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Rapid determination of nitrophenol isomers in polluted water based on multi-walled carbon nanotubes modified screen-printed electrode

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Abstract: A sensitive screen-printed electrode modified with multi-walled carbon nanotubes (MWCNTs/SPE) was applied to determine simultaneously *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol. The electrochemical response showed that *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol were entirely separated at the MWCNTs/SPE interface. Under the optimized conditions, it was found that the detection limits were 8.1×10^{-8}, 5.5×10^{-7} and 2.0×10^{-7} M and the linear calibration ranges were 1.0×10^{-6}~1.9×10^{-5} M, 2.5×10^{-6}~2.1×10^{-5} M and 2.0×10^{-6}~2.0×10^{-5} M for *m*-nitrophenol, *o*-nitrophenol and *p*-nitrophenol respectively, proving that the electrode presented here could be easily used to determine nitrophenol isomers simultaneously with high sensitivity within pH range from 4.8 to 8.0. The applications in water samples showed that no interferences appeared with deviations below 5% to the determination of nitrophenol isomers with 1000 fold excess, indicating a good response of this method for nitrophenol isomers detection. This disposable modified SPE combining with a portable electrochemical device were performed for wastewater samples on-field rapid determination.

Keywords: Nitrophenol isomer; Multi-walled carbon nanotube; Screen-printed electrode; Differential pulse voltammetry; On-field simultaneous determination

Introduction

Nitrophenol isomers usually coexist in biological and environmental samples, which are important and versatile organic compounds in industrial, agricultural and defense applications. These chemicals are frequently used as intermediates in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, rubber chemicals and fungicides etc. However, their toxicity and potential propagation through the environment via leaching and seepage, especially for *o*-nitrophenol and *p*-nitrophenol, make them to be considered as hazardous wastes and priority toxic pollutants[1,2]. Facing rampant degradation of the ecosystem due to human or nonhuman activities, in order to reduce the toxic discharges, there is need and a great challenge to establish a fast, selective, sensitive and low-cost technique to simultaneously and quantitatively monitor nitrophenol isomers[3].

Many methods, such as flow-injection analysis, electrochemical methods, spectrophotometry, gas chromatography, high performance liquid chromatography and

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capillary electrophoresis have been the most attractive methods and widely used[4-9]. But chromatography takes a long time to make previous separation for mixture sample and need complex treatments to analytical signals, while with spectrophotometry, the polluted detection in colored samples is complicated, making them less convenient in practice. Among these methods, electrochemical sensors have a great impact on the monitoring of pollutants[10]. Such devices allow the instrument to be taken to the on-field sample, avoiding bringing the sample to the laboratory. Electrochemical sensors could perform automated chemical analyses in complex matrices and meet the demand for rapid, reliable and inexpensive measurements of varieties of pollutants[11]. However, nitrophenol isomers peak potentials, as well as other electroactive isomers, are too close to be separated entirely, so it is difficult to simultaneously determine them only by using conventional electrochemistry sensors.

Recently, electrochemical sensors based on new electrode materials have been published to separation and determination of nitrophenol isomers. The early investigation was the voltammetric behaviour as a method for the simultaneous determination of nitro-substituted aromatic compounds, based on a hanging mercury drop electrode (HMDE)[12]. Further research was performed at the new single wall nanotubes compound poly(4-aminopyridine) modified electrode (SWNTs/POAPE) prepared at glass carbon electrode (GCE), which obtained three well-defined oxidation peaks of o-, m-, p-nitrophenol[13]. In a recent study, simultaneous determination of nitrophenol isomers was also achieved at a GCE modified with carbon nanotubes without pre-separation process, which yield the promising results[14]. Indeed, carbon nanotubes with its unique properties such as high aspect ratio, high electrical conductivity and high surface area, provide high sensitivity in electroanalysis and sensor development[15,16]. Accordingly, carbon nanotubes have been employed as a useful material to modify electrode surface in order to enlarge the electrochemical response, approach the low detection limit, obtain high selectively and avoid interference of other electrochemical species[17]. Associated to screen-printed electrode (SPE), it opens new paths in the field of electrochemical sensors in many different applications[18,19]. In addition to ease of its applicability and portability, screen-printing technique is a simple process for the mass production of single used electrodes and inexpensive manufacture procedure[20,21]. As a consequence of these advantages and the miniaturization, small sample volume can be required in-situ or on-line measurements[22,23].

In this paper, a novel electrochemical sensor based on multi-walled carbon nanotubes (MWCNTs) modified SPE (MWCNTs/SPE) was applied to determine simultaneously and sensitivity nitrophenol isomers in polluted water on field. Our approach is to distinguish reduction peaks of nitrophenol isomers. The MWCNTs/SPE was characterized in morphology and electrochemical properties. With differential pulse voltammetry (DPV), the developed MWCNTs/SPE was investigated to quantity and simultaneous determination of the nitrophenol isomers, showing a promising performance on the on-field analysis of nitrophenol isomers.

Results and Discussion

Voltammetric behaviors of nitrophenol isomers at MWCNTs/SPE

The electrochemical behaviors of nitrophenol isomers at SPE and MWCNTs/SPE were explored with cyclic voltammetry. Fig. 1 showed the results in 0.10 M pH 7.0 phosphate buffer solution (PBS) within potential range of -1.0 to +0.4 V. In Fig. 1A, without nitrophenol isomers (curve 1), no potential peak was observed, showing that PBS did not give any electrochemical response in this potential range. In contrary, after adding nitrophenol isomers, well-defined peaks were observed (curve 2 and curve 3) around -0.80 V (R_4), -0.19 V (R_2) and -0.05 V (R_1) for reduction peaks and; -0.15 V (OX_2) and 0.04 V (OX_1) for oxidation peaks. Also, comparing at bare electrode (curve 2), the current peaks at MWCNTs/SPE (curve 3) were more obvious and one new redox peak at -0.38 V (OX_3) and -0.41 V (R_3) appeared, indicating that the electrode process was enhanced at MWCNT/SPE due to great deal of active sites, better conductivity and favorable electrocatalytic power of MWCNTs[24].

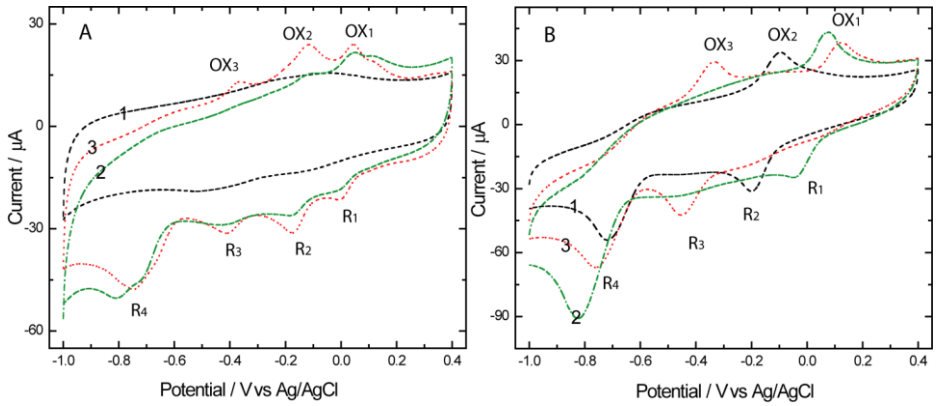


Fig. 1 A: Cyclic voltammograms without nitrophenol isomers (1), with nitrophenol isomers mixture at bare SPE (2) and at MWCNTs/SPE (3); **B**: Cyclic voltammograms of *p*-nitrophenol (1), *m*-nitrophenol (2), *o*-nitrophenol (3) in pH 7.0 PBS at MWCNTs/SPE. Concentration of each isomer: 2.5×10^{-4} M, Scan rate: 100 mV s^{-1}.

This result showed the possibility to choose the potential within this range for simultaneous detection of nitrophenol isomers. Furthermore, cyclic voltammogram shown in Fig. 1B predicted each isomeric peak. The same peaks at MWCNTs/SPE appeared at the same potential indicating the independence of these isomer peaks in the mixture. Here, it is evident that OX_1/R_1 (Fig. 1 B, curve 3), OX_2/R_2 (Fig. 1 B, curve 1) and OX_3/R_3 (Fig. 1 B, curve 2) could be attributed to *p*-, *m*- and *o*-nitrophenol redox peaks respectively. The irreversible peak R_4 was attributed to nitro group of nitrophenol reduction[25].

According to this figure, the large redox peaks (OX_1 and R_4) in the mixture (Fig. 1A) were *o*, *p*-nitrophenol oxidation peaks overlapping (OX_1) and nitro group of nitrophenol isomers reduction peak overlapping (R_4) in the mixture.

In contrary to previous report[26], the difference between the potential reduction peaks for *o*-nitrophenol and *m*-nitrophenol and for *m*-nitrophenol and *p*-nitrophenol was estimated at 200 mV. Also, the investigation of irreversible peak R_4 influence on the reversible peaks of nitrophenol isomers (Supplementary B) showed that the nitrophenol isomers redox peaks resulted from the electrochemical irreversible reduction peak R_4 which was consistent with the literatures[27-29].

Influence of scan rate and pH

The scan rate influence was investigated with cyclic voltammetry. The Fig. 2B showed the result from the cyclic voltammograms (Fig. 2A) obtained at MWCNTs/SPE in pH 7.0 PBS containing 1.0×10^{-4} M of each nitrophenol isomer. It was found that the increase of scan rate resulted in slight shifting of oxidation peak potentials towards positive value and the reduction peak potential towards negative value. Meanwhile, the oxidation and reduction peak currents of nitrophenol isomers at the MWCNTs/SPE are linearly with the square root of scan rate within the range from 20 to 140 mV s^{-1}, respectively, suggesting that the nitrophenol isomers underwent a diffusion-controlled process[29].

According to the slopes ratio and the different concentrations at MWCNTs/SPE and at bare SPE lines (Supplementary table C_1), the apparent area of the MWNTs/SPE modified electrode was about 50 times as large as that of the SPE electrode. Meanwhile, the peak current could reach 7 times as high as that of the bare SPE electrode (when the concentration at bare SPE was 5 fold high than that of MWCNTs/SPE), which could be attributed to the significant enhancement of apparent area, better conductivity[30], great deal of active sites, better conductivity and favorable electrocatalytic power of MWCNTs[24].

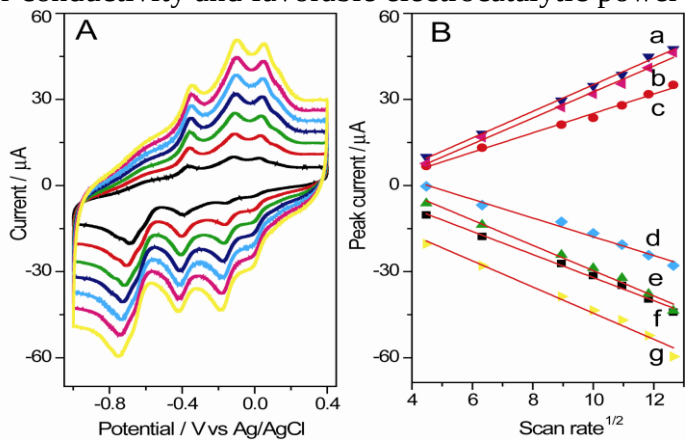


Fig. 2 Cyclic voltammograms of 1.0×10^{-4} M of nitrophenol isomers mixture in pH 7.0 PBS at scan rate 20, 40, 80, 100, 120 and 140 mV s^{-1} **(A)**. Relationship between peak currents and scan rates **(B)**: oxidation peak current of *m*-nitrophenol (a), *p*-nitrophenol (b) and *o*-nitrophenol (c); reduction peak current of *p*-nitrophenol (d), *m*-nitrophenol (e), *o*-nitrophenol (f) and nitro group for the three isomers (g).

The effect of pH was also explored using cyclic voltammetry and differential pulse voltammetry. NaOH and H_3PO_4 solutions were used to adjust the pH of the buffer from 3.5 to 9.0. The cyclic voltammogram results (Fig. C_2) showed that no obvious peak current was found for nitrophenol isomers, especially o- and p-nitrophenol, beyond the pH range 4.8~8.0 due to instability of the electrode and high interference out of this pH range[24]. So the differential pulse voltammetry experiments were carried out within the pH range 4.8~8.0 (Fig. 3).

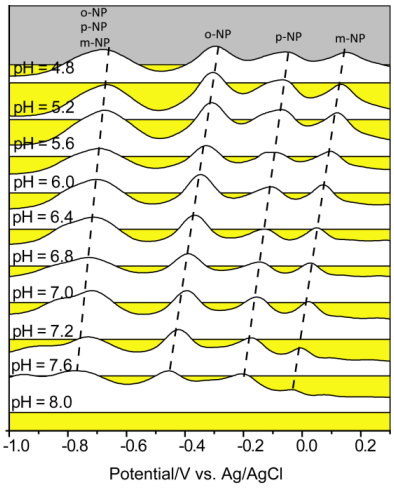


Fig. 3 Differential pulse voltammogram of reduction of *p*-nitrophenol (p-NP), *m*-nitrophenol (m-NP), *o*-nitrophenol (o-NP) in PBS at the pH range of 4.8~8.0; Scan rate: 100 mV s^{-1}; Concentration of each isomer: 1.5×10^{-4} M.

As shown in Fig. 4A, increase in current peak was found within pH range of 4.8 to 6.4, and decreased with pH from 6.4 to 8.0, the highest peak current was observed at pH 6.4. Furthermore, Fig. 4B showed that the peak potentials decreased linearly with the increase of pH values. The relationships between peak potential and pH were given by: $E_p = 0.172 - 0.048pH$ (R = 0.9988), $E_p = 0.442 - 0.059pH$ (R = 0.9969), $E_p = -0.044 - 0.050pH$ (R = 0.9910) and $E_p = -0.520 - 0.030pH$ (R = 0.9966) for m-NP, p-NP, o-NP and nitro group reduction respectively and with -48 mV pH^{-1}, -59 mV pH^{-1}, -50 mV pH^{-1} and -30 mV pH^{-1} as slope.

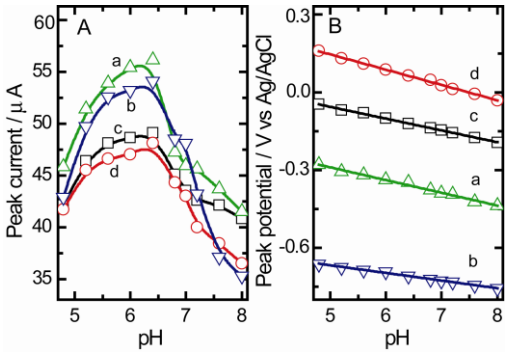


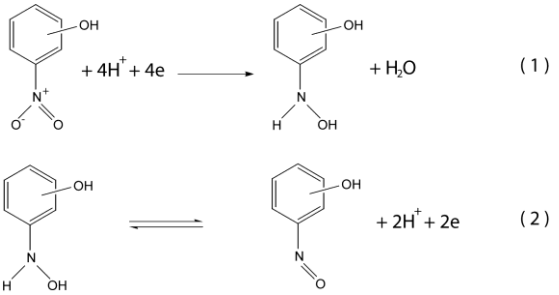
Fig. 4 Influence of pH on the reduction peak currents (**A**) and potentials (**B**) of *o*-nitrophenol (a), nitro group of nitrophenol isomers (b), *m*-nitrophenol (c) and *p*-nitrophenol (d). Scan rate: 100 mV s^{-1}, concentration of each isomer: 1.5×10^{-4} M.

The slope values for *m*, *o*, *p*-nitrophenol reversible reduction peaks suggest that the number of electrons and protons, involved in these three isomers reduction, were equal[27]. In parallel, taken in aggregate in the mixture, nitro group reduction plot with slope of -30 mV pH^{-1}, suggested that two electrons involved in nitrophenol reduction process. This value was confirmed by the relationship reduce[31] for an n electron process (E_p^a and E_p^r are respectively, oxidation and reduction peak potential of the isomer):

$$E_p^a - E_p^r = \frac{59}{n}(mV)$$

These results were consistent with the literature[25] in which it was suggested that for two

electrons process, the following equations below (Scheme 1) as the nitrophenol isomers reduction process.



Scheme 1 Electrochemical reduction process of nitrophenol isomers on MWCNT/SPEs.

The first step (1) was associated with nitro group of nitrophenol isomers irreversible reduction peak and the second step (2), with the characteristic peak of nitrophenol isomers. The half equations were different from those proposed in moderate acid media[32,33]. Indeed, according to our experiments, in weak base, the peaks were still obviously perspicuous.

Moreover, the lines of nitrophenol isomers (Fig.4B) were almost parallel showing that the difference of the potentials was stable and the change in pH would not compromise the resolution[24,29].

Interferences

Some inorganic compounds KCl, $FeCl_3$, $CaCl_2$, and $CuSO_4$ and organic compounds CH_3COONa, p-aminophenol, 1,4-dihydroxyanthraquinone (1,4-DOA) and dihydroxy-benzene isomers were tested in 1.0×10^{-5} M of each nitrophenol isomer, 0.1 M PBS was chosen as buffer solution (Fig. 5). The results showed that at a concentration below 1000 fold excess for these compounds, they did not have any obvious interference with deviations below 5% to the determination of nitrophenol isomers. It was also found that catechol redox peak was closed to p-nitrophenol redox peaks and had serious interference (In fact, with 1500 fold excess of catechol, the interference was slightly above 5%) on its measurement in high concentration of catechol[25].

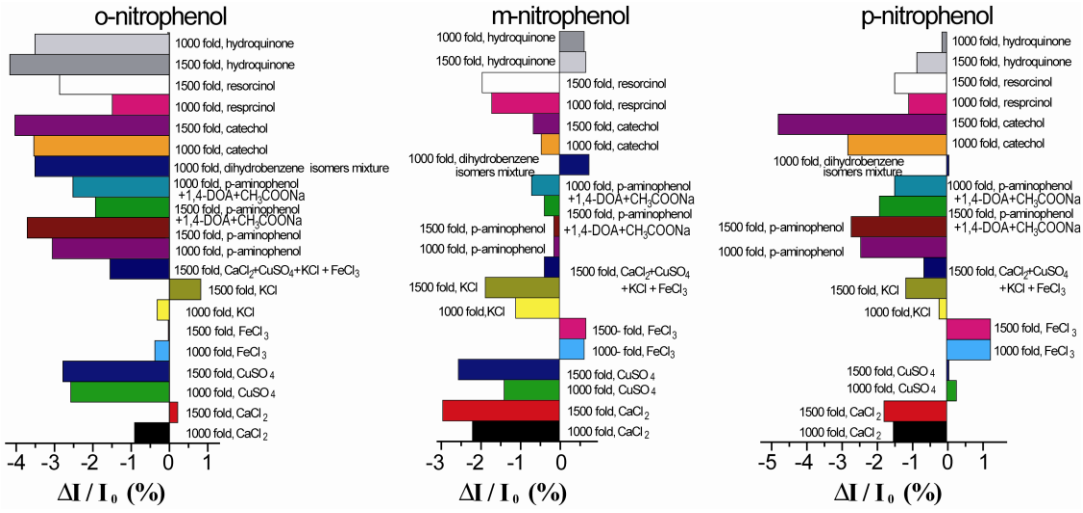


Fig. 5 Interferences of some compounds on the determination of nitrophenol isomers in pH 7.0 PBS.

Simultaneous determination of nitrophenol isomers

In order to evaluate the sensitivity and selectivity of the MWCNTs/SPE for the simultaneous determination of nitrophenol isomers, differential pulse voltammograms (Fig. 6A, B and C) was recorded for different concentrations of one isomer at the MWCNT/SPE in the presence of a constant concentration (1.2×10^{-5} M) of the other two isomers in pH 7.0PBS and at a scan rate of 100 mV s^{-1}. The results obtained in Fig. 6A, B and C showed a monotonically increased peak current for reduction of one nitrophenol isomer with its increasing concentration and reduction peak current of others remained almost constant, indicating the independent reduction of three isomers at MWCNTs/SPE[34]. The Fig. 6D resulting from the Fig. 8A, B and C, indicated that the oxidation peak current of each component was linearly proportional to its concentration in the range of 2.0×10^{-6}~2.0×10^{-5} M for p-nitrophenol, 1.0×10^{-6}~1.9×10^{-5} M for m-nitrophenol and 2.5×10^{-6}~2.1×10^{-5} M for o-nitrophenol and their regression equations were I (A) = $12.3\times10^{-6}+1.8\times$C ($\mu$M), R = 0.9914; I (A) = $27.8\times10^{-6}+0.9\times$C ($\mu$M), R = 0.9989, and I (A) = $9.2\times10^{-6}+2.2\times$C ($\mu$M), R = 0.9977 for *p*- nitrophenol, *m*-nitrophenol and *o*-nitrophenol respectively.

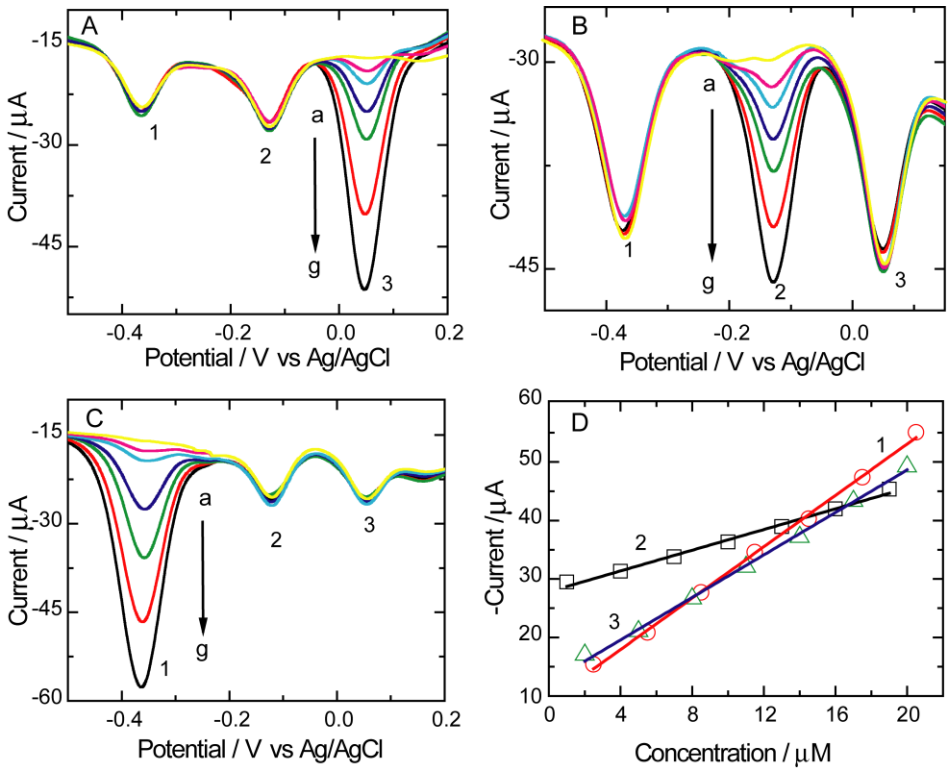


Fig. 6 Differential pulse voltammograms at MWCNTs/SPE with different concentrations of *p*-nitrophenol (**A**), *m*-nitrophenol (**B**) and *o*-nitrophenol (**C**) in the presence of a constant concentration (1.2×10^{-5} M) of the other two nitrophenol isomers in pH 7.0 PBS and at a scan rate of 100 mV s^{-1}. Concentrations for **A**: 2.0 μM (a), 5.0 μM (b), 8.0 μM (c), 11.0 μM (d), 14.0 μM (e), 17.0 μM (f), 20.0 μM (g); **B**: 1.0 μM (a), 4.0 μM (b), 7.0 μM (c), 10.0 μM (d), 13.0 μM (e), 16.0 μM (f), 19.0 μM (g) and **C**: 2.5 μM (a), 5.5 μM (b), 8.5 μM (c), 11.5 μM(d), 14.5 μM (e), 17.5 μM (f), 21.0 μM (g). **D**: Plot of differential pulse voltammogram peak current at MWCNTs/SPE containing different concentrations of *o*-nitrophenol (1), *m*-nitrophenol (2) and *p*-nitrophenol (3).

In these correlation, the slope of *o*-nitrophenol and *p*-nitrophenol current are almost in the same magnitude order and *o*-nitrophenol ~ *p*-nitrophenol > *m*-nitrophenol, showing that the reduction of *o*-nitrophenol ~ *p*-nitrophenol > *m*-nitrophenol when their concentration increased. In this last case, the results are similar of previous works where the reduction of *p*-nitrophenol > *o*-nitrophenol > *m*-nitrophenol[35]. Also, it was found 8.1×10^{-8} M, 5.5×10^{-7} M and 2.0×10^{-7} M as detection limits (LOD) for *m*-, *o*-, *p*-nitrophenol respectively using the following equation[36]: $\mathrm{LOD}=\frac{3\sigma}{\alpha}$, where σ and α are the standard deviation in the peak current-intercept and the slope of the line (peak current versus analyte concentration), respectively.

Clearly, this method might imply an excellent response of nitrophenol isomers simultaneous detection in polluted water in pH range 4.8~8.0.

Applications in real water samples

To evaluate the practical application of this MWCNTs/SPE method; laboratory tap water (pH~7.1), living tap water (pH~7.0) and river water (pH~8.0) were tested. The determination of nitrophenol isomers concentration was performed by addition of 6.4 μM of each isomer in these samples. The results were shown in Table 1. As shown in Table 1, 96~105% was recovered after adding into the water samples, known amounts of nitrophenol isomers.

In addition, it was investigated that it was possible to assay for approximately ten successive times using the prepared electrode with a relative standard deviation (R.S.D.) value of 4.2%, showing that this sensor had a good repeatability.

Finally, by measuring sensor's response to 6.4 μM of each isomer for 1 month, its storage stability and lifetime were examined. The data showed that the sensor retained 87%, 79% and 82% of their original responses for m-NP, p-NP, o-NP, respectively.

Table 1 Determination of nitrophenol isomers in water samples.

Sample	Compound	Added (μM)	Found[a] (μM)	Recovery (%)
Laboratory tap water	m-NP	6.4	6.6	103.1
	o-NP	6.4	6.5	101.6
	p-NP	6.4	6.5	101.6
River water[b]	m-NP	6.4	6.5	101.6
	o-NP	6.4	6.3	98.4
	p-NP	6.4	6.2	96.9
Waste water[c]	m-NP	6.4	6.5	101.6
	o-NP	6.4	6.6	103.1
	p-NP	6.4	6.7	104.7

[a] Average value of five determinations.

[b] River water samples from Qingchun River.

[c] Waste water samples discharged from factories.

Conclusion

This work showed the efficacy of using MWCNT/SPE electrode to determine nitrophenol isomers simultaneously and quantitatively. In a mixture solution, the isomer reduction peaks became well resolved and separated. This method provided a highly selective and fast route to detect the concentrations of nitrophenol isomers, which are significant to environmental control, the chemical industry, pharmaceutical and agricultural detection or in emergency detection and in particular the rapid determination of nitrophenol isomers in polluted water.

Acknowledgements

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Experimental Section

Reagents

2-nitrophenol (o-NP), 3-nitrophenol (m-NP) and 4-nitrophenol (p-NP) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China) and were prepared freshly before used. All reagents were of analytical reagent grade and all solutions were prepared with deionized water (with ρ 18.2 MΩ cm) obtained by a Mili-Q System (Millipore, USA). MWCNTs were supplied by Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China) with a typical diameter of 10~30 nm, length of 5~15 μm and purity of 95~98%. Besides silver ink, carbon ink, silver/silver chloride ink (Camnano Technology Ltd., Xuzhou, China) and insulating ink (Jujo Chemical Co., Ltd., Japan) were also used to fabricate the SPEs.

Apparatus and fabrication of multi-walled carbon nanotubes modified screen-printed electrode (MWCNTs/SPE)

A disposable SPE, with a standard three-electrode system and a 3.1 mm^2 working area, was manufactured onto a glass fiber plate with an AT-25P screen printing machine (ATMA CHAMP ENT. Corp., Taiwan)[37]. Before used, this SPE was pre-treated in pH 7.0 phosphate buffer solution (PBS) by applying an anodic potential of 2.0 V for 200 s. All the electrochemical experiments were carried out with a portable detecting system composed of a CHI-1211A electrochemical workstation (Chenhua Instrument Company, Shanghai, China), a laptop and a SPE. A JSM-6360LV scanning electron microscope (JEOL Ltd., Japan) were used to obtain scanning electron microscopy (SEM) images.

MWCNTs were purified by refluxing in concentrated nitric acid for 12 h at a constant temperature according to a previously described procedure which caused segmentation and carboxylation of the MWCNTs at their terminus[38]. Then, 2.0 mg purified and functionalized MWCNTs were dispersed into 1.0 mL 1.0% HAc (acetic acid) with ultrasonic agitation and a black colloidal solution was formed. To prepare MWCNTs-modified SPE (MWCNTs/SPE), 3 μL (Supplementary A) of MWCNTs colloid was dropped onto the working area of the

manufactured bare SPE. After drying in air, MWCNTs/SPE was rinsed with deionized water three times to remove the impurities. Fig. 7 showed the scanning electron micrograph of bare SPE and MWCNT modified on a SPE. Comparing with the bare SPE, it could be observed that a large number of randomly tangled MWCNT with a typical diameter of 10-30 nm forming stereo porous interspaces (the illustration of the on-site monitoring device and USB connection of the screen-printed electrode was shown in Fig. 8).

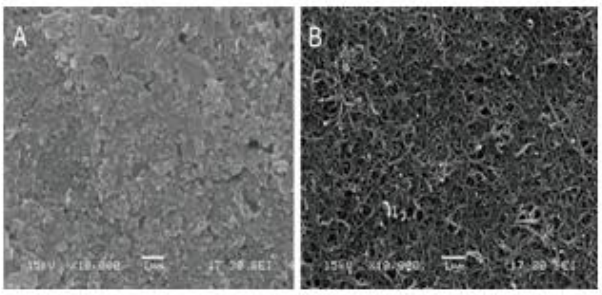

Fig. 7 SEM images of bare SPE **(A)** and MWCNTs/SPE **(B)**.

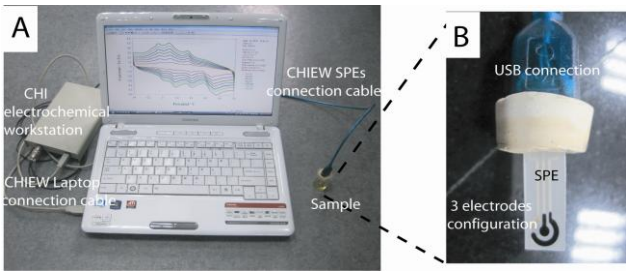

Fig. 8 Illustration of on-site monitoring device (**A**) and USB connection of the screen-printed electrode (**B**).

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