Design of a sensing platform with dual performance for detection of hydrogen peroxide and Fe³⁺ based on a new fluorescent oligo N-phenylpyrrole derivative

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ABSTRACT

Fe^{3+} ion and hydrogen peroxide (H_2O_2) have attracted tremendous research interests in the field of analytical chemistry, due to their vast area of use. We report herein the design of fluorescence sensor with dual performance toward detection of H_2O_2 and Fe^{3+} utilizing a novel oligo N-phenylpyrrole (ONPP) derivative. ONPP was synthesized using the oxidation of N-phenylpyrrole by Cu^{2+} as a mild oxidant agent. The fluorescence of ONPP could be selectively quenched by Fe^{3+} ion, resulting in a recognition platform for Fe^{3+} ion. The quenching of ONPP emission by Fe^{3+} was also applied as a strategy for design of a H_2O_2 fluorescence sensor based on the oxidative generation of Fe^{3+} by H_2O_2 in the presence of optimized concentration of Fe^{2+} ion in solution. The developed fluorescence sensor provides a simple and cost effective approach for detection of Fe^{3+} and H_2O_2 traces with linear ranges of 0.2-6.1 and 0.1-0.57 $\mu\text{mol L}^{-1}$ and detection limits of 0.17 and 0.03 $\mu\text{mol L}^{-1}$, respectively. The results of this research will open up new vistas in the synthesis of fluorescent oligomer materials and their application for development of sensitive, simple, low cost and reliable sensing platforms with versatile performance.

Key words: Mild oxidant, Oligo N-phenylpyrrole, Fe^{3+} , H_2O_2 , Fluorescence sensor

1. Introduction

The development of new analytical strategies for sensitive and selective recognition of cations, anions and molecular compounds in different media has long been a subject of interest for both academic and industrial reasons. The unique and astonishing properties of fluorescence-based techniques make them extremely attractive for design of chemical sensors [1, 2] and biosensors [3]. A number of different advanced materials have been recently applied as fluorescence sensing elements including: quantum dots [4, 5], carbon materials [6-8], ionic liquids [9-11], metal–organic frameworks [12], noble metal nanoclusters [13-15] and conjugated polymers, oligomers and molecules [16, 17]. Conjugated fluorescent materials offer some highly desired properties such as non-toxicity [18] and exceptional photostability and brightness [19]. Conjugated polymers based on pyrrole and its derivatives have recently gained tremendous popularity for development of fluorescence sensor platforms. The research devoted to this class of conjugated materials has been led to fabrication of fluorescence sensors for ions [20], molecules [21] and proteins [22].

Iron plays a vital role in many biological processes including oxygen transport, cellular growth, tissue generation and transportation of nerve signals [23] and therefore is an essential chemical for the good performance of almost all living organisms, including human, animal and bacteria [24]. Both the overload or deficiency of this ion from normal

concentration level could result in physiological disorders and diseases such as neurological and Parkinson's diseases [25]. Moreover, uncontrolled releasing of iron, especially Fe^{3+} ion, into the ground water resources would lead to serious environmental problems. According to the U.S. Environmental Protection Agency (EPA), the maximum allowable level of iron in drinking water is $5.357\ \mu\text{M}$ [26]. Therefore, development of analytical techniques capable of selective, sensitive and reliable detection of iron ions is of great importance. Fluorescence spectroscopy has attracted tremendous attention for development of iron ion sensors owing to its outstanding features [27].

H_2O_2 is a simple molecule of hydrogen and oxygen which acts as a versatile compound. H_2O_2 has widespread use in industry, food, medicine, biology and environmental analysis owing to its strong oxidizing ability [28]. In addition, H_2O_2 is a catalytic by-product of a large number of reactions catalyzed by oxidase enzymes which finally leads to release of this compound to water and air, giving rise to serious environmental contamination [29]. Hence, development of sensors and biosensors for reliable and sensitive determination of H_2O_2 has attracted a great deal of attention throughout the world [30-34].

Here we report the synthesis and characterization of a new oligo N-phenylpyrrole (ONPP) derivative by the mild oxidation of N-phenylpyrrole using Cu^{2+} cation, according to a synthesis procedure reported in our previous work [35]. The ONPP showed fluorescence when excited at a wavelength of 250 nm. The fluorescence measurements showed that Fe^{3+} can effectively quench the emission of ONPP. Since H_2O_2 can generate Fe^{3+} by oxidation of Fe^{2+} , the fluorescence of ONPP could indirectly be quenched by H_2O_2 . The fluorescence quenching of ONPP was applied

to develop recognition systems for Fe^{3+} ion and H_2O_2 molecule. The developed sensor platform offered potential for the sensitive, simple, low cost and reliable assessment of Fe^{3+} and H_2O_2 .

2. Experimental

2.1. Reagents

All chemicals used in this work were of analytical grade and used without further purification. N-phenylpyrrole was purchased from Sigma-Aldrich. All metal salts, H_2O_2 , hydrochloric acid and n-hexane, were obtained from Merck. Acetonitrile was obtained from Duksan. Doubly distilled deionized water was used throughout.

2.2. Apparatus

All fluorescence measurements were performed on a Perkin-Elmer model LS 50B spectrofluorimeter (PerkinElmer, U.K.), using emission and excitation band passes of 10 and 10 nm and a scan rate of 100 nm min^{-1} . UV-vis absorption spectra were recorded using a Model Scinco UV S-2100. A Nicolet 100 FT-IR spectrometer was used to measure the infrared spectrum of the sample in the $4000\text{--}400 \text{ cm}^{-1}$ range. The mass spectrum was recorded on a 5973 Network Mass Selective detector, Agilent Technology (HP).

2.3. Synthesis of ONPP

First, 6 mL of 0.050 mol L^{-1} N-phenylpyrrole in acetonitrile was added to 1 mL of 0.050 mol L^{-1} Cu^{2+} in acetonitrile. The mixture was magnetically stirred for 48 h at room temperature which resulted in complete evaporation of solvent. The brown colored solid product was finally washed with double distilled water (25 mL) and n-hexane (25 mL) to remove undesirable residues.

2.4. Detection of Fe^{3+} ion in real samples

Tap water, collected from our laboratory, mineral water, obtained from a local store and Persian Gulf water were used as real samples. Before analysis, all water samples were filtered through a 0.45 μm micropore membrane to remove any suspended particles. Quantitative analysis of the Fe^{3+} ion in real samples was performed by standard addition method to eliminate any matrix effect. Aliquots (2 mL) of water samples were spiked with standard Fe^{3+} solution and then analysed using the ONPP fluorescence probe.

3. Results and discussion

3.1. Studying the synthesis procedure of ONPP

A general procedure for the synthesis of conjugated polymers and oligomers is the oxidation of monomers using chemical oxidants. The chemical structure and also the morphology of resultant polymer or oligomer are dependent on the solvent and the strength of oxidant. Using a mild oxidant in acetonitrile solvent promotes the formation of oligomers instead of polymers. Therefore, in this work ONPP was synthesized using Cu^{2+} as a mild oxidant and acetonitrile as solvent. The molar ratio of N-phenylpyrrole to Cu^{2+} and synthesis time are two essential parameters which must be optimized. Fig. 1a shows the reaction vessels containing different molar ratios of N-phenylpyrrole to Cu^{2+} at various times. It is evident from Fig. 1a that in the first stages of the reaction all reaction vessels have a light green color which gradually changes to dark brown. After 48 h the color of all reaction vessels became fixed and neither of them showed a change in color, indicating the completion of the reaction.

Fig.1

UV-vis spectroscopy was used to explore the effect of molar ratio of N-phenylpyrrole to Cu^{2+} on the synthesis process. The UV-vis spectra of reaction solutions with N-phenylpyrrole to Cu^{2+} molar ratios of 0-8 at 420 nm after 72 h are illustrated in Fig. 1b. Since, neither Cu^{2+} nor N-phenylpyrrole solutions absorb at 420 nm, this wavelength was chosen to explore the synthesis products (see Fig. S1 in the supporting information for visualization of UV-vis spectrum of N-phenylpyrrole and Cu^{2+}).

The absorbance of reaction solution at 420 nm increases as the N-phenylpyrrole to Cu^{2+} ratio rises and reaches a maximum at the molar ratio of 6:1 (Fig. 1b). This finding confirms that the maximum product could be obtained by using a N- phenylpyrrole to Cu^{2+} ratio of 6:1. As a result, ONPP was synthesized within 48 h with a N-phenylpyrrole to Cu^{2+} ratio of 6:1.

3.2. Characterization

Mass and Fourier transform infrared spectroscopies (FT-IR) were utilized for characterization of ONPP. The molecular ion peak of the product was observed at $m/z = 316$ which is consistent with the molecular formula of $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$. FT-IR spectroscopy was used to further investigate the chemical structure of the product (Fig. 1c). The peak at 3060 cm^{-1} corresponds to the aromatic C-H groups. The existence of aliphatic C-H groups in the product is evident from 2923 cm^{-1} peak. The peaks at 1324 and 1380 cm^{-1} are assigned to C=C bonds. The C-N stretching vibration which is in resonance with carbon-carbon double bond and amide C-N vibrations are observed at 1038 and 1300 cm^{-1} , respectively. The peaks at 1074 and 1188 cm^{-1} are attributed to etheric functional groups which are in resonance with carbon-carbon double bond. Finally the peak at 1709 cm^{-1} corresponds to a carbonyl group in the structure of the product. Regarding the information obtained by mass and FT-IR spectroscopies, we proposed the structure (I) for the product (Scheme 1). The proposed structure could be supported by the results

of Richard W Frank's studies on the singlet oxygen oxidation of N-phenylpyrroles [36]. In the other hand the observation of an absorption peak at the wavenumber of 3420 cm^{-1} in the FT-IR spectrum of the product suggests the existence of O-H functional group. Therefore the structure (II) is also possible for the product (Scheme 1). The structures (I) and (II) could exist at the same time through a tautomeric equilibrium. Such tautomeric equilibriums have already been reported for the similar structures [37, 38]. In summary, the synthesis procedure shown in scheme 1 could be proposed for the ONPP.

Scheme 1

3.3. Spectroscopic properties of ONPP

The UV-vis spectrum of ONPP shows a broad absorption band which spans the region from 190-590 nm (Fig. S2). This broad absorption band is composed of a strong peak at 200 nm and a weak shoulder at 420 nm. When ONPP was illuminated by a 250 nm UV light it showed dual emission at 346 and 420 nm (Fig. S3). The fluorescence peak at 346 nm corresponds to a locally excited (LE) state of ONPP and the peak at 420 nm is due to an intramolecular charge transfer (ICT) between the nitrogen lone-pair electrons of pyrrole ring (HOMO) and the phenyl unit (LUMO) [39, 40].

Photostability is an essential feature of a fluorescent material to be used as a probe. The fluorescence intensity measurement of ONPP at 346 nm revealed no significant change in emission intensity in a time period of 60 min (Fig. 2a), suggesting the excellent photostability of ONPP.

Fig. 2

3.4. Fe^{3+} sensing

3.4.1. Effect of different cations and anions on the fluorescence intensity of ONPP

We recorded the fluorescence spectrum of ONPP in the presence of different cations and anions and the results have been shown in Fig. 2b. In all measurements the concentration of ONPP was equal to 2 mg L^{-1} ; the concentration of Fe^{3+} was $5\text{ }\mu\text{mol L}^{-1}$ while the concentration of other ions was $20\text{ }\mu\text{mol L}^{-1}$. Of all the ions tested only Fe^{3+} caused a considerable fluorescence quenching which shows the potential of ONPP probe to be used as a selective fluorescence assay platform for determination of Fe^{3+} ion.

3.4.2. Optimization of influencing parameters in determination of Fe^{3+}

The pH of solution is an important parameter that can affect the spectroscopic properties of ONPP and should be studied. Hydrochloric acid was used for acidification of the ONPP solution. A constant decrease in the fluorescence intensity of ONPP at 346 nm was observed as the pH of solution was lowered in the range of 7-4, which could be assigned to the protonation of nitrogen atoms of pyrrole rings in strong acidic solution. (Fig. 2c). Moreover, in basic pH Fe^{3+} precipitates in the form of ferric oxide, therefore, the pH 7 was selected for the further experiments.

In order to study the response time of ONPP to Fe^{3+} , $4.8\text{ }\mu\text{mol L}^{-1}$ of Fe^{3+} ion was added to the fluorescence cell containing 2 mL of 2 mg L^{-1} ONPP and the response was

measured over time. Our results show that addition of Fe^{3+} ion to the fluorescence cell leads to instant quenching of ONPP.

The ONPP concentration is another important parameter which should be optimized. Fig. 2d shows the response of different concentrations of ONPP probe to $4.8 \mu\text{mol L}^{-1}$ of Fe^{3+} . As the results show the maximum response obtained with 2 mg L^{-1} of ONPP probe. Therefore, ONPP with a concentration of 2 mg L^{-1} was used for determination of Fe^{3+} .

The influence of ionic strength on the Fe^{3+} sensing was also investigated. The effect of ionic strength was evaluated by measuring the response of ONPP to $4.8 \mu\text{mol L}^{-1}$ of Fe^{3+} in the presence of $0\text{-}2.5 \text{ mmol L}^{-1}$ of sodium chloride salt (Fig. S4). As seen, no significant change in the response of ONPP to Fe^{3+} was observed in the presence of high concentrations of sodium chloride, suggesting the potential applicability of the proposed method to determination of Fe^{3+} in real samples containing high concentrations of ionic species.

3.4.3. Quantitative evaluation of Fe^{3+}

In order to explore the potential of ONPP probe as a sensitive fluorescence sensor for determination of Fe^{3+} , the quenching of ONPP fluorescence by Fe^{3+} ion was tested over concentration of $0 - 6.1 \mu\text{mol L}^{-1}$ and the results were presented in Fig. 2e. The changes in the fluorescence intensity of ONPP, $(F_0/F)-1$, were plotted vs. Fe^{3+} concentration and the results were shown in Fig. 2f. The response of ONPP probe toward Fe^{3+} shows linearity in the range of 0.2 to $6.1 \mu\text{mol L}^{-1}$ with a detection limit of $0.17 \mu\text{mol L}^{-1}$.

The particular response of ONPP sensor to Fe^{3+} ion makes it a suitable candidate for fluorescence sensing applications to determine Fe^{3+} in real samples. Therefore, we applied the ONPP probe to the analysis of Fe^{3+} in tap, mineral, and Persian Gulf water samples, using the standard addition method and the results are summarized in Table 1. As seen, we detected Fe^{3+} ion in all water samples and the obtained relative recoveries were rather Satisfactory.

Table 1

3.4.4. Mechanism of ONPP response to Fe^{3+}

Fluorescence quenching by Fe^{3+} ion is a well-known event which has been attributed to its paramagnetic character [41]. UV-vis spectroscopy was used to further explore the mechanism of ONPP quenching by Fe^{3+} . Fig. S5 depicts the UV-vis spectra of various concentrations of Fe^{3+} . The effect of Fe^{3+} on the UV-vis spectrum of ONPP has been illustrated in Fig. S6. As seen, neither shift nor new absorption peak in the UV-vis spectrum of ONPP was observed upon addition of Fe^{3+} , suggesting that the paramagnetic Fe^{3+} ions interact with ONPP molecules in the excited state which results in fluorescence quenching of ONPP.

Table 2 compares the analytical figures of merits of this sensor with a number of techniques developed for determination of Fe^{3+} . As the results show the linear range of this method which is in the range of $\mu\text{mol L}^{-1}$ is comparable with the other techniques. In the other hand, the detection limit obtained in this work is better than most of the other techniques presented in Table 2.

Table 2

3.5. H_2O_2 sensing

We investigated the effect of H_2O_2 on the fluorescence emission of ONPP probe over a concentration range of 1.5-10 $\mu\text{mol L}^{-1}$ (Fig. S7). After addition of H_2O_2 to the fluorescence cell the mixture was allowed to reach equilibrium for 15 min and then the fluorescence spectrum was recorded. As seen, the addition of H_2O_2 with high concentrations results in a subtle decrease in the emission intensity of the ONPP probe. Hence, ONPP is not able to directly respond to H_2O_2 in a sensitive manner and another strategy must be used for development of a sensitive and selective H_2O_2 sensor based on ONPP probe.

H_2O_2 acts as an oxidizing agent to oxidize Fe^{2+} cation to Fe^{3+} according to the following equation:

Thus, in the next step, we planned to design a sensing strategy for H_2O_2 using the oxidation of Fe^{2+} to Fe^{3+} by H_2O_2 . Fig. S8 depicts the effect of H_2O_2 on the ONPP probe in the presence of 25 $\mu\text{mol L}^{-1}$ Fe^{2+} . As seen (Fig S6 and S7) a small fluorescence quenching was observed for high concentration of H_2O_2 and Fe^{2+} which could be attributed to collisional effects. Although neither Fe^{2+} nor H_2O_2 can solely quench the fluorescence intensity of ONPP probe Significantly ($[\text{H}_2\text{O}_2] < 3.5 \mu\text{mol L}^{-1}$ and $[\text{Fe}^{2+}] \leq 10 \mu\text{mol L}^{-1}$), but a considerable fluorescence quenching was observed when H_2O_2 was added to the mixture of ONPP and Fe^{2+} . In order to ensure the proposed mechanism for the quenching of ONPP fluorescence, the sequence of Fe^{2+} and H_2O_2 addition to the

fluorescence cell was reversed, so that $25 \mu\text{mol L}^{-1} \text{Fe}^{2+}$ was added to ONPP in the presence of $2 \mu\text{mol L}^{-1} \text{H}_2\text{O}_2$ and the changes in the fluorescence intensity was recorded (Fig. S9). A significant decrease in the fluorescence intensity was also occurred by reversing the order of Fe^{2+} and H_2O_2 addition, confirming the oxidation of Fe^{2+} to Fe^{3+} by H_2O_2 and a subsequent decrease in the fluorescence intensity.

3.5.1 Optimization of influencing parameters in determination of H_2O_2

The only source for the formation of Fe^{3+} by H_2O_2 is Fe^{2+} , thus the concentration of Fe^{2+} in the fluorescence cell is a very important parameter which should be optimized to obtain the maximum response. Fig. 3a indicates the quenching of ONPP fluorescence by $0.29 \mu\text{mol L}^{-1} \text{H}_2\text{O}_2$ in the presence of different concentrations of Fe^{2+} . As seen, using $10 \mu\text{M} \text{Fe}^{2+}$ resulted in the maximum fluorescence quenching. Therefore $10 \mu\text{mol L}^{-1} \text{Fe}^{2+}$ cation was used for the further studies.

In order to investigate the fluorescence quenching over time, the response of ONPP probe to $0.29 \mu\text{mol L}^{-1} \text{H}_2\text{O}_2$ in the presence of $10 \mu\text{mol L}^{-1} \text{Fe}^{2+}$ cation was recorded for 30 min. As demonstrated in Fig. 3b, the response increased from 5 to 15 min and then reached a constant level. Therefore a time of 15 min was selected as the optimum value.

Fig. 3

3.5.2. Quantitative evaluation of H_2O_2

In the next step, the influence of H_2O_2 concentration as the target analyte on the fluorescence intensity of the ONPP probe was studied and the results are presented in Figure. 3c. As seen, the plot of $(F_0/F)-1$ vs. H_2O_2 concentration gives a linear range from $0.10\text{-}0.57 \mu\text{mol L}^{-1}$ and a detection limit of $0.03 \mu\text{mol L}^{-1}$ (Fig. 3d). Table 3 summarizes the linear ranges and limit of detections obtained from various methods applied for

determination of H_2O_2 . Although the linear range of this research is smaller than other works but the detection limit of developed method is in the nmol L^{-1} range and therefore is far superior to the others.

Table 3

4. Conclusions

In summary, N-phenylpyrrole was oxidized to a new fluorescent oligomer, ONPP, using Cu^{2+} as a mild oxidant. The chemical structure of the product was determined using mass and FT-IR spectroscopies. Fluorescence studies proved that the synthesized ONPP could be used as a sensing material with dual performance. The fluorescence quenching of ONPP by Fe^{3+} ion provided us with a sensing platform which can selectively respond to this ion with a linear range of 0.2 to $6.1 \mu\text{mol L}^{-1}$ and detection limit of $0.17 \mu\text{mol L}^{-1}$. Meanwhile, the oxidative formation of Fe^{3+} by H_2O_2 was applied to design a recognition system for H_2O_2 . Fe^{2+} was oxidized to Fe^{3+} in the presence of H_2O_2 which resulted in a considerable fluorescence quenching of ONPP. Using this strategy H_2O_2 could be detected with a linear range of 0.10- $0.57 \mu\text{mol L}^{-1}$ and an excellent detection limit of $0.03 \mu\text{mol L}^{-1}$.

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Biography

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Figure captions:

Fig. 1 (a) Photographs of solutions with different N-phenylpyrrole (PP) to Cu^{2+} molar ratios at various time. (b) UV-vis spectra of solutions with different PP to Cu^{2+} molar ratios; the inset shows the changes in absorbance at 420 nm. (c) FT-IR spectrum of ONPP.

Scheme 1. Synthesis of ONPP and tautomeric equilibrium between the products.

Fig. 2 Photostability of 2 mg L^{-1} ONPP at 346 nm over the time period of 60 min (a). Response of ONPP probe to $5 \text{ } \mu\text{mol L}^{-1} \text{ Fe}^{3+}$ and $20 \text{ } \mu\text{mol L}^{-1}$ of other cations and anions (b). Optimization of influencing parameters affecting the response of ONPP probe to Fe^{3+} : pH (c), ONPP concentration (d), Fluorescence quenching of ONPP probe upon

addition of different concentrations of Fe^{3+} (0.2, 0.50, 1.0, 1.5, 2.0, 2.9, 3.9, 4.8 and 6.1 $\mu\text{mol L}^{-1}$) (e), Calibration curve for fluorescence quenching of ONPP toward Fe^{3+} (f).

Fig. 3 Optimization of influencing parameters affecting the response of ONPP probe to 0.29 $\mu\text{mol L}^{-1}$ H_2O_2 : Fe^{2+} concentration (a), Time (b); Fluorescence quenching of ONPP probe upon addition of different concentrations of H_2O_2 (0.1, 0.19, .29, .39, .48 and .57 $\mu\text{mol L}^{-1}$) (c), Calibration curve for fluorescence quenching of ONPP toward H_2O_2 at 346 nm (d).

Fig. 1

Scheme. 1

Fig. 2

Fig. 3

Table 1Determination of Fe^{3+} ion in tap, mineral and Persian Gulf water samples using ONPP

Sample	Spiked amount (μM)	Found amount(μM)	Recovery (%)
Tap water	0.00	1.77 (± 0.18)	-
	1.00	1.19 (± 0.07)	119.0
	2.00	1.92 (± 0.19)	96.0
	4.00	4.17 (± 0.28)	104.2
Mineral water	0.00	0.79 (± 0.08)	-
	1.00	1.07 (± 0.06)	107.3
	2.00	1.86 (± 0.15)	93.0
	4.00	4.03 (± 0.19)	100.7
Persian Gulf water	0.00	0.69 (± 0.03)	-
	1.00	1.16 (± 0.13)	116.0
	2.00	2.22 (± 0.19)	111.0
	4.00	3.78 (± 0.21)	94.5

fluorescence sensor ($n = 3$).

Table 2

Comparison of analytical performance of the proposed sensing platform and other techniques in determination of Fe^{3+} .

Method ^a	System	LDR (μM)	DL (μM)	Ref.
A	pyrazoline derivative	10-100	3.0	[42]
A	naphthalimide derivative	10-1000	4.5	[43]
A	gold nanoclusters	5-2000	2.0	[44]
A	poly(1-amino-5-chloroanthraquinone)	0.0001-100	0.00002	[45]
B	anthracene-based schiff base	2-60	2.95	[46]
C	Au nanoparticles -thiourea	1.8-8.9	0.90	[47]
D	carbon paste electrode	0.0055-0.45	0.0017	[48]
E	[HPDTP]	3.5-400	2.5	[49]
A	oligo N-phenyl pyrrole (ONPP)	0.2-6.1	0.17	This work

^a Methods: (A) Turn-off fluorescence, (B) Turn-on fluorescence, (C) Colorimetry, (D) Voltammetry, (E) Potentiometry.

Table 3

Comparison of analytical performance of the proposed method and other techniques in determination of H₂O₂.

Method ^a	System	LDR (μM)	DL (μM)	Ref.
A	Au nanoclusters	20-1000	12	[50]
A	terbium ions and phthalic acid	0.3-2560	0.15	[51]
A	Cu nanoclusters	0.5-10	0.4	[52]
A	polymer nanoparticles	6-1000	2.0	[53]
B	cupric oxide nanoparticles	0.5-200	0.34	[54]
C	CGP and Au nanoparticles	10-100	20	[55]
C	positively-charged Au nanoparticles	2-200	0.5	[56]
D	carbon fiber microelectrodes	50-250	1.9	[57]
E	MnO ₂ -doped carbon paste electrode	0.3-360	0.12	[58]
A	oligo N-phenyl pyrrole (ONPP)	0.1-0.57	0.03	This Work

^a Methods: (A) Turn-off fluorescence, (B) Turn-on fluorescence, (C) Colorimetry, (D) Voltammetry, (E) Potentiometry.

Graphical abstract: