C, N, O, Co elements can be detected. The peaks of C, O and N are high, while the Co peak is extremely weak, which indicates that there may be a small amount of incompletely encapsulated Co<sub>3</sub>O<sub>4</sub> in the composite. Therefore, the Co 2p signal is still detected, which is also beneficial to investigate the electronic interactions between Co<sub>3</sub>O<sub>4</sub> and PPy. Fig. 2c and d respectively show the N 1s and Co 2p XPS spectrum. After surface polymerization, the peak of N 1s shifts to lower binding energy, while the peak of Co<sub>3</sub>O<sub>4</sub>@PPy (Co 2p) moves towards higher binding energy. It shows that there is electron transfer from Co<sub>3</sub>O<sub>4</sub> to PPy, which improves the coupling interaction between PPy and Co<sub>3</sub>O<sub>4</sub>, thus enhancing the efficiency of charge transfer. Additionally, Co donates electrons to the N position in PPy, giving Co<sub>3</sub>O<sub>4</sub>@PPy abundant



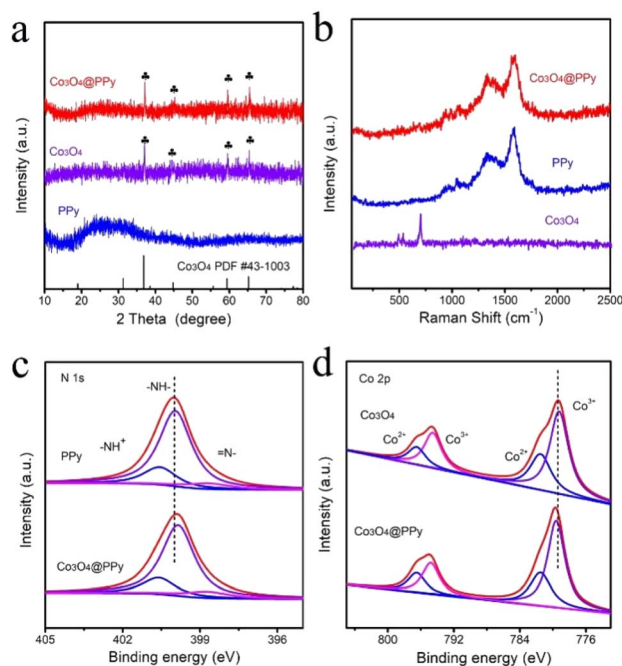


Fig. 2 (a) XRD patterns of  $\text{Co}_3\text{O}_4$ , PPy and  $\text{Co}_3\text{O}_4@\text{PPy}$ . (b) Raman spectrum of  $\text{Co}_3\text{O}_4$ , PPy and  $\text{Co}_3\text{O}_4@\text{PPy}$ . (c) High resolution N 1s XPS spectrum of PPy and  $\text{Co}_3\text{O}_4@\text{PPy}$ . (d) High resolution Co 2p XPS spectrum of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4@\text{PPy}$ .

electron delocalization centers and creating rich active sites in  $\text{Co}_3\text{O}_4@\text{PPy}$ .

### Electrochemical properties of core-shell $\text{Co}_3\text{O}_4@\text{PPy}$

Electrochemical impedance spectroscopy (EIS) is implemented to investigate charge transport characteristics. In the high-frequency region, the semicircle part of the EIS diagram is related to electron transfer, while in the low-frequency region, the linear part represents the diffusion process. As shown in Fig. 3a, bare GCE, PPy,  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4@\text{PPy}$  exhibited decreasing in semicircle part gradually. Compared to other modified electrodes, the semicircle diameter of  $\text{Co}_3\text{O}_4@\text{PPy}$  is much smaller. This result proved that the modification of  $\text{Co}_3\text{O}_4$  or PPy could reduce the resistances slightly, which could attributed to their

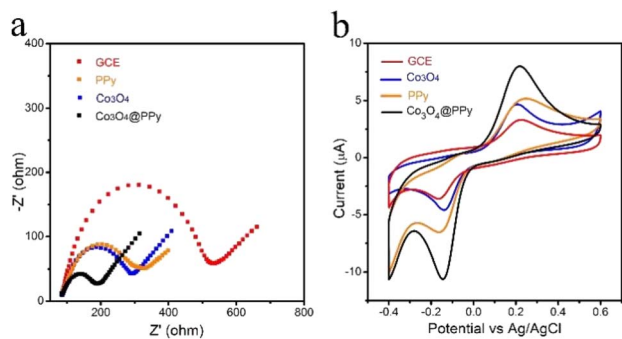


Fig. 3 (a) EIS of GCE, PPy,  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4@\text{PPy}$  in 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  solution containing 0.1 M KCl. (b) CVs of GCE, PPy,  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4@\text{PPy}$  containing 100  $\mu\text{M}$  TBHQ in 0.1 M PBS solution (pH = 7).

own excellent conductivity. And the resistance drastically reduce after modification of  $\text{Co}_3\text{O}_4@\text{PPy}$ , demonstrating that the synergistic effects of  $\text{Co}_3\text{O}_4$  and PPy further facilitated electron transfer. On the whole,  $\text{Co}_3\text{O}_4@\text{PPy}$  has smaller resistance and higher electron transfer ability.

The electrochemical responses of different electrodes for TBHQ (100  $\mu\text{M}$ ) in 0.1 M PBS (pH = 7) solution are examined by the CV, as shown in Fig. S5.† In the blank buffer solution, there are no redox peaks on  $\text{Co}_3\text{O}_4@\text{PPy}$ ,  $\text{Co}_3\text{O}_4$ , PPy and GCE. However, after adding TBHQ, a pair of distinct redox peaks can be observed on all electrodes, which is clearly derived from the electro-redox of TBHQ. Fig. 3b compares the electrocatalytic oxidation of TBHQ on  $\text{Co}_3\text{O}_4@\text{PPy}$ ,  $\text{Co}_3\text{O}_4$ , PPy and GCE. The small redox peak current of bare GCE is observed, showing poor electrocatalytic performance of bare GCE for TBHQ. After coated by  $\text{Co}_3\text{O}_4$ , the oxidation peak current of  $\text{Co}_3\text{O}_4/\text{GCE}$  increase slightly, which may be attributed to the high electrocatalytic capacity of  $\text{Co}_3\text{O}_4$ . However, after loading PPy,  $\text{Co}_3\text{O}_4@\text{PPy}$  electrode exhibits further increased peak current (6.15  $\mu\text{A}$ ), which is about 3-fold higher than bare GCE (1.98  $\mu\text{A}$ ). Besides, the response peak current increases linearly with the increase of TBHQ concentration from 0 to 250  $\mu\text{M}$  (Fig. S6†). These results suggest that the  $\text{Co}_3\text{O}_4@\text{PPy}$  electrode has excellent synergistic effect of fast charge transfer, rich active surface area and more active sites, which are beneficial to achieve the effective determination of TBHQ.

### Electrochemical reaction mechanism of TBHQ

The  $\text{Co}_3\text{O}_4@\text{PPy}$  sensing performance is evaluated by CV method with different buffer solution (HAc-NaAc,  $\text{Na}_2\text{HPO}_4\text{-CA}$  and PBS) and different pH (6.0–8.0) to find the optimal sensing platform. As shown in Fig. S7,† the highest current response is obtained in PBS buffer solution. This observation might be associated with higher migration rate of TBHQ in PBS, accelerating the electron transfer between the electrode and the solution.<sup>35</sup> As shown in Fig. 4a, the peak current increases from pH 6.0 to pH 7.0 and decreases progressively from pH 7.0 to pH 8.0. The strongest response is attained at pH 7.0 for TBHQ sensing (Fig. 4b). Thus, subsequent experiments are performed with an optimum pH of 7.0. Besides, the oxidation peak potential ( $E_{\text{pa}}$ ) shifts linearly with the pH value, showing that protons are involved in the electrochemical reaction of TBHQ. According to the linear relationship between pH value and the anode peak potential, the regression equation is  $E_{\text{pa}} (\text{V}) = -0.064 \text{ pH} + 0.686$ . The slope value is 64  $\text{mV pH}^{-1}$ , which is consistent with the theoretical value of 0.059 V, suggesting that an equal number of protons and electrons transferred in the TBHQ oxidation process.<sup>36</sup>

The electrooxidation behavior of TBHQ in  $\text{Co}_3\text{O}_4@\text{PPy}$  is also explored by CV method with different scan rate to investigate the sensing mechanism (Fig. 4c). Obviously, the oxidation peak current ( $I_{\text{pa}}$ ) of TBHQ increases gradually with the scan rate increasing in the range of 20–100  $\text{mV s}^{-1}$ , and proportional to the linear relationship of  $I_{\text{pa}} (\mu\text{A}) = 1.548 + 48.62\nu$  (Fig. 4d). The result reveals that typical adsorption-controlled process occurs on the  $\text{Co}_3\text{O}_4@\text{PPy}$  electrode. For adsorption-controlled



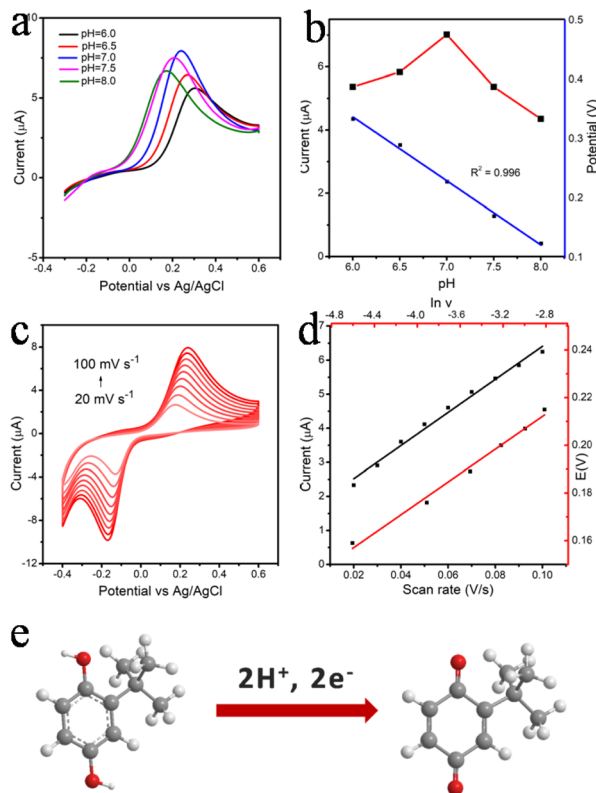


Fig. 4 (a) Positive voltammograms of 100  $\mu\text{M}$  TBHQ at the  $\text{Co}_3\text{O}_4\text{@PPy}/\text{GCE}$  in 0.1 M PBS solution under different pH values (6.0–8.0). (b) The relationship between pH and peak potential  $E_p$ , and the effect of pH on the anodic peak current. (c) CVs of the  $\text{Co}_3\text{O}_4\text{@PPy}/\text{GCE}$  in 0.1 M PBS solution containing 100  $\mu\text{M}$  TBHQ at different scan rates. (d) Corresponding calibration plot of  $I_p$  vs.  $\nu$  and  $E(V)$  vs.  $\ln \nu$ . (e) Electrochemical reaction mechanism diagram of TBHQ.

electrode process,  $E_p$  and  $\nu$  is defined by the following equation according to Laviron's equation:<sup>37</sup>

$$E_p = E^0 + \frac{RT}{\alpha nF} \ln \left( \frac{RTk^0}{\alpha nF} \right) + \frac{RT}{\alpha nF} \ln \nu \quad (1)$$

where  $\alpha$  is the transfer coefficient,  $k^0$  is the standard rate constant of the reaction,  $n$  is the electron transfer number, and  $E^0$  is the formal potential. Therefore,  $n$  and  $\alpha$  values can be easily obtained by eqn (1), respectively. Assuming that the value of  $\alpha$  is 0.42, the value of  $n$  is calculated to be 2. Thus, two electrons have participated in the electrochemical oxidation of TBHQ. As mentioned above, an equal number of protons and electrons transferred in the TBHQ oxidation process. Therefore, the electrooxidation mechanism of TBHQ at  $\text{Co}_3\text{O}_4\text{@PPy}$  electrode may be proposed in Fig. 4e.

### Analytical performance of $\text{Co}_3\text{O}_4\text{@PPy}$ to TBHQ

Accumulation method is applied before determination to enhance the sensitivity. As shown in Fig. S8.† It is obviously observed that accumulation time and accumulation potential have a great impact on electrochemical sensing ability of the  $\text{Co}_3\text{O}_4\text{@PPy}$  electrode for TBHQ. Fig. S8a† shows the oxidation peak current has been increasing with accumulation time from

30 s to 90 s. However, the oxidation peak current increases slowly after 60 s, which may be because the adsorption capacity of TBHQ on the electrode has reached saturation with the increase of accumulation time. Based on this, 60 s is chosen as the best accumulation time. The influence of accumulation potential is also investigated in Fig. S8b.† Apparently, the maximum oxidation peak current is obtained at 0.1 V, which is determined as the best accumulation potential for TBHQ detection.

Differential pulse voltammetry (DPV) technique is used to investigate the electrooxidation responses of the  $\text{Co}_3\text{O}_4\text{@PPy}$  for TBHQ quantitative detection (Fig. 5a). With the increase of TBHQ concentration in the range of 0.2–600  $\mu\text{M}$ , the oxidation peak current increases steadily with no significant shift in potential, showing good determination ability of TBHQ based on  $\text{Co}_3\text{O}_4\text{@PPy}$ . Fig. 5b describes the linear relationship between TBHQ concentration and oxidation peak current, and its linear equation are  $I_{pa} (\mu\text{A}) = 0.00410 + 0.0569C$  ( $R^2 = 0.992$ ) and  $I_{pa} (\mu\text{A}) = 0.641 + 0.0100C$  ( $R^2 = 0.996$ ). The sensitivity of the

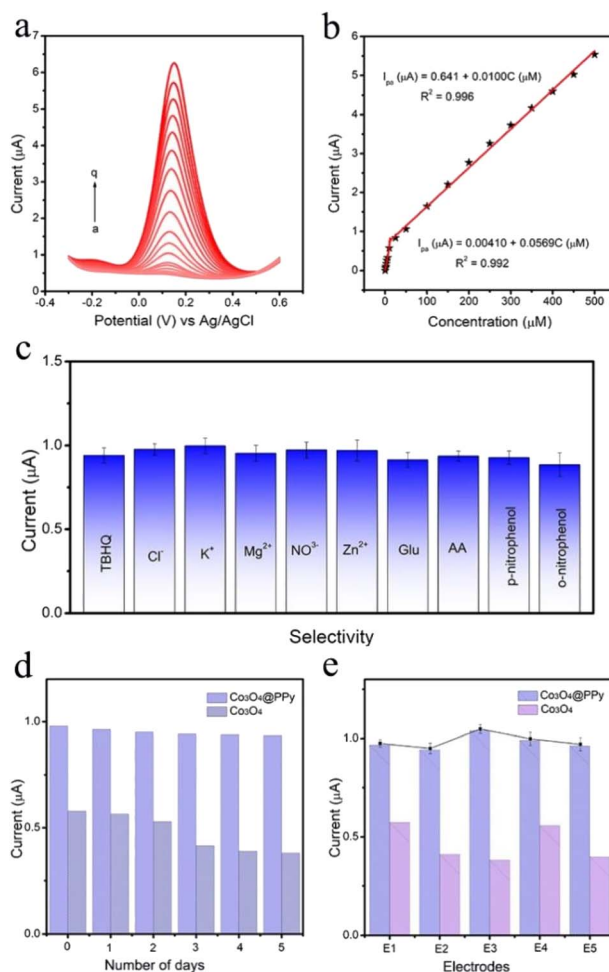


Fig. 5 (a) DPV of  $\text{Co}_3\text{O}_4\text{@PPy}$  composite at different concentrations. (b) The linear relationship between the corresponding peak current and TBHQ concentration. (c) Anti-interference of  $\text{Co}_3\text{O}_4\text{@PPy}/\text{GCE}$ . (d) Stability of  $\text{Co}_3\text{O}_4\text{@PPy}/\text{GCE}$  and  $\text{Co}_3\text{O}_4/\text{GCE}$ . (e) Repeatability of  $\text{Co}_3\text{O}_4\text{@PPy}/\text{GCE}$  and  $\text{Co}_3\text{O}_4/\text{GCE}$ .



first linear range is  $0.803 \mu\text{A} \mu\text{M}^{-1} \text{cm}^2$ , and the sensitivity of the second linear range is  $0.141 \mu\text{A} \mu\text{M}^{-1} \text{cm}^2$ . The decrease of sensitivity in the second linear range may be attributed to the fact that the active sites on the electrode surface tends to be saturated with the successively increasing TBHQ concentrations, which limits the adsorption control process of TBHQ.<sup>38</sup> According to the first linear equation, the detection limit (LOD) is calculated as  $0.05 \mu\text{M}$  ( $S/N = 3$ ). Table S2† lists other reported sensor for TBHQ determination, and the proposed sensor outperforms them in terms of wider linear range and lower LOD. Therefore,  $\text{Co}_3\text{O}_4@\text{PPy}$  electrode shows satisfactory capability toward TBHQ determination. The improved activity may be ascribed to the excellent electron transfer ability and increased active sites of core-shell structure composites, promoting the electrochemical chemical reaction kinetics.

### Anti-interference, stability, reproducibility

Anti-interference study of  $\text{Co}_3\text{O}_4@\text{PPy}$  is performed by adding several potential interfering substances ( $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Zn}^{2+}$ , AA, Glu, *p*-nitrophenol and *o*-nitrophenol) to observe the effect on the TBHQ determination. Fig. 5c illustrates that the interferences have barely influence on the current response, and the as-prepared sensor has highly specific response toward TBHQ. The long-term stability is examined to evaluate current response of the  $\text{Co}_3\text{O}_4@\text{PPy}$  electrode for 5 days (Fig. 5d), and the current response remains 98% of the initial current after 5 days, proving the proposed sensor exhibits good stability.

For the reproducibility test, DPV is recorded by five times with  $\text{Co}_3\text{O}_4@\text{PPy}$  electrode under identical conditions. The results shows that the current response does not change significantly, and the RSD value of their peak current range from 1.2–3.6% (Fig. 5e), confirming admirable reproducibility of the proposed sensor. In addition, it can be observed from Fig. 5d and e that the stability of  $\text{Co}_3\text{O}_4@\text{PPy}$  composite is greatly improved compared with  $\text{Co}_3\text{O}_4$  alone, which is mainly attributed to the existence of the shell buffer layer of PPy. The results prove that the PPy shell plays a key role in improving electrochemical stability, ensuring a longer service life for the  $\text{Co}_3\text{O}_4@\text{PPy}$  sensor.

### Determination of TBHQ in real samples

Feasibility of the established sensor in determining practical samples is tested by assaying TBHQ in sesame blend oil *via* the standard addition method. A certain amount of TBHQ (50, 80, 100  $\mu\text{M}$ ) is added to the pretreated sesame oil, and the current response of the developed sensor in the actual sample is recorded, and the detailed information is listed in Table S3.† Its recoveries ranging from 99.0 to 101% and RSD value varying from 2.0% to 3.6% show satisfied accuracy of  $\text{Co}_3\text{O}_4@\text{PPy}$  in real sample determination, indicating the great potential in practical application.

## Conclusion

$\text{Co}_3\text{O}_4@\text{PPy}$  composite material with cored shell structure is synthesized for electrochemical determination of TBHQ, with

wide detection range, low detection limit and good stability. The excellent sensing performance benefits from the strong coupling interaction of inner  $\text{Co}_3\text{O}_4$  and outer PPy, which contribute to facilitate the electron transfer and create more active sites. In addition, the PPy shell is beneficial to increase the stability of the sensor. Thus, the proposed electrochemical sensor can also be applied for practical application. Considering the outstanding performance of the core-shell structure of  $\text{Co}_3\text{O}_4@\text{PPy}$ , this sensing platform will have a broad application prospect in the detection of other substances.

## Author contributions

Yuxi Zhang: resources, funding acquisition, project administration. Cunli Wang: data curation, methodology, writing – original draft. Yalin Zhao: writing – review & editing. Zhe Yu: visualization. Fengchun Yang: supervision, funding acquisition. Xin Zhang: writing – review & editing, conceptualization, project administration.

## Conflicts of interest

There are no conflicts to declare.

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