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

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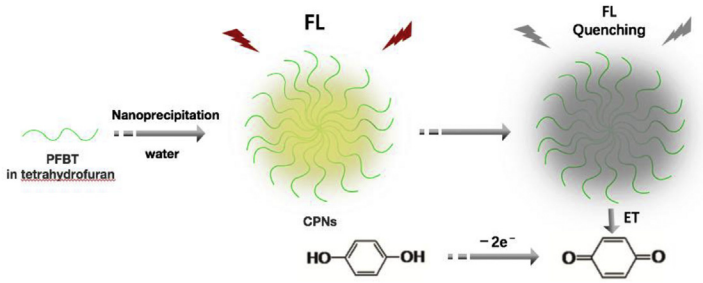
HIGHLIGHTS

- 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

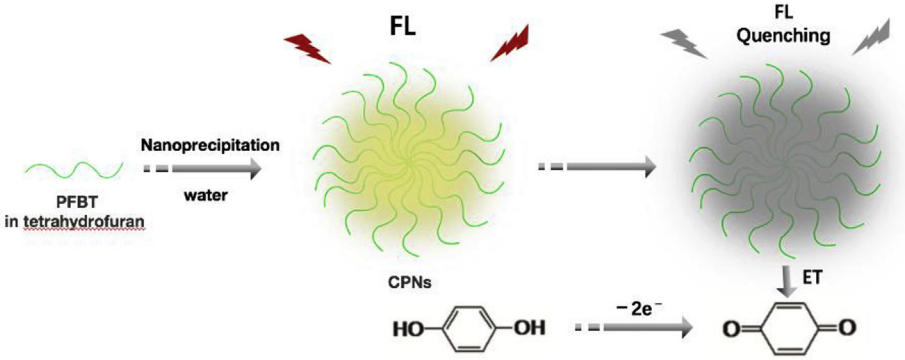
Hydroquinone, glucose, resorcin, phenol, NaCl, $NaNO_3$, Na_2SO_4, Na_2CO_3, KCl, $ZnCl_2$, $NiCl_2·6H_2O$, $MnCl_2·4H_2O$, $CaCl_2·2H_2O$, $FeCl_3·6H_2O$, $Na_2HPO_4·12H_2O$, $NaH_2PO_4·2H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cysteine, uric acid were obtained 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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