A novel Prussian blue/PANI nanostructure-based biosensor for ultrasensitive determination of trace hydroquinone

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ABSTRACT
A sensitive, accurate, and low-cost hydroquinone detection method is always desired due to the great threat of hydroquinone to human beings and environment. In this work, we proposed an ultrasensitive electrochemical hydroquinone biosensor relying on a nano-architecture of oriented Prussian blue/Polyaniline (PB/PANI) nanoarrays, which can achieve precise and specific detection within only 15 s. The oriented nanoarray architecture of the PANI was in-situ constructed on a carbon cloth substrate to shorten the electron pathway. To overcome the poor electrocatalysis of PANI, the well-defined PB nanocubes were exactly synthesized on those PANI to construct a novel PB/PANI nanostructure. This special nanostructure enables to arouse strong synergistic effects owning both excellent electrocatalysis and conductivity derived from PB and PANI, along with a remarkably high surface area to create abundant active sites for the laccase immobilization. After the immobilization of laccase, the as-prepared biosensor performs a high sensitivity of 931.39 μM·cm⁻², together with outstanding detection limit of 250 nM (0.027 ppm) and reliability in the analysis of real lake samples.

1. Introduction
Phenolic compound is an essential chemical raw material to be widely applied in chemical industry, pharmaceutical industry, and food industry. Its pollution problem is becoming more and more serious with the rapid development of global industrialization process. Main emission sources of phenolic compounds are traditional industries like petroleum oil refineries (2.8–1220 mg L⁻¹), coal mining (9–6800 mg L⁻¹), and coke oven plant (28–1200 mg L⁻¹) [1,2]. Phenolic family possesses high toxicity to normally damage functions of human organs, immune system and nervous system, causing muscle fatigue, diarrhea, and skin rashes [3–5]. Moreover, it is difficult in degradation leading to the environmental accumulation. Currently, the phenolic compound has been identified as a priority pollutant by World Health Organization (WHO). According to US Environmental Protection Agency (EPA) and European Union (EU), the threshold quantity for phenolic compound in wastewater is 1 ppm [6,7]. Therefore, fast and on-site detection of the phenolic compound is essential to timely control the damage of ecological water quality caused by industrial pollution.

Among various phenolic compounds, hydroquinone (HQ) is widely used as a stabilizer in paints, developing agent in photography, dye intermediate, varnishes oils [8], and can also be used to produce important pharmaceutical intermediate p-benzoquinone. It has been reported that the leaking of hydroquinone will cause fatigue, headache, tachycardia and kidney damage. Moreover, hydroquinone is listed as the possible human carcinogen according to the International Agency for Research on Cancer [9]. Nowadays, high-performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS) are two main techniques in the analysis of hydroquinone [10,11]. However, bulky and high-cost instruments are always required with time-consuming response period (normally beyond 30 min), which cannot realize on-site and immediate pollutant detection [12]. Compared with above traditional methods, the electrochemical sensor is superior in the short response time, low-cost and portable feature [13–15]. However, the nonenzymatic sensor always exhibits poor selectivity because it usually requires high detection potential to promote the oxidization of interfering substances coexisting in the system [16]. To achieve the more accurate recognition of hydroquinone and its isomers, enzymatic principle is commonly used to oxidize HQ through oxidases, such as laccase, peroxidase or tyrosinase [17–19]. Laccase belongs to a family of multicopper-oxidase enzymes which can catalyze

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the oxidation of phenols at the T1 copper site with the concomitant reduction of molecular oxygen to water at the T2/T3 cluster. Its application in the biosensing fabrication benefits the improvement of the specific recognition of hydroquinone [20]. In recent years, the laccase-based biosensors have been applied for the detection of hydroquinone and its isomers [21–25]. The utilization of laccase significantly improves the sensitivity and selectivity of the biosensor, endowing biosensor with better practical value for real environment detection [26–29]. However, the signal intensity of the biosensor could not be satisfactory if the adopted electrode material cannot possess both high electrocatalysis and conductivity. In the last decade, more and more regular nanostructures of electrode materials have been confirmed to present great promotion in both electrocatalysis and conductivity. In this case, to simultaneously realize the precise, on-site, reusable and immediate detection of HQ, it is desired to design an advanced nanomaterial to possess both performance and stability during the practical water analysis.

In this work, we proposed an ultrasensitive and reusable biosensor by constructing an oriented nano-architecture of Prussian blue/polyaniline nanoarrays to achieve high-precision analysis of trace HQ within 15 s (Fig. 1). The oriented nanoarray architecture of the PANI can shorten the electron pathway to reduce the transfer resistance. On these PANI nanoneedles, we exactly controlled the grow of PB to construct well-defined PB nanocubes which have been proved to own superior electrocatalysis than the irregular morphology [30]. Therefore, this nanocomposite enables to produce an electrochemical synergetic effect harvesting both high electrocatalysis and conductivity to significantly improve the response current intensity and detection period. Moreover, all above nanostructures of the PANI and PB are created by the in-situ growth strategies which should overcome the strong influence of the substrate to realize the oriented feature. It can also provide a high surface area to benefit the immobilization of laccase, creating more recognition sites based biosensing interface. During the analysis of HQ in real lake samples, the as-prepared biosensor shows an ultrahigh sensitivity and low detection limit, along with long-term stability to support reusable tests for more than 20 days.

2. Experimental

2.1. Chemical reagents

Aniline, sulfuric acid, ammonium persulphate, phenol, catechol, resorcin, hydroquinone, toluene, potassium ferricyanide, and glutaraldehyde (25 % aqueous solution) were purchased from Sinopharm Chemical Reagent Co. Ltd. Dipotassium hydrogen phosphate (K₂HPO₄), potassium dihydrogen phosphate (KH₂PO₄), and potassium chloride (KCl) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. (China). Polyvinyl pyrrolidone (PVP, K30), trisodium citrate dihydrate (SC), sodium dodecyl benzene sulfonate (SDBC), sodium humate (SH), and laccase (EC 1.10.3.2, 285.7 unit/mg, from Rhus vernicifera) were purchased from Sigma-Aldrich. Carbon cloth (CC, W0S1009) was provided by Phychemi company, Hong Kong. All the chemicals in this work were directly used without further purification. All aqueous solutions were prepared with deionized water (≥18.2 MΩ, Smart2Pure 6, Thermo Fisher Scientific, USA).

2.2. Preparation of oriented PANI nanoarrays electrode

Polyaniline nanoarrays were prepared by a simple low-temperature chemical synthesis method. First, the carbon cloth was ultrasonically cleaned with acetone, ethanol, and deionized water to remove the impurities on the surface. Then, 0.0931 g aniline was dissolved in 50 ml 0.5 M sulfuric acid solution, and 0.3423 g ammonium persulfate was dissolved in 50 ml 0.5 M sulfuric acid solution, similarly. Carbon cloth was immersed into the aniline solution and then ammonium persulfate solution was slowly injected into the aniline solution and stirred uniformly. The mixed solution was put into the refrigerator at 2 °C for 24 h. After the reaction, the carbon cloth was taken out and carefully washed several times with deionized water to prepare oriented Polyaniline nanoarrays/Carbon cloth electrode (PANI/CC).

2.3. Preparation of oriented PB/PANI/CC electrode

Prussian blue nanoparticles were synthesized by hydrothermal method. First, the previously prepared PANI/CC was washed with deionized water and put into 40 ml 0.01 M hydrochloric acid solution, then 2.73 g PVP and 0.09 g potassium ferricyanide were added into the solution and fully stirred. Then, the solution was put into a 100 ml Teflon container and reacted at 85 °C for 3 h. After the hydrothermal reaction, the prepared electrode was carefully washed with deionized water for several times, and dried at 60 °C for 6 h. The prepared electrode was named as Prussian blue/PANI nanoarrays/Carbon cloth (PB/PANI/CC).

2.4. Immobilization of laccase

Laccase (100 U) was dissolved in 1 ml of phosphate buffer solution (PBS, 0.1 M, pH = 6.5), and then 12.5 μL of 25 % glutaraldehyde was added to crosslink the enzyme. Glutaraldehyde served as a molecular bridge between PB and laccase. One aldehyde group covalently bonded with amino group of laccase through dehydration condensation reaction, while the other one

![Fig. 1. Schematic of the synthesis strategy of PB/PANI based HQ biosensor.](image-url)
interacted with -OH group on PB surface through aldol condensation [31]. After that, 40 μL of enzyme solution was dropped on the as-prepared PB/PANI/CC electrode, PANI/CC electrode and CC electrode. Then electrodes were stored at 4 °C overnight and washed with distilled water. After drying in nitrogen, Lac-PB/PANI/CC, Lac-PANI/CC and Lac-CC were successfully prepared. After the measurement, the electrode was fully rinsed by PBS for three times. When not used, the electrode was stored at 4 °C in air.

2.5. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) characterization was carried out using 5 mM [Fe(CN)6]3-/4- solution containing 0.1 M KCl at the frequency range of 0.1 Hz~1 MHz with a signal amplitude of 5 mV. Cyclic voltammetry (CV) tests were performed in the probe solution containing 10 mM [Fe(CN)6]3-/4- with 0.1 M KCl at room temperature from −0.2 to 0.8 V. The scan rate in CV was 100 mV s⁻¹. The effective area was tested in solution containing 10 mM K3[Fe(CN)6]3-/4- and 3 M KCl. In addition, chronoamperometry characterization was carried out in 10 mM of phosphate buffer solution containing 0.1 M KCl [32,33]. A conventional three electrode configuration was employed during the experiment. The modified carbon cloth electrode, a Pt wire and an Ag/AgCl (saturated KCl) electrode were utilized as the working electrode, counter electrode and reference electrode, respectively.

3. Results and discussion

3.1. Nanostructure construction of PB/PANI/CC

To realize the orientation growth of PANI, the carbon cloth (CC) was selected as a preferred substate due to its high surface area composed by woven carbon fibers which enables to produce π-π conjugation and chemical bonding effects with aniline monomers [34], and other substrates were also confirmed to show rare this function (Fig. S1). Furthermore, the key to form an oriented nanostructure is the density of the prepared PANI nano-units, which can be well controlled by the reactant concentration. As shown in Fig. 2A, when we just used ultralow aniline concentration (5 mM) for polymerization, the prepared PANI enabled to present a nanoneedle feature but showing a twisted morphology due to the loose growth cites. Further increase of the concentration can produce more PANI nanoarrays towards the vertical direction. The results illustrated that the formation of more nanoneedles creates higher resistance to the radial growth, hence, each needle prefers the extension along axial direction (Fig. 2B). However, the excessively dense distribution of PANI nanoarrays have caused the agglomeration of each nanoneedle, almost losing nanoarrays morphology (Fig. 2C). Besides, the length of the PANI nanoarrays can also be feasibly regulated by varying the reaction time. As showed in Fig. 2D, when the reaction time was set to 6 h, the PANI deposited on the CC existed in the form of

Fig. 2. FESEM images of the PANI arrays prepared at different concentrations: (A) 5 mM, (B) 10 mM, (C) 50 mM. FESEM images of the PANI arrays prepared at different time: (D) 6 h, (E) 24 h, (F) 48 h. (G) Fourier transform infrared spectra of PANI arrays prepared at different time. (H) CC and PANI/CC after resting the water droplet on the surface for 10 s and 1 s, respectively.
short protrusions attributed to the lack of reaction time. This protrusion shape was transformed to a needle-like nanoarrays showing an average length of 50 nm when the reaction time was prolonged to 24 h (Fig. 2E), and could further change to a complete plane with the polymerization time reaching 48 h (Fig. 2F). The characteristic peaks changes of polyaniline during above synthesis process were observed by Fourier transform infrared (FTIR) spectra. As showed in Fig. 2G, the PANI films prepared at different time all shows four adsorption peaks at 1243, 1297, 1483, and 1569 cm$^{-1}$, which can be contributed to the bonds of C-N, C$\equiv$N, and C-C of PANI, respectively [35], and the intensity of these peaks increased with the time. Besides, after the deposition of PANI, the hydrophobic property of CC has been significantly reversed to present a superhydrophilic interface (Fig. 2H), which is because PANI possesses abundant amino groups which can easily establish hydrogen bonds to benefit further modification of extra materials [36].

Due to the poor electrocatalysis of PANI, it is not a good choice to only employ PANI as the satisfactory biosensing material. In this case, Prussian blue was adopted to eliminate the deficiency of PANI. In our previous work, we have verified that PB owning regular nanostructures can present superior electrocatalysis [37–39]. Therefore, well-defined nanocubes of PB were in-situ formed on the before prepared nanoarrays. As showed in Fig. 3A and B, lots of PB nanocrystals with the diameter of ca. 100 nm were uniformly distributed on each carbon fiber without any aggregation as independent islands. Focusing on a single PB nanocube, High Resolution Transmission Electron Microscope (HRTEM) revealed an oriented growth towards (2 2 0) crystal plane (Fig. 3C). Further mapping this PB crystal using EDX scan can confirm that the nanocube is composed of Fe, C, N atoms (Fig. 3D-G) derived from the unit Fe$\equiv$C$\equiv$N-Fe in PB. Furthermore, the XRD patterns also exhibited the typical peaks at 17.92°, 35.74° and 40.1° which correspond to the PB crystal faces of (200), (400), and (420), respectively (Fig. 3H). FTIR was also applied to indicate that a very strong absorption peak at 2090 cm$^{-1}$ was generated to indicate the -C=R group in Prussian blue [40] (Fig. S2). Then, the chemical composition and element valences of the CC, PANI/CC and PB/PANI/CC films were studied by X-ray photoelectron spectroscopy (XPS). According to the full survey spectra of Fig. 3I, the XPS data of PB/PANI/CC was mainly composed of C, N, O, and Fe. Compared with the bare CC, the PANI/CC contains an additional characteristic peak of N1s, which is attributed to the introduction of PANI. Moreover, the PB/PANI/CC contains a new produced peak of Fe2p due to the crystallization of PB. The peak of N1s (Fig. S3) of PB/PANI/CC can be fitted to four peaks at 397.58 eV, 399.48 eV, 400.08 eV, and 401.88 eV, which were corresponding to the C-N of PB and the typical bonds of PANI [41,42]. Furthermore, the Fe2p spectrum (Fig. 3J) showed four main peaks at 708.8 eV (Fe$^{2+}$ 2p$^{3/2}$), 712.4 eV (Fe$^{3+}$ 2p$^{3/2}$), 721.4 eV (Fe$^{2+}$ 2p$^{1/2}$), and 723.8 eV (Fe$^{3+}$ 2p$^{1/2}$), proving the crystallization of PB on the PANI/CC [43]. Above results demonstrate the successful formation of PB crystals without any obvious influence to the chemical structure and composition of PANI. The high electrocatalytic ability of PB and remarkable conductivity of PANI can be expected to

![Fig. 3.](image-url) (A-B) FESEM images of the PB/PANI. (C) SAED pattern of the PBNPs. (D-G) The mapping results of the PBNPs for three characteristic elements (C, Fe and N). (H) The XRD patterns of CC, PANI/CC and PB/PANI/CC. (I-J) XPS survey map and element analysis of Fe2p.
arouse synergetic effects to the signal generation and transfer resulting in the improvement of current intensity during biosensing reactions.

3.2. Electrochemical behaviors of the biosensor

Before the electrochemical test, the stability of the as-prepared PB/PANI/CC was first examined to ensure the accuracy of the electrochemical signal. This electrode was repetitively oxidized and reduced by CV technique for 30 cycles. As shown in Fig. 4A, after the continuous scanning between –0.8 and 0.8 V, only 2.09 % and 5.15 % decreases were respectively produced to the current intensities of oxidation and reduction peaks, confirming that the combination of PB nanocubes and PANI nanoarrays can form a stable film attributed by the electrostatic attraction between negative charge of PB and positive charge of PANI.

Then the electrocatalytic activities of PB, PANI and CC were compared using [Fe(CN)₆]³⁻/⁴⁻ as the probe. It can be observed in Fig. 4B, with the successive depositions of PANI and PB on CC, the redox currents kept rising to indicate the excellent electrocatalytic ability of PB/PANI to the reaction between active pairs of [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻. To directly observe the difference of the current signal before and after the synthesis of PB nanocubes, two electrodes of PANI/CC and PB/PANI/CC were 3D imaged via a scanning electrochemical microscopy (SECM). As compared between Fig. 4C and D, more sharp current peaks appeared after the deposition of PB, which was owing to the independent distribution of each big PB nanocrystal to produce a heterogeneous signal in contrast to small PANI nanoarrays. The peak currents of PB/PANI and

![Fig. 4.](image-url) (A) Repetitive CV tests of PB/PANI/CC from –0.8 to 0.8 V at a scan rate of 0.1 V/s. (B) Comparison of cyclic voltammetry (CV) values of the CC, PANI/CC and PB/PANI/CC from –0.2 to 0.8 V at a scan rate of 0.1 V/s in the probe solution. (C-D) SECM diagrams of the PANI electrode and PB/PANI electrode. (E) EIS diagram of the above three electrodes with the frequency range from 0.1 Hz to 1 MHz. (F) Calibration curves of the peak current versus the square root of the scanning rate of these three electrodes.
PANI were tested to 3.948 and 3.755 nA, showing the higher electrochemical activity of PB. However, the introduction of PB has slightly increased the peak potential difference (ΔEp), revealing the semiconductor characteristics of PB with lower conductivity than PANI and bare CC. For clarity, EIS tests of above three electrodes were carried out to investigate the values of the electron transfer resistance $R_{ct}$. According to the fitting of Nyquist curves in Fig. 4E, the $R_{ct}$ of CC, PANI/CC, and PB/PANI/CC were respectively calculated as 11.548, 10.98 and 13.616 Ω, which is consistent with the results of CV characterization. Overall, it can be proved that PB nanocube enables to present high electrocatalysis through Fe(II) and Fe(III) transformation but owns low conductivity due to its semiconductor characteristic, thus leading to both increases of redox peak current and $R_{ct}$ value [44], and PANI possesses better conductivity than PB nanocube and CC. Therefore, the combination of PB and PANI have successfully produced synergetic effects to obtain both advantages of these two nanomaterials.

As our expectation, the unique architecture of the PANI nanoarrays were considered to remarkably increase the surface area of the electrode. To prove this, the electrochemical surface areas of CC, PANI/CC and PB/PANI/CC were studied using CV according to the Randles Sevcik equation:

$$I_p = \frac{(2.69 \times 10^5)n^{3/2}D^{1/2}C_oA}{\nu^{1/2}}$$

where $I_p$ is the redox peak current, $\nu$ is the scan rate, $n$ is the total number of electrons transferred during the redox process, and $D^{1/2}$, $C_o$, and $A$ correspond to the molecular diffusion coefficient, probe molecule concentration and electrode area, respectively. In this equation, there is a linear relationship between the peak current and the square root of scan rates, hence, the surface area was proportional to the slope of calibration curves according to Eq. (1). After the synthesis of PANI nanoarrays, the effective surface area of the PANI/CC electrode enormously increased from 0.5 cm$^2$ (bare CC) to 2.086 cm$^2$, verifying the great promotion of the nanoarray feature to the effective surface area.

Besides, the area enabled to be further increased to 2.569 cm$^2$ after the introduction of PB (Fig. 4F). This high surface area can provide an abundant support for the immobilization of laccase during the biosensor fabrication.

### 3.3. Biosensing performance of the Laccase-PB/PANI/CC

After the immobilization of laccase, the kinetic control mechanism of this biosensor was investigated by CV characterization in the presence of 100 μM hydroquinone. As shown in Fig. 5A, with the increase of scanning rate, both intensities of redox peak currents were enhanced. Through fitting according to the CV results (Fig. 5B), two linear dependences between the root of scan rates and peak currents were observed to confirm that the detection of hydroquinone is a diffusion-controlled process. In order to illustrate the role of laccase during the test, we compared the electrochemical performance of PB/PANI/CC and laccase-immobilized PB/PANI/CC (Lac-PB/PANI/CC), as showed in Fig. S4A-B. The sensitivity of Lac-PB/PANI/CC is higher than PB/PANI/CC and glutaraldehyde-treated PB/PANI/CC (GA/PB/PANI/CC), indicating the laccase is capable for the electrocatalytic oxidation of HQ to increase current intensity. In addition, the use of laccase can also improve the selectivity of the sensor (Fig. S4C), which was mainly attributed to the selectivity and the barrier effect of the immobilized enzyme [37,45]. Therefore, the utilization of laccase is essential for the practical detection of HQ. Besides, to demonstrate the superior performance of our proposed Lac-PB/PANI/CC, the Lac-PANI/CC and Lac-CC were simultaneously examined for comparison. Under the same potential of 0.15 V, the Lac-PB/PANI/CC exhibited much higher current response than both Lac-PANI/CC and Lac-CC when adding 0.1 mM hydroquinone (Fig. 5C), which can be attributed to the excellent electrocatalytic ability of PB nanocubes facilitating the electron transfer process through the transformation between Prussian White (PW) and PB [46]. Besides, the interaction between HQ and PANI through van der Waals forces and π-π interactions also benefits the detection [47].

![Fig. 5](image-url)

(A) CV curves of the as-prepared biosensor at different scanning rates in PBS containing 100 μM of HQ from −0.8 to 0.8 V. (B) Calibration curves for the peak current vs. the square root of scan rate. (C) Amperometric responses of the Lac-CC, Lac-PANI/CC and Lac-PB/PANI/CC after the injection of equivalent HQ. (D) Amperometric responses of the biosensor at different working potential. (E) The signal responses and (F) linear calibration of the Lac-PB/PANI/CC at 0.15 V in PBS, insets showing magnifications of the curve from 100 to 600 s and the detection time.
Because hydroquinone owns two isomers including catechol and resorcinol which often coexist together, therefore, we further studied the influence of working potential on the selectivity of the Laccase-PB/PANI/CC based biosensor. It can be found in Fig. 5D, with the increase of potential from 0.1 to 0.25 V, the response to hydroquinone was improved. However, when using 0.2 and 0.25 V as the working potential, the addition of catechol can also produce strong response currents. This is because HQ with duel phenolic hydroxyl groups located at the para-position owing much lower steric effect than orthoposition, which is easier to contact laccase for the oxidation [48]. Although the current values of hydroquinone were higher than catechol, the specific recognition was not realized to strongly affect the detection accuracy. Therefore, to achieve both satisfactory sensitivity and selectivity, 0.15 V was selected as the preferable working potential. We further investigated the effect of pH and laccase concentration during the detection process. As shown in Fig. S5, a higher current signal was obtained under the condition of pH = 7.0 and laccase loading amount of 4 U, which was set as the optimized operation parameters.

Then, the sensitivity, detection limit, and linear detection range of the as-prepared biosensor were carefully tested by using the successive additions of hydroquinone from low to high concentrations. As shown in Fig. 5E, even injecting an ultralow concentration of 250 nM, a stable and evident current step was obtained within only 15 s. With the rapid rise to 100 μm, the current response can be always distinguished to show steady increase until the concentration in the system reaching to 0.9 mM. By fitting the signal change (Δi) with the hydroquinone concentrations, a linear detection range from 250 nM to 0.9 mM was achieved, along with an ultralow detection limit of 250 nM and a high sensitivity of 931.39 μA mM⁻¹ cm⁻².

3.4. Anti-interference ability, reproducibility, and stability

The anti-interference performance of the biosensor is essential for the practical application in the pollution monitor. Here, 75 μM of interfering pollutants in water, such as catechol, resorcinol, phenol, aniline, toluene, sodium citrate (SC), sodium dodecyl benzene sulfonate (SDBC), and sodium humate (SH) were employed to study the specific detection ability of the biosensor. It can be observed in Fig. 6A, all above substances cannot produce obvious interference to the current signal generated by hydroquinone. Moreover, after these additions, again injection of hydroquinone can also arouse similar current intensity of the generated current, illustrating that the Lac-PB/PANI/CC enables to endure these interfering compounds without any damages. Besides, we further tested the reusable stability of this biosensor. As shown in Fig. 5B, after 20 days of repetitive tests, the biosensor can still maintain 56.74% of the original sensitivity, indicating its excellent usage stability. To explore its reproducibility, the sensitivities of six different electrodes were compared to show a relatively low RSD of 6.34% (Fig. 6B). Importantly, the sensitivity and detection limit of our biosensor were compared with those of other reported hydroquinone biosensors (Fig. 6C and Tab. S1). It can be found that our biosensor presents high sensitivity with low detection limit which is derived from the construction of this special nano-architecture to integrate both high electrocatalysis and conductivity of PB and PANI, respectively.

3.5. Analysis of real lake water samples

To test the possibility of this hydroquinone biosensor for practical applications, three samples from lakes in Nanjing Tech University were collected to evaluate the performance through the standard addition method. The lake water was collected by beaker and stored at 4 °C when not used. Before the test, the lake water was filtered by PES microfiltration membranes (0.22 μm) to remove the impurities, then the hydroquinone with different amounts was added to obtain the water samples. First, a standard hydroquinone aqueous solution with a known concentration was added to the detection system to obtain a standard signal, and then lake water samples with different concentrations of hydroquinone were added to record response currents. According to Table 1, the RSD of the biosensor to these samples can locate in the range of 2.50–3.07 %, and the recovery was 100.17–102.53 %. In addition, the untreated real samples could not cause signal interference (Fig. S7). These results proved that this biosensor is reliable for hydroquinone detection in real water samples.

4. Conclusions

In this work, we have designed an ultrasensitive hydroquinone biosensor through constructing a functional architecture of PB nanocubes/PANI nanoarrays to achieve accurate and specific recognition of trace hydroquinone within only 15 s. This oriented nanostructure enables to integrate both high electrocatalysis and conductivity of PB and PANI, promoting the generation and transfer of the current signal produced by the laccase reaction. The performance including the sensitivity, detection limit, and linear detection range is remarkably competitive to exhibit outstanding anti-interference, reproducibility, and reusage ability, along with high accuracy in the analysis of real lake samples.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (μM)</th>
<th>Found (μM)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
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<td>40</td>
<td>40.47</td>
<td>2.50</td>
<td>101.17</td>
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Fig. 6. (A) Anti-interference ability of the Lac-PB/PANI/CC to catechol (CC), resorcinol (RC), phenol (PE), aniline (AN), methylbenzene (MB), trisodium citrate dihydrate (SC), sodium dodecyl benzene sulfonate (SDBC), and sodium humate (SH). All the addition concentration of interfering substances and HQ was 75 μM. (B) Sensitivity comparison of the prepared 6 independent biosensors. (C) Comparison of detection performance of this prepared biosensor with those HQ sensors reported in literature, the abscissa and ordinate respectively represent the sensitivities and detection limits of the previously reported literatures and the as prepared HQ biosensor.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2023.134137.

References

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