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Conjugated polymer nanoparticles-based fluorescent biosensor for ultrasensitive detection of hydroquinone

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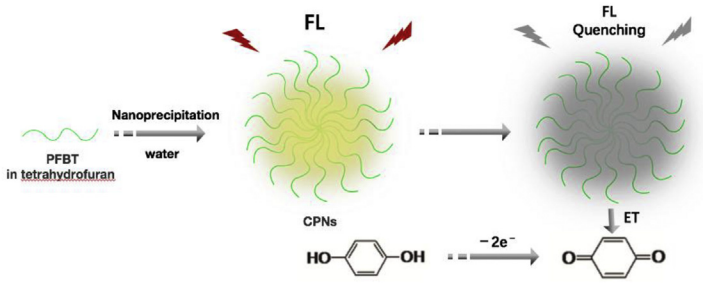
HIGHLIGHTS

- Fluorescent conjugated polymer nanoparticles have been synthesized via a facile nano-precipitation method.
- The conjugated polymer nanoparticles functionalized both as catalystand the fluorescent probe for biosensor construction.
- The biosensor demonstrated significant improvement in detection sensitivity compared to previous hydroquinone assay.

GRAPHICAL ABSTRACT



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ABSTRACT

This work describes a simple and sensitive fluorescent method for detection of hydroquinone utilizing conjugated polymer nanoparticles (CPNs). The CPNs serve both as a catalyst to accelerate the conversion of hydroquinone to benzoquinone and a fluorescent probe. In the presence of hydroquinone, the fluorescence of CPNs can be effectively quenched by benzoquinone. The detection limit of hydroquinone was down to 5 nM and excellent selectivity toward possible interferences was obtained. This method was successfully applied for hydroquinone detection in lake water and satisfactory results were achieved.

1. Introduction

Hydroquinone is a kind of phenol compound pollutant produced by manufactured industry [1]. It has been widely used as reducing agent in areas of photography, lithography, x-ray films, rubber and food. Besides man-made processes, which is the major source of hydroquinone release, plants and animals can also release small amount hydroquinone into the environment. Hydroquinone is toxic for many organisms in the environment, and the toxicity effect varies from different species [2–4]. Because of its harmful effect, development of sensitive and selective methods for

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hydroquinone detection is important [5]. At the moment, spectrophotometry, high performance liquid chromatography (HPLC), electrochemistry, and gas chromatography (GC) are the commonly used techniques for hydroquinone detection [6–15]. These conventional methods involve complicated and expensive instruments, and sample pretreatment processes are often tedious and time-consuming. Biosensors represent a promising way to achieve facile, rapid, sensitive, and selective detection of analytes at low-cost because of its unique advantages. Fluorescent-based biosensor is widely used due to its inherent sensitivity and high selectivity. Recently, several fluorescent-based biosensors have been successfully applied for hydroquinone detection including employing water-soluble fluorescent conjugated polymer-enzyme hybrids system, carbon dots, quantum dots, silver nanoclusters, and nanocrystals electrode [16–20]. Although desirable sensitivity and analysis time were achieved, these methods still suffer from some limitations such as high cost of enzyme, complex synthesis process, fluorescence brightness and stability issue.

Conjugated polymer nanoparticles (CPNs) are promising fluorescent probes for biosensor construction owing to their favorable characteristics such as easy preparation, high fluorescence brightness, low toxicity, stable photoluminescence and small particle sizes [21,22]. The CPNs are easy to synthesis, and the optical properties can be easily tuned by size and components. Herein, we have explored synthesis of CPNs utilizing conjugated polymer: Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,4-benzo-{2,1′,3}-thiadiazole)] (PFBT) via a nano-precipitation method [23]. PFBT is a widely used conjugated polymer and is commercial available nowadays. Due to its excellent properties, PFBT has been applied as a major component for various functionalized fluorescent CPNs synthesis and biosensing in vitro and in vivo [24–32].

In this work, we have developed a simple and sensitive fluorescent approach for hydroquinone detection utilizing PFBT CPNs as fluorescent probe. As illustrated in Scheme 1, the assay was based on the quenching of the fluorescent CPNs by bezoquinone, which was the oxidation product of hydroquinone. Bezoquinone was known as an effective photoluminescence (PL) quencher due to its electron-rich property and conjugated structure [17]. Moreover, previous report indicated that hydroquinone can be oxidized to bezoquinone in alkaline environment under the catalysis of peroxidase or nanoparticles possessed peroxidase-mimicking catalytic activity [18]. Hence, in this system, CPNs were functioned as catalyst to accelerate the oxidation process of hydroquinone into bezoquinone and the fluorescent probe. The fluorescent quenching level was dependent on the concentration of hydroquinone. The proposed assay can be performed in homogenous solution format, which was in favor of its convenience and robustness.

2. Experimental

2.1. Chemicals and materials

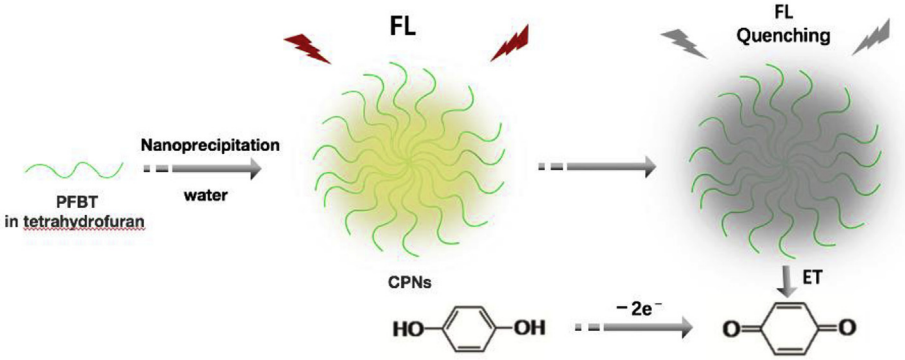
Hydroquinone, glucose, resorcin, phenol, NaCl, $NaNO_3$, Na_2SO_4, Na_2CO_3, KCl, $ZnCl_2$, $NiCl_2·6H_2O$, $MnCl_2·4H_2O$, $CaCl_2·2H_2O$, $FeCl_3·6H_2O$, $Na_2HPO_4·12H_2O$, $NaH_2PO_4·2H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cysteine, uric acid were obtained from Sigma-Aldrich (U.S.A.). Benzoic acid was bought from Aladdin Chemistry Co., Ltd. (Shanghai, China). Tetrahydrofuran was bought from Titan Scientific Co., Ltd. (Shanghai, China). Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,4-benzo-{2, 1, 3}-thiadiazole)] (PFBT, polydispersity 1.7) were purchased from ADS Dyes, Inc. (Quebec, Canada), structure of this polymer was shown in Figure S1, ESI. Spectra/Por® biotech dialysis membranes were purchased from Sangon Biotech Co., Ltd. (Shanghai, China). All reagents were analytically pure and without further purification before being used. All the solutions were prepared with the ultrapure water, which was supplied from a Millipore Milli-Q water purification system with the resistance $>18.2\ M\Omega\ cm^{-1}$.

2.2. Instruments

In this work, the fluorescence spectra were recorded at room temperature in a quartz cuvette with an optical path of 1.0 cm on an F-7000 fluorescence spectrometer (Hitachi, Japan). The slit width of excitation and emission was set at 5.0 nm. The emission spectra were collected by exciting the sample at 455 nm, with a recording emission range from 470 to 650 nm. The UV-vis spectrum were recorded at room temperature on the 2450 UV-visible spectrometer (Shimadzu, Japan). Tecnai G2 F20 Transmission electron microscope (E.A. Fischione Instruments, USA) and dynamic light scattering (DLS) were used to characterize the size and morphology of the CPNs. DLS image and zeta potential image were carried out by using a Malvern Zetasizer 3000 HS particle size analyzer (Malvern Instruments, UK). Fourier transform infrared (FTIR) spectra were acquired on a Lambda FTIR-6700 spectrophotometer (Lambda, Australia).

2.3. Synthesis of CPNs

The synthesis of PFBT CPNs was based on a nano-precipitation, where conjugated polymers were first dissolved in a “good” solvent and then added to an excess of “poor” solvent under ultrasonic dispersion [23]. The formation of CPNs was due to the significant change of solvent polarity. In this work, appropriate amount of



Scheme 1. Illustration of the hydroquinone assay based on fluorescent CPNs.

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conjugated polymer PFBT was dissolved in tetrahydrofuran (THF) solution to the final 400 μL solution with concentration of 0.1 mg/ml. Subsequently, the solution was co-precipitated into 10 mL ultrapure water in conditions of ultrasonic. Finally, THF in the system were removed by dialysis with MWCO 3.5K dialysis membranes six times in 2 days. The as-prepared CPNs solution was stored at 4 °C before use.

2.4. Reaction of CPNs and hydroquinone

140 μL water, 20 μL phosphate buffer (200 μM, pH 7.7), 20 μL CPNs solution, and 20 μL hydroquinone(10 mM) were pipetted into a 200 μL vial sequentially. Then the mixture was incubated at 60 °C for 1 h. The solution was then desiccated by LNG-T88 rapid centrifugal concentration dryer (Taicang Huamei, China). The product was then subject to FT-IR measurement.

2.5. Procedure of hydroquinone assay

A stock solution of hydroquinone (10 mM) was freshly prepared in water and various concentrations of hydroquinone were obtained by serial dilutions from the stock solution. For the determination of hydroquinone, 70 μL water and 10 μL of phosphate buffer (200 μM, pH 7.5) were pipetted into a 200 μL vial, then 10 μL of CPNs and 10 μL of hydroquinone with different concentrations were added. The mixture was incubated at 60 °C for 1 h. Then the fluorescence measurements were performed at an excitation wavelength of 455 nm with the slit widths of excitation and emission of both 5 nm.

3. Results and discussion

The CPNs have excellent water solubility certificated by the clear solution. Then CPNs were characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS) and fluorescence spectrometer. As shown in Fig. 1, DLS results and TEM images demonstrated the CPNs had excellent dispersibility in water. Since sizes given by DLS represented hydrodynamic diameter and were often larger then TEM, the average diameter of CPNs was estimated to be 6 nm according to the TEM image. A negative zeta potential of −18.2 mV was observed for the CPNs solution, indicating a negatively charged surface, which helped to maintain good dispersibility. The fluorescence spectra under the excitation of 455 nm indicated CPNs had strong fluorescence emission and the maximum emission wavelength was 540 nm.

The quenching ability and mechanism of hydroquinone toward the fluorescent CPNs were thoroughly investigated. The fluorescent responses of CPNs under different conditions were shown in Fig. 2A. In the presence of hydroquinone, the fluorescent intensity of CPNs was significantly decreased, signal-to-background ratio was ~90%. Benzoquinone was hypothesized as fluorescent quencher of CPNs based on previous study [17]. Hence, we then incubated CPNs and hydroquinone mixture with glutathione and the fluorescence was recovered. The fluorescence recovery was due to the strong antioxidant property of glutathione so the benzoquinone was reduced into hydroquinone. The oxidation reaction of hydroquinone was further validated by FT-IR measurements. The FT-IR spectrum of hydroquinone, CPNs and reaction product of hydroquinone and CPNs were recorded and shown in Fig. 2B. For hydroquinone, the vibration band at 1519 cm^{-1} was corresponding to the C-O stretching vibration (plot a, Fig. 2B). The characteristic peak at 1519 cm^{-1} disappeared in the FT-IR spectra of product of hydroquinone and CPNs (plot b, Fig. 2B). Moreover, a new peak appeared at 1633 cm^{-1} for product of hydroquinone and CPNs, suggesting conversion of hydroquinone to benzoquinone. These results confirmed the oxidation reaction of hydroquinone and the

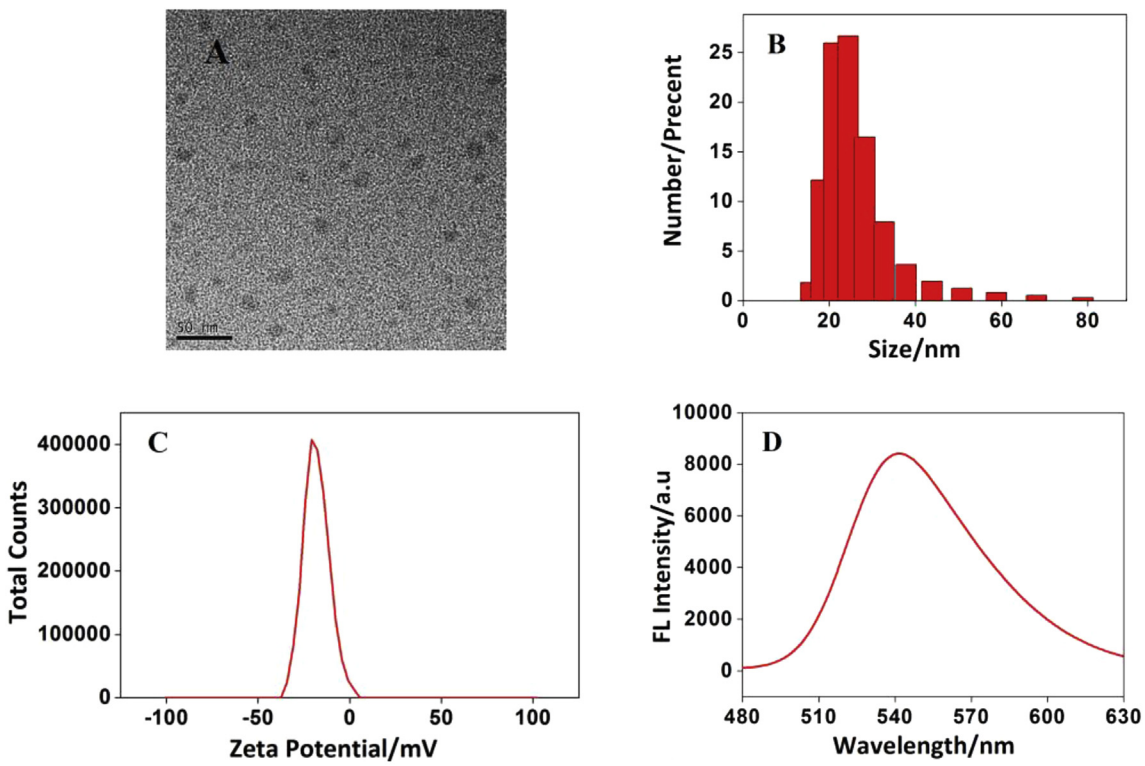

Fig. 1. (A) TEM image of the CPNs. (B) Zeta potential of the CPNs solution. (C) DLS analysis of the CPNs solution. (D) Fluorescence spectra of the CPNs solution under the excitation of 455 nm.

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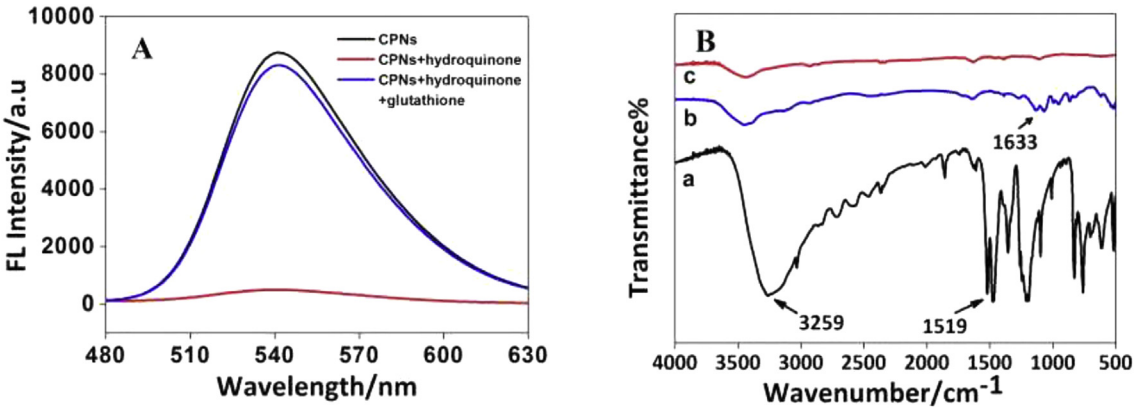

Fig. 2. (A) Fluorescence emission spectra of CPNs, CPNs in the presence of hydroquinone, and CPNs in the presence of hydroquinone and glutathione. Excitation wavelength was 455 nm. (B) FT-IR spectra of hydroquinone (a), product of CPNs and hydroquinone (b), and CPNs (c).

product could effectively quench the fluorescence of CPNs. To investigate the effect of dissolved oxygen, we used nitrogen to remove dissolved oxygen and protect the reaction process free of oxygen. Under nitrogen protection, solution of CPNs and hydroquinone mixture showed strong fluorescence, indicating hydroquinone could not quench the fluorescence of CPNs. On the other hand, hydroquinone's oxidation product benzoquinone could effectively quench the fluorescence of CPNs (Figure S2, Supporting Information). We then investigate the effect of catalytic activity of CPNs by observing color change of hydroquinone in the presence or absence of CPNs since hydroquinone was a colorless solution and benzoquinone was a brown solution. The UV-Vis absorption spectrum of hydroquinone and its oxidation product benzoquinone were shown in Figure S3 in Supporting Information. And as shown in Figure S4 in Supporting Information, without CPNs, the transformation process of hydroquinone into benzoquinone was quite slow as demonstrated by the slow color change. On the other hand, in the presence of CPNs, the color of hydroquinone solution and the absorbance spectroscopy turn quickly. These results demonstrated CPNs could effectively catalyze the oxidization process of hydroquinone into benzoquinone.

The experimental conditions were then optimized for hydroquinone detection. Since the oxidation process required alkaline environment, the reaction pH was investigated first. According to Figure S3 in Supporting Information, the reaction pH was set at 7.5 (Figure S5). The reaction temperature was set at 60 °C and assay time was set for 1 h according to (Figure S6 and S7 in Supporting Information). Under the optimized conditions, the ability of the CPNs-based biosensor for quantitative detection of hydroquinone was investigated with different concentrations of hydroquinone. As shown in Fig. 3, the fluorescence peak at 540 nm decreases gradually with increasing concentrations of hydroquinone in the range from 0.01 μM to 1000 μM. A linear relationship ($y = 0.052x+0.113$, $R_2 = 0.997$) was observed between the fluorescence intensity and hydroquinone concentration range from 0.01 μM to 50 μM. The detection limit for hydroquinone was estimated to be 0.005 μM according to the 3σ rule. The developed method showed a wide linear range and improved sensitivity compared to previous fluorescent and electrochemical biosensors for hydroquinone detection as shown in Table 1. Moreover, the developed method was simple, rapid and with excellent reproducibility due to the homogeneous format. We also investigated the possibility of quantifying hydroquinone concentrations based measurement of absorbance. Although there is a good linear correlation between absorbance and hydroquinone concentrations, the detection limit was found to be 8 μM, much higher than the fluorescent method (Figure S8, Supporting Information).

The selectivity of the developed assay was then evaluated by analyzing a series of possible interferences including ions (Na^+, K^+, NO_3^-, CO_3^{2-}, SO_4^{2-} (50 mM each); Ni^{2+}, Mn^{2+}, Ca^{2+}, Zn^{2+}, Fe^{3+} (0.5 mM each)), glucose (50 mM), benzoic acid, phenol, cysteine, and uric acid (5 mM each), resorcin, catechol, and dopamine

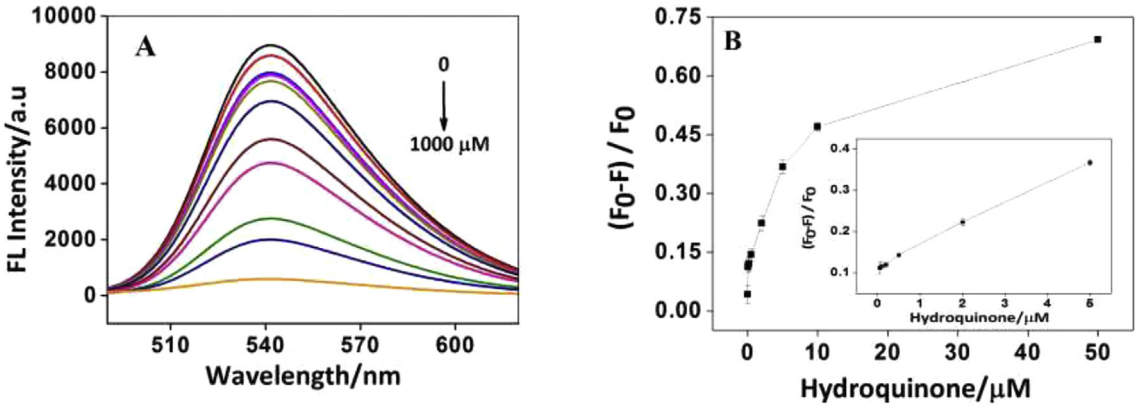

Fig. 3. (A) Fluorescence spectra upon addition of different concentrations of hydroquinone rang from 0.01 μM to 1000 μM. (B) Fluorescence peak intensities versus the hydroquinone concentration. Inset: linear relationship between the fluorescence peak intensity and the logarithm of hydroquinone concentration. Error bars are standard deviation of three repeated experiments.

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Table 1
Comparison of different biosensors for the detection of hydroquinone.

Methods/Materials	Linear range (μM)	Detection limit (μM)	References
Fluorescence/CdTe QDs	0.5–500	0.5	[19]
Fluorescence/C-dots	0.1–50	0.1	[17]
Fluorescence/Polymer	1.0–2000	0.5	[16]
Electrochemistry/CuS nanocrystals	4.5–4500	1.5	[14]
Electrochemistry/Copper complex	60–2500	30	[15]
Fluorescence/CPNs	0.01–50	0.005	This work

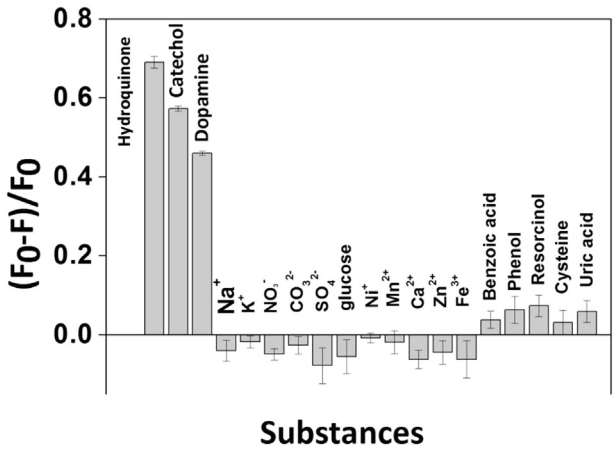

Fig. 4. The selectivity of the developed biosensor for ALP detection over other possible interferences. The concentration of hydroquinone was 0.05 mM, Ni^{2+}, Mn^{2+}, Ca^{2+}, Zn^{2+}, Fe^{3+} were 0.5 mM each, Na^{+}, K^{+}, NO_3^{-}, CO_3^{2-}, SO_4^{2-} were 50 mM each, resorcin, catechol, and dopamine were 0.05 mM each, benzoic acid, phenol, cysteine, and uric acid were 5 mM each, and glucose was 50 mM. Error bars are standard deviation of three repeated experiments.

(0.05 mM each) under the optimal conditions. The results was shown in Fig. 4. Compared to signal of 0.05 mM hydroquinone, signals of most substances can be ignored., indicating desirable selectivity for hydroquinone detection. Catechol and dopamine also had significant responses, probably because these compounds could form quinone structure under oxidation to quench the fluorescence. Resorcin showed no interference because it could not form quinone structure. These results were consistent with previous report utilizing fluorescent graphene quantum dots for hydroquinone detection [18]. Nevertheless, dopamine is a neurotransmitter and the amount in water is very little, hence, its interference is insignificant in real sample analysis. The results indicated the developed method was able to analyze total hydroquinone and catechol in the presence of catechol.

In order to testify the feasibility of the proposed method for the determination of hydroquinone in real samples, three kinds of water sample (tap water, lake water, sewage water that discharged into river) were analyzed. Table 2 shows that the recovery value of the real samples are in the range of 93.1–114.0%, which proved that the coexistent substances have negligible impact on hydroquinone detection.

Table 2
Analysis of hydroquinone in water samples.

Samples	Hydroquinone (μM)		Recovery (%)
	Amount added	Amount found[a]	
Tap water[b]	1	1.05 ± 0.02	105.0
	5	5.03 ± 0.01	100.6
Lake water[c]	1	0.91 ± 0.02	91.0
	5	4.92 ± 0.01	98.4
Sewage water[d]	1	1.14 ± 0.02	114.0
	5	5.05 ± 0.03	101.0

[a] Average of three determinations ± standard deviation.
[b] Tap water from the laboratory.
[c] Lake water at Taozi Lake, Changsha.
[d] Sewage water that discharged into Xiangjiang River, Changsha.

4. Conclusions

In summary, we have developed a simple and sensitive fluorescent method for hydroquinone detection utilizing CPNs. The CPNs were characterized by TEM, DLS, zeta potential, and FT-IR. The mechanism of the assay was thoroughly investigated. The detection limit of hydroquinone was down to 0.005 μM and excellent selectivity was achieved. Real sample analysis demonstrated the method was suitable for practical application. It is envisioned that the developed biosensor will be useful for monitoring hydroquinone level in environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.aca.2018.01.027.

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