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Electrochemical Synthesis of PtAu Bimetallic Nanoparticles on Multiwalled Carbon Nanotubes and Application for Amperometric Determination of Nitrite

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In the present work, we report the amperometric detection of nitrite using the composite of PtAu nanoparticles decorated multiwalled carbon nanotubes (MWCNT) modified electrode. The MWCNTs/PtAu composite was prepared by simultaneous electrochemical deposition of Pt and Au nanoparticles on MWCNT electrode surface using 2 mM of H_2PtCl_6 and 1.8 mM $HAuCl_4$ mixed solutions as precursors. The surface morphology of the fabricated composite modified electrode was characterized by the scanning electron microscopy. The MWCNT/PtAu composite modified electrode shows an enhanced catalytic activity towards nitrite when compared to the response observed for Pt and Au modified MWCNT modified electrodes. Under optimum conditions, the fabricated MWCNT/PtAu composite modified electrode shows a stable amperometric response for nitrite in the linear response ranging from 0.2 µM to 4.85 mM with the sensitivity of 1186.3 $\mu A\ mM^{-1}\ cm^{-2}$. The MWCNT/PtAu composite modified electrode shows quick response time (5s), low limit of detection (0.09 µM) and high selectivity for the detection of nitrite.

Keywords: Multiwalled carbon nanotubes, Pt, Au, nitrite oxidation, amperometric method.

1. INTRODUCTION

Nitrite is an environmental precursor in the formation of nitrosamines and can greatly affects the environment and human health [1]. Nitrite is also widely used in our daily life and can be easily contaminating with drinking water [2]. Furthermore, nitrite is one of the primary pollutant in the ground water due to the anthropogenic activity from agriculture and waste water from industries [3].

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So far different methods are reported for the determination of nitrite, such as calorimetry [4], by chemiluminescent flow-injection analysis [5], capillary electrophoresis with fluorescence [6], high-performance liquid chromatography with post-column photochemical reaction and chemiluminescence detection [7], and electrochemical methods [8, 9]. Compared with other available traditional methods, the electrochemical methods are widely used for the highly sensitive determination of nitrite due to its unique advantages such as low cost, highly sensitivity, simplicity and portability [10, 11].

In electrochemical sensors, biosensors and energy devices, the metal nanoparticles are received much attention due to their high surface area and a large fraction of metal atoms that are exposed to reactant molecules, which makes them as a promising catalyst materials in diverse applications [12–14]. On the other hand, multiwalled carbon nanotubes (MWCNT) have also been widely used for the electrochemical sensor and biosensors due to its high surface area, good mechanical stability and high electronic conductivity [15]. The metal nanoparticles decorated MWCNT offers enhanced electrocatalytic activity towards the detection of many small molecules including nitrite than that of individual MMCNT and metal nanoparticles [16–21]. By taking the advantages of the past, we have decorated bimetallic nanoparticles such Pt and Au on MWCNT surface, which offers more sensitivity than that individual nanoparticles decorated MWCNT. In addition, the Pt and Au nanoparticles can simultaneously have electrodeposited on MWCNT surface by single step electrochemical method. The resulting MWCNTs/PtAu composite electrode is further used for sensitive amperometric determination of nitrite.

In the present study, we report an enhanced sensing platform for amperometric detection of nitrite using PtAu decorated MWCNT modified electrode. The fabricated Pt/Au decorated MWCNT modified electrode shows an enhanced oxidation peak current response towards nitrite than that of MWCNT/Pt and MWCNT/Au modified electrodes. The selectivity, operational stability, storage stability and practicality of MWCNTs/PtAu composite electrode towards the detection of nitrite also been studied and discussed in detail.

2. EXPERIMENTAL

2.1. Reagents

Dihydrogen hexachloroplatinate (IV) (H_2PtCl_6), gold (III) chloride ($HAuCl_4$), and multi-walled carbon nanotubes (MWCNTs) were purchased from Sigma-Aldrich (USA) and used as received. All other chemicals (Merck) used were of analytical grade (99%). Double-distilled deionised water (> 18.1 $M\Omega\ cm^{-1}$) was used to prepare all solutions. The phosphate buffer solution of was prepared by using 0.1 M Na_2HPO_4 and NaH_2PO_4 solutions. All other reagents were of analytical grade and used without further purifications.

2.2. Apparatus and measurements

The surface morphology of the composite was characterized by Hitachi S-3000 H scanning electron microscope (SEM). The electrochemical experiments were conducted using a CHI 1205a electrochemical workstation (CH Instruments, USA) with a conventional three-electrode setup using glassy carbon electrode (GCE) with the surface area of 0.3 cm^2 as the working electrode, an Ag/AgCl (3 M KCl) as reference electrode and a platinum wire as counter electrode. All potentials reported in this paper were referred to a Ag/AgCl electrode.

2.3. Preparation of the MWCNT/PtAu composite modified electrode

The MWCNTs/PtAu composite was prepared by the simultaneous electrodeposition of Pt and Au on MWCNT surface. Briefly, 10 µL of MWCNT (2 mg/mL) suspension was drop coated GCE and the resulting GCE was immersed into 0.5 M H_2SO_4 solution containing 2 mM of H_2PtCl_6 and 1.8 mM $HAuCl_4$. Then, 20 consecutive cyclic voltammograms were performed in the potential range between -0.6 to 1.05 V with a scan rate of 0.1 V/s. After the 20 consecutive cyclic voltammograms, the Pt and Au nanoparticles were simultaneously electrodeposited on MWCNT surface. The resulting MWCNT/PtAu composite modified electrode was dried in air oven and used for further electrochemical studies. The Pt, Au, PtAu modified electrodes were prepared by the same method without MWCNT.

3. RESULTS AND DISCUSSION

3.1. Electrochemical preparation of MWCNT/PtAu composite

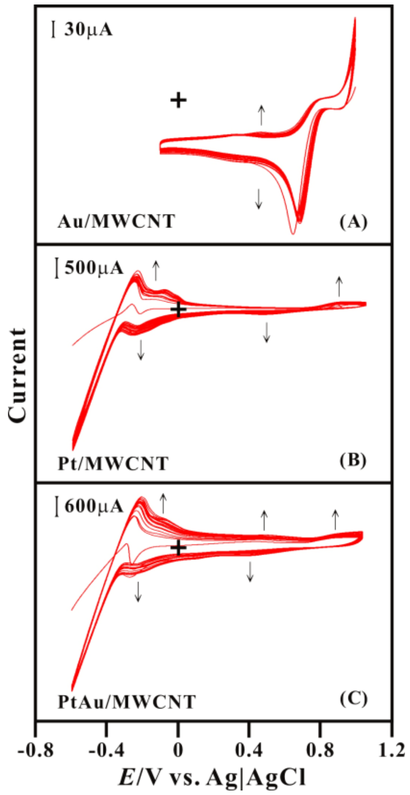

Figure 1. Consecutive cyclic voltammograms (20 cycles) of MWCNT modified electrode in 0.5 M H_2SO_4 solution containing (A) 2 mM H_2PtCl_6, (B) 1.8 mM $HAuCl_4$ and (C) 2 mM H_2PtCl_6 + 1 8 mM $HAuCl_4$, respectively. Scan rate = 0.1 Vs^{-1}.

Fig. 1 shows the cyclic voltammograms of Pt, Au, and PtAu electrodeposition on MWCNTs modified electrode in 0.5 M H_2SO_4 solution containing 2 mM of H_2PtCl_6 and 1.8 mM $HAuCl_4$. Fig. 1A shows the cyclic voltammograms of Au electrodeposition on MWCNT modified electrode, and two characteristic peaks (E_{pa} = 0.47 V and E_{pc} = 0.68 V) are clearly observed. The observed redox peaks are due to the Au redox processes on MWCNT modified electrode surface. Both anodic and cathodic peak currents increase with the increasing in the cycles, indicating the Au nanoparticles are electrodeposited on MWCNTs modified electrode [22]. Fig. 1B depicts the similar characteristic cyclic voltammograms for Pt electrodeposition on MWCNT surface. Fig. 1C shows the consecutive cyclic voltammograms of the simultaneous electrodeposition of PtAu on MWCNTs modified electrode. It shows similar redox behaviour for Pt and Au on MWCNTs modified electrode. This phenomenon clearly indicates that the electrodeposition of PtAu has similar electrochemical processes of Pt and Au on MWCNT electrode surface. Moreover, the electrodeposition of PtAu on MWCNT modified electrode shows an enhanced current profile than that of other electrodeposited single metals (Au and Pt) on MWCNTs modified electrode. The result clears that the successful electrodeposition of PtAu on MWCNT surface.

3.2. Characterizations

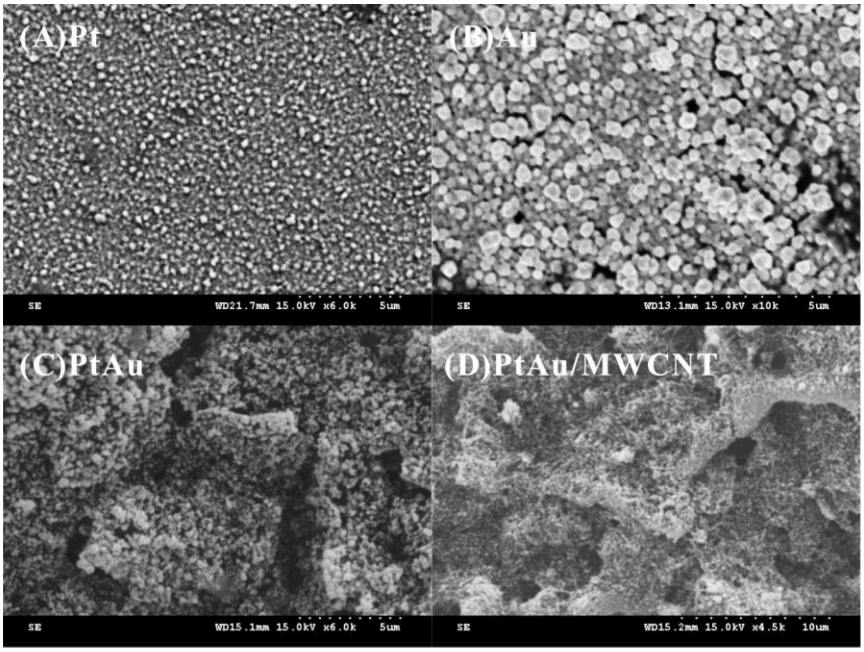

Figure 2. (A) SEM images of (A) Pt, (B) Au, (C) Pt/Au and (D) MWCNT/PtAu composite modified electrodes.

The morphology of the different modified electrodes was studied by SEM. Fig. 2 shows the SEM images of (A) Pt, (B) Au, (C) PtAu and (D) MWCNT/PtAu modified electrodes. Based on the comparison of SEM, the Pt and Au nanoparticles shows an aggregated morphology when compared to the SEM images PtAu nanoparticles decorated MWCNT. On the other hand, a uniform morphology of Pt and Au were observed on the SEM image of MWCNT/PtAu modified electrode. The result indicates that MWCNT may provide more suitable active sites for the formation of uniform sized PtAu on electrode surface.

The average particle size of electrodeposited Pt and Au nanoparticles was analysed by AFM (not show in figure) and the results were compared with electrodeposited Pt and Au nanoparticles on MWCNT surface. The average diameters of Pt, Au, PtAu, and MWCNT/PtAu were observed as 22, 57, 46, and 35 nm, respectively. The result clears that ultra-small size of Pt and Au nanoparticles were deposited on MWCNT electrode surface.

3.3. Electrocatalytic oxidation of nitrite at MWCNT/PtAu electrode

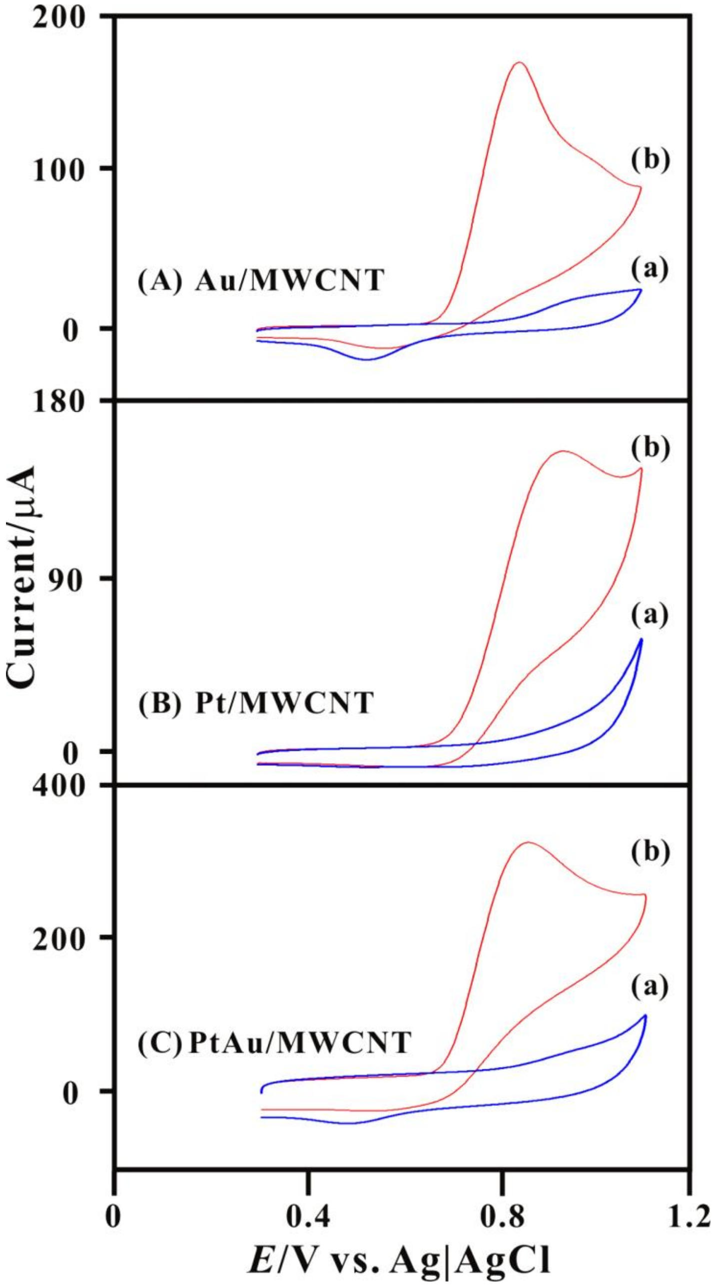

Figure 3. Cyclic voltammograms of (A) MWCNT/Pt, (B) MWCNT/Au, (C) MWCNT/PtAu modified electrodes in the (a) absence and (b) presence of 2 mM nitrite (pH 7 PBS). Scan rate = 0.1 Vs^{-1}.

To explore the catalytic activity of the PtAu/MWCNT composite electrode, the electrocatalytic activity of the different modified electrodes towards nitrite oxidation was investigated by cyclic voltammetry.

Fig. 3 shows the cyclic voltammograms of (A) MWCNT/Pt, (B) MWCNT/Au and (C) MWCNT/PtAu modified electrodes in the absence and presence of 2 mM nitrite in PBS. As shown in Fig. 3A, the MWCNT/Au modified electrode shows an obvious electrocatalytic oxidation peak at 0.846 V. While, the MWCNT/Pt modified electrode shows an oxidation peak of nitrite at 0.936 V. On the other hand, MWCNT/PtAu modified electrode shows oxidation peak of nitrite at quite low overpotential as 0.807 V when compared with other modified electrodes. Furthermore, MWCNT/PtAu modified electrode shows 1.5 and 2 folds enhanced oxidation peak current response for nitrite than that of MWCNT/Pt and MWCNT/Au modified electrodes. The combined unique properties of Au and Pt at MWCNT electrode is resulting to the low overpotential and enhanced sensitivity towards the detection of nitrite. Hence, MWCNT/PtAu modified electrode is more suitable for electrocatalytic oxidation of nitrite than that of other modified electrodes.

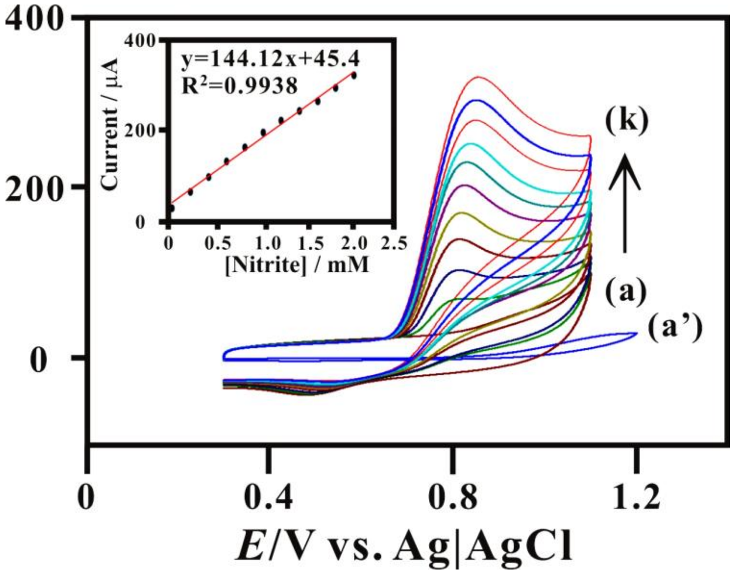

Figure 4. Cyclic voltammograms of MWCNT/PtAu modified electrode in PBS containing nitrite ((a) 0, (b) 0.2 mM, (c) 0.4 mM, (d) 0.6 mM, and (e) 0.8 mM, (f) 1.0 mM, (g) 1.2 mM, (h) 1.4 mM, (i) 1.6 mM, (j) 1.8 mM, (k) 2 mM). Scan rate = 0.1 Vs^{-1}. Inset: the plot of the anodic peak current vs. [nitrite].

Fig. 4 shows the cyclic voltammograms of MWCNT/PtAu modified electrode in PBS with addition of various concentrations of nitrite. It can be seen that the oxidation peak current response of nitrite increase linearly with increasing the concentration of nitrite (inset), which indicates the efficient electro-oxidation of nitrite on MWCNT/PtAu modified electrode. The response of the nitrite was linear up to 2.1 mM with the correlation coefficient of 0.9938. The result suggests that MWCNT/PtAu modified electrode is more suitable for the determination of nitrite.

3.4. Amperometric determination of nitrite

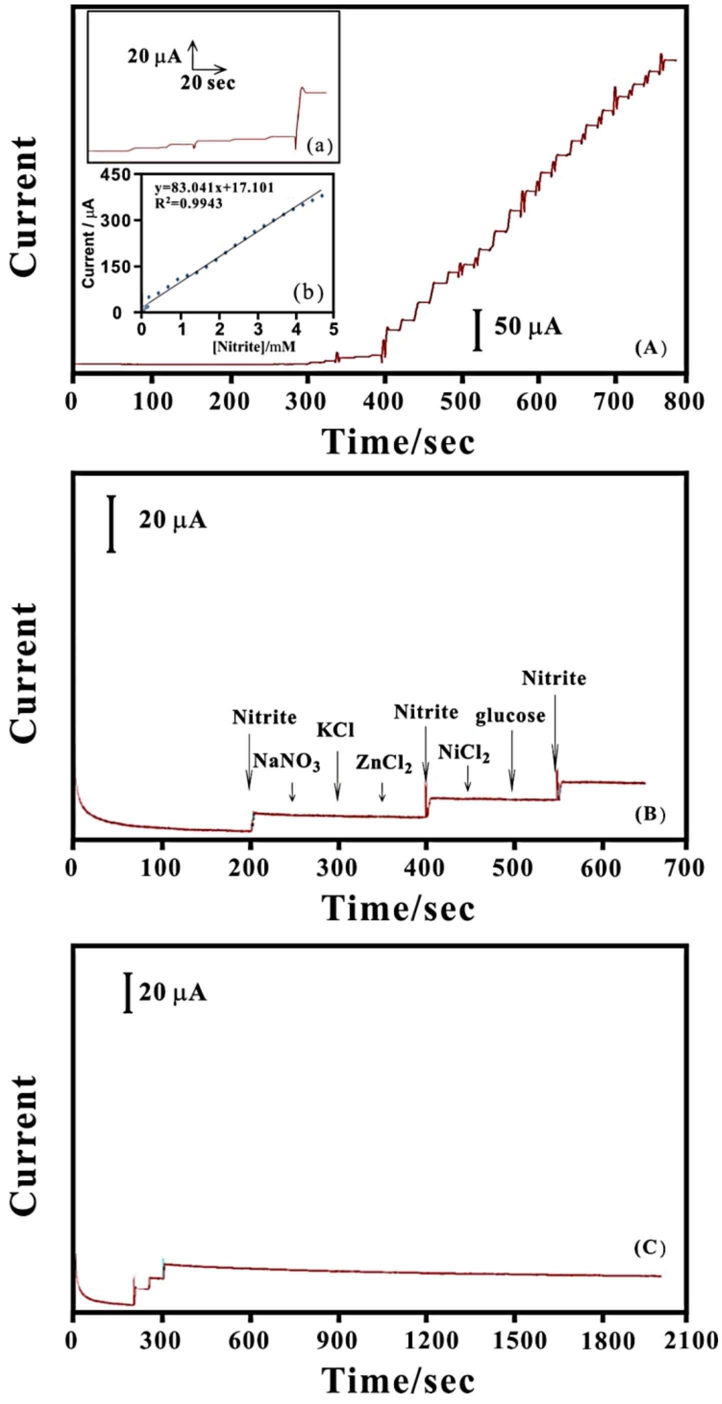

Figure 5. (A) Amperometric responses of sequential additions of nitrite (0.2–4.85 mM) at the MWCNT/PtAu modified electrode in phosphate buffer (pH 7.0). The rotating speed = 2000 rpm, E_{app} = 0.78 V. Inset (bottom): current response vs. [nitrite]; inset (upper): enlarged amperometric response for the additions of 0.2, 0.5, 1.0 and 50 µM nitrite. (B) Amperometric responses of MWCNT/PtAu modified electrode for sequential additions of 25 µM nitrite and 1 mM of $NaNO_3$, KCl, $ZnCl_2$, NiCl and glucose. C) Amperometric i–t response of MWCNT/PtAu modified electrode for 25 µM nitrite into continuously stirred N_2 saturated PBS and background current up to 2000 s.

Fig. 5A shows the amperometric responses of nitrite at MWCNT/PtAu modified electrode for the addition of different concentration of nitrite (0.2 µM – 4.85 mM) into the PBS. Rotating speed = 2000 rpm and $E_{app.}$ = 0.78 V. A well-defined amperometric response was observed for each addition 0.2, 0.5, 1.0 and 50 µM additions of nitrite into the PBS (inset). The response time of the sensor was calculated as 5 s. The amperometric response of nitrite was linear over the concertation ranging from 0.2 µM to 4.64 mM. The sensitivity and detection limit (LOD) were estimated as 1186.3 $\mu AmM^{-1} cm^{-2}$ and 0.09 µM, respectively. The analytical performance of the MWCNT/PtAu modified electrode was compared with previously reported nitrite sensors and the companion results are shown in Table 1. Table 1 clearly reveals that the calculated LOD and sensitivity of the fabricated sensor are higher than previously reported nitrite sensors [23–33]. Hence, the fabricated MWCNT/PtAu composite may be used sensitive detection of nitrite.

Table 1. Comparison of analytical performance of the MWCNT/PtAu modified electrode with previously reported modified electrodes for determination of nitrite.

Modified electrode	**Detection method**	**Eapp (V)**	**LOD (µM)**	**Linear range (mM)**	**Ref.**
Au/ZnO/MWCNTs/GCE	Amperometry	0.75	0.4	up to 400.0	23
GR/CD/SPCE	Amperometry	0.81	0.26	up to 2.15	24
CS@PB/GNS–CNS/GCE	Amperometry	0.86	0.001	up to 0.39	25
RGO-MWCNTs/GCE	DPV	–	25	up to 6.06	26
EAG/SPCE	Amperometry	0.8	0.038	up to 16.4	27
CuO/graphite electrode	CV	–	0.6	up to 1.25	28
CRGO/GCE	Amperometry	0.8	1	up to 0.167	29
RGO/Pd/GCE	DPV	–	0.23	up to 1.0	30
Cu-NDs-RGO/GCE	Amperometry	-0.2	0.4	up to 13	31
GR/PPy/CS/GCE	Amperometry	0.9	0.1	up to 0.722	32
GR-CS/AuNPs/GCE	Amperometry	0.7	0.25	up to 0.38	33
MWCNT/PtAu/GCE	Amperometry	0.78	0.09	up to 4.64	This work

The selectivity of the sensor was examined by amperometry. Fig. 5B shows the amperometric response of MWCNT/PtAu modified electrode in PBS containing 25 µM nitrite and 1 mM of $NaNO_3$, KCl, $ZnCl_2$, $NiCl_2$ and glucose (E_{app} = 0.78 V; rotation speed = 2000 rpm). An obvious current response was observed for the addition of 25 µM nitrite, while 1 mM additions of $NaNO_3$, KCl, $ZnCl_2$ $NiCl_2$, and glucose did not show any response on the modified electrode. The result indicates that MWCNT/PtAu modified electrode exhibit its high selectivity for the detection of nitrite. The operational stability of the MWCNT/PtAu modified electrode was also further examined by amperometric method and the results are shown in Fig. 5C. Fig. 5C clearly reveals that the MWCNT/PtAu modified electrode lost its 0.92% of initial amperometric i-t response when it is continuously run up to 2000 s in 25 μM nitrite, which indicates appropriate operational stability and better antifouling properties of the fabricated electrode. The storage stability of MWCNT/PtAu modified electrode was further examined towards the detection of 1 mM nitrite by CV. The MWCNT/PtAu modified electrode retains 96.4% of its initial current response towards nitrite after 24 days storage in PBS, which indicates the good stability of the proposed sensor. The repeatability and reproducibility of the proposed sensor was examined for the detection of l mM nitrite. The relative standard deviation (RSD) for 5 successive determinations of nitrite was found 1.4% and 3 independent electrodes was found 2.7%. The obtained result indicates the appropriate repeatability and reproducibility of the proposed sensor. The practical ability of the MWCNT/PtAu modified electrode towards the detection of 25 μM of nitrite by amperometry and the results are summarized in Table. 2. The average recoveries of nitrite in the river and tap water are found as 97.2% and 98.7%, respectively. The obtained result authenticates that MWCNT/PtAu modified electrode has good practical ability towards the detection of nitrite in water samples.

Table 2. Determination of nitrite in river and tap water samples using MWCNT/PtAu modified electrode by amperometry.

Sample	Added (μM)	Found (μM)	Recovery (%)
River water	–	–	–
	10.0	9.72	97.2
Tap water	–	–	–
	10.0	9.87	98.7

4. CONCLUSIONS

A simple electrochemical method was used for fabrication of PtAu nanoparticles on the surface of MWCNTs modified electrode. The electrochemical behaviour of different modified electrodes toward the oxidation of nitrite was studied by cyclic voltammetry. The proposed MWCNT/PtAu modified electrode offers the high sensitivity and selectivity for detection of nitrite. The modified electrode also shows good practicality and operational stability towards the detection of nitrite. As a future perspective, the fabricated MWCNT/PtAu composite can be used for sensitive detection of nitrite in environmental samples.

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