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Sensitive Voltammetric Detection of Metol with a TiO_2 Nanowire Modified Carbon Ionic Liquid Electrode

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In this work a TiO_2 nanowire modified carbon ionic liquid electrode (CILE) was constructed and used for the sensitive electrochemical detection of metol. Electrochemical performances of the modified electrode were investigated by the classical techniques including cyclic voltammetry and electrochemical impedance spectroscopy, which indicated that the presence of TiO_2 nanowire on the CILE surface could greatly improve the electrochemical signal. Electrochemical behaviors of metol were further studied on TiO_2/CILE and the appearance of a pair of well-defined redox peaks indicated the excellent electrocatalytic activity. Electrochemical parameters of the electrode reaction of metol, including the electron transfer coefficient (α), the electron transfer number (n) and the heterogeneous electron transfer kinetic constant (k_s), were obtained as 0.46, 1.8, 1.48 s^{-1}, respectively. On the modified electerode the oxidation peak currents of metol increased proportional with the concentration in the range of 0.08 μmol L^{-1}~ 800.0 μmol L^{-1} accompanied by a detection limit of 0.0237 μmol L^{-1} (3σ). Moreover, the analytical performance of the proposed method for artificial water samples was evaluated with good sensitivity and acceptable recoveries.

Keywords: Metol; Carbon ionic liquid electrode; TiO_2 nanowire; 1-hexylpyridinium hexafluorophosphate; Electrochemistry

1. INTRODUCTION

Metol (N-methyl-p-aminophenol sulfate) is a main developing agent in photographic developers, which has been widely used in published developer formulas and commercial products. As a chemical that has been used for over 100 years, the contact with metol can cause a lot of health problems for its toxicity and persistence [1]. Therefore it is important to find sensitive and convenient approaches for metol determination. Many methods including spectrophotometry [2], oscillopolarographic titration [3], liquid chromatography-mass spectrometry [4], ceric oxidimetry [5] and electroanalytical technique [6] have been developed to detect metol in various samples. However, some of these methods suffered from different disadvantages such as expensive, time-consuming and complicated procedure, etc. In contrast to the traditional methods, electrochemical methods have exhibited some advantages including low cost, time-saving, simple operation, fast response, good sensitivity, high selectivity and so on. Wang et al. fabricated a L-cysteine modified gold electrode to recognize and detect metol by differential pulse voltammetry [7]. Li et al. studied the electrochemical behaviors and voltammetric detection of metol using a multi-walled carbon nanotube modified electrode as working electrode [8]. Our group applied ionic liquid (IL) modified carbon paste electrode (CPE) for the electrochemical determination of metol [9, 10].

Carbon ionic liquid electrode (CILE) was manufactured by incorporating IL in the traditional CPE. The electrochemical performance of CILE can be greatly enhanced by adding IL into the CPE, which was owing to the excellent electrochemical properties of IL such as wide electrochemical windows, negligible vapor pressure, high chemical and thermal stability, high ionic conductivity, etc [11]. As a new sort of working electrode, CILE has the advantages of wide electrochemical windows, inherent electrocatalytic ability and anti-fouling ability. Maleki et al. studied the electrochemical performance of 1-octylpyridinium hexafluorophosphate based CILE, which showed better responses than the conventional carbon electrodes [12]. Our group also utilized various IL based CILE for the electrochemical enzyme sensors or DNA detection [13-16]. Zheng et al. fabricated CILE for the electrochemical determination of calcium dobesilate [17]. In recent years chemically modified CILEs have also been fabricated and used in the field of electrochemical sensors. By combining the synergistic effects of modifier and CILE, the modified CILE also exhibited excellent performances with wide applications. Haghighi et al. fabricated a prussian blue modified CILE that was applied to H_2O_2 and glucose measurement [18]. Ping et al. applied a copper oxide nanoparticles modified CILE for the direct electrocatalytic reduction of H_2O_2 in alkaline medium [19]. Liu et al. constructed a colloidal gold modified CILE to immobilize glucose oxidase and further used for the amperometric determination of glucose [20]. Sun et al. also investigated various nanomaterials such as graphene composites modified CILE for studying the electrochemistry of DNA and hemoglobin [21-24].

As an commonly used semiconductor, titanium oxide (TiO_2) has attracted much attentions due to its widely applications in different domains such as sensors, solar cells photocatalysis, biomaterials and catalyst [25]. Due to its good biocompatibility, high surface area and relatively electronic properties, nanosized TiO_2 has been used for fabricating chemically modified electrodes and electrochemical biosensors [26]. Zhan et al. investigated the direct electrochemistry of horseradish peroxidase immobilized in TiO_2 nanoparticle films on pyrolytic graphite electrode [27]. Bao et al. applied a porous TiO_2 nanomaterial for the direct electrochemistry of glucose oxidase and glucose detection [28]. Wang et al. applied a TiO_2/graphene composite modified CILE for the electrochemical detection of specific *tlh* gene [29]. Song et al. investigated the direct electrochemistry of hemoglobin with the usage of TiO_2 whisker [30]. Therefore nanostructured TiO_2 has exciting prospects in applications as a modifier in various chemical modified electrodes.

In this paper a TiO_2 nanowire was synthesized according to a hydrothermal method and further modified on the surface of CILE with the help of chitosan film to get the modified electrode (CTS-

TiO_2/CILE). The electrochemical behaviors of metol were further studied on CTS-TiO_2/CILE with relative electrochemical parameters calculated. A new electrochemical method for the sensitive determination of metol with CTS-TiO_2/CILE as the working electrode was proposed and further utilized to water samples detection with satisfactory results.

2. EXPERIMENTAL

2.1 Apparatus and Chemicals

General electrochemical experiments such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a CHI 1210A electrochemical workstation. Electrochemical impedance spectroscopy (EIS) experiments were carried out on a CHI 750B electrochemical workstation (Shanghai Chen Hua Instrument, China). A traditional three-electrode system was used in the electrochemical experiments with CTS-TiO_2/CILE as the working electrode, saturated calomel electrode (SCE) as the reference electrode and platinum wire as the auxiliary electrode. Scanning electron microscopic (SEM) observation was taken on a JSM-6700F scanning electron microscopy (JEOL, Japan).

Metol (Shanghai Chemical Reagent Station, China), 1-hexylpyridinium hexafluorophosphate ($HPPF_6$>99%, Lanzhou Greenchem. ILS. LICP. CAS., China), chitosan (CTS, minimum 92 % deacetylated, Dalian Xindie Co. Ltd., China), glucose, ribonucleic acid and deoxyribonucleic acid (Sinopharm Chemical Reagent Co. Ltd., China), L-arginine, glycine, L-cysteine and m-nitrophenol, hydroquinone (Aladdin Reagent Co. Ltd., China), β-cyclodextrin (Tianjin Guangfu Fine Chemical Research Institute, China), sodium dodecyl sulfate (Tianjin Kemiou Chemical Reagent Co. Ltd., China) and graphite powder (average particle size 30 μm, Shanghai Colloid Chem. Co., China) were utilized as received without further purification. TiO_2 nanowire was synthesized according to the method reported in the literature with a little modification [31]. The supporting electrolyte was 0.1 mol L^{-1} Britton-Robinson (B-R) buffer and the pH values were adjusted with 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl. All the other chemicals in this study were all of analytical reagent grade and used as received. Doubly distilled water were used throughout the investigation.

2.2 Fabrication of CTS-TiO_2/CILE

CILE was fabricated according to a previous work we had reported [32]. Briefly 1.6 g of graphite powder and 0.8 g of $HPPF_6$ were mixed thoroughly in a mortar to conform a homogeneous carbon paste. Then a portion of the carbon paste was filled into one end of a glass tube (Φ=4 mm) with a copper wire inserted through the opposite end as the electrode wire.

The modified CILE was prepared as follows. A 6.0 μL of 0.5 mg mL^{-1} TiO_2 nanowire and 1.0 mg mL^{-1} CTS (in 1.0 % HAc) mixture solution was cast on the surface of newly prepared CILE and left it to dry at ambient temperature. In order to slow down the water evaporation, a small beaker was covered on the electrode surface throughout this process. The fabricated electrode was denoted as CTS-TiO_2/CILE and laid in 4 °C refrigerator when it was not in use.

3. RESULTS AND DISCUSSION

3.1 Characterizations of CTS-TiO_2/CILE

Figure 1A showed the SEM image of TiO_2 nanowire, which displayed massive thin wires with a length within a range of several micrometers. Electrochemical properties of the modified electrodes were explored by CV and EIS. A 1.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ and 0.5 mol L^{-1} KCl mixture solution was used to record the cyclic voltammograms of different modified electrodes with the scan rate of 100 mV s^{-1}, and the results were shown in Figure 1B. On CILE a pair of redox peaks appeared with smallest redox currents and the peak-to-peak separation (ΔE_p) as 91 mV (curve a), indicating the slowest electron transfer rate. While on CTS/CILE both the redox peak currents increased with the ΔE_p value reduced to 86 mV (curve b), which could be attributed to the presence of CTS film on the electrode surface. CTS is in positive charged and can adsorb negatively charged $[Fe(CN)_6]^{3-/4-}$ on the electrode surface, which results in the increase of the electrochemical response. On CTS-TiO_2/CILE the redox peak currents were further increased with the ΔE_p decreased to 73 mV, which indicated that the presence of TiO_2 nanowire was favorable for the electrochemical reaction of $[Fe(CN)_6]^{3-/4-}$. TiO_2 nanowire is a semiconductor with certain conductivity and the effective surface of the modified electrode is increased due to the large surface area of TiO_2, which is benefit for the electron transfer. Therefore the electrochemical responses of $[Fe(CN)_6]^{3-/4-}$ was enhanced on CTS-TiO_2/CILE.

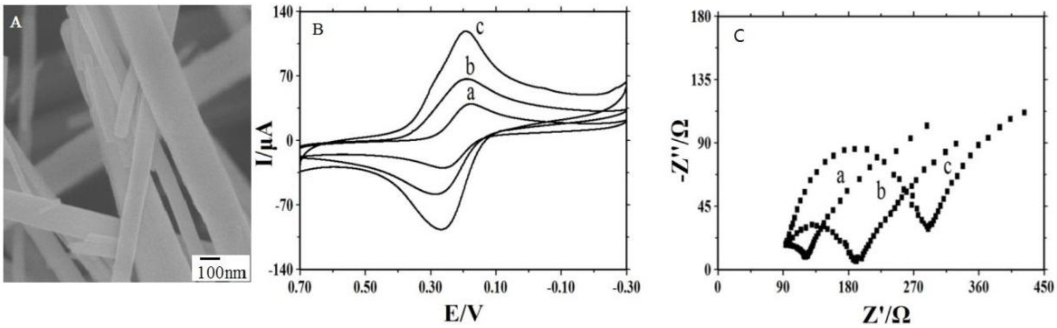

Figure 1. (A) SEM images of TiO_2 nanowire; (B) Cyclic voltammograms of (a) CILE; (b) CTS/CILE and (c) CTS-TiO_2/CILE in 1.0 mmol L^{-1} $K_3[Fe(CN)_6]$ solution containing 0.5 mol L^{-1} KCl, Scan rate: 100 mV s^{-1}; (C) EIS of (a) CILE, (b) CTS/CILE and (c) CTS-TiO_2/CILE in a solution of 10.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol L^{-1} KCl with the frequencies swept from 10^5 to 10^{-1} Hz.

EIS is a powerful technique to analysis the impedance changes of the electrode interface after modification, which is commonly used for exploring the interfacial information. The semicircle diameter of Nyquist plots reflected the electron transfer resistance (Ret) on the electrode surface. EIS measurement was actualized by applying an AC voltage with 5 mV amplitude in the frequency range swept from 10^5 to 10^{-1} Hz. Figure 1C presented the EIS results from 0.1 mol L^{-1} KCl and 10.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ mixture solution at CILE, CTS/CILE and CTS-TiO_2/CILE. It could be seen that the Ret value was got as 202.5 Ω (curve a) on CILE and that of CTS/CILE decreased to 98.7 Ω (curve b). While on CTS-TiO_2/CILE the Ret value was further decreased to 29.08 Ω, which was attributed to the presence of TiO_2 nanowire on the surface of electrode that could decrease the interface resistances.

3.2 Electrochemical response of metol on the modified electrode

Electrochemical behaviors of metol on CILE and CTS-TiO_2/CILE in pH 5.0 B-R solution with 5.0×10^{-4} mol L^{-1} metol were investigated by CV and the results were shown in Figure 2. It could be seen that on both electrodes a pair of well-defined redox peaks appeared, indicating the electrochemical reaction of metol had took place on the working electrode [9]. On CILE (curve a) the redox peak potentials were got as at 0.224 V (E_{pa}) and 0.116 V (E_{pc}) with the redox peak currents as 58.03 μA (I_{pa}) and 66.71 μA (I_{pc}). The value of ΔE_p was calculated as 108 mV. While on CTS-TiO_2/CILE (curve b) the redox peak potential was get as 0.204 V (E_{pa}) and 0.135 V (E_{pc}) with the ΔE_p value of 69 mV. Also the redox peak currents were got as 106.7 μA (I_{pa}) and 119.3 μA (I_{pc}), which was about 1.9 times higher than that of CILE. The increase of redox peak currents was ascribed to the presence of TiO_2 nanowire on the electrode surface that exhibited high surface area with improved conductivity. Consequently, highly enhanced electrochemical responses of metol appeared on TiO_2 nanowires modified electrode with better reversibility, which could be used to the sensitive detection of metol.

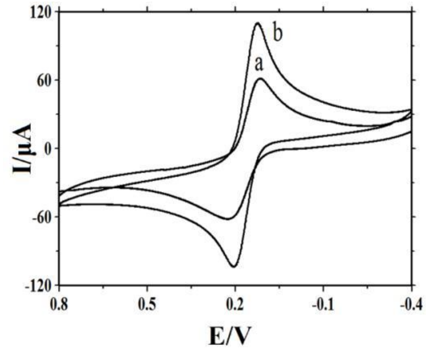

Figure 2. Cyclic voltammograms of 5.0×10^{-4} mol L^{-1} metol on (a) CILE and (b) CTS-TiO_2/CILE in pH 5.0 B-R buffer solution with the scan rate of 100 mV s^{-1}.

3.3 Effect of pH on the electrochemical response

The effect of buffer pH on the voltammetric responses of 5.0×10^{-4} mol L^{-1} metol on CTS-TiO_2/CILE was investigated by CV with the pH values from 2.5 to 7.0, and the results were displayed in Figure 3A. Then the relationships between the formal peak potential ($E^{0'}$), the oxidation peak currents and pH were established respectively, with the results shown in Figure 3B and C. With the increase of buffer pH, the redox peak potentials of metol moved negatively along with the change of the peak shape, which indicated that protons were involved in the electrode reaction. The linear regression equation between $E^{0'}$ and pH was calculated as $E^{0'}$(V)=-0.0635 pH+0.555 (γ=0.995). The slope value of -63.5 mV pH^{-1} was close to the theoretical value of -59.0 mV pH^{-1}, indicating that the same amount of protons and electron transferred number involved in the electrode reaction. In the solution pH range of 2.5~7.0, the I_{pa} value increased from 2.5 to 5.0 and then decreased with the maximum value got at pH 5.0. Therefore buffer solution at pH 5.0 was selected as the supporting electrolyte for all the electrochemical experiments. The results also illustrated that proton was involved in the electrochemical reaction, and the electrochemical reaction would become difficult without the proton existed in alkaline solution.

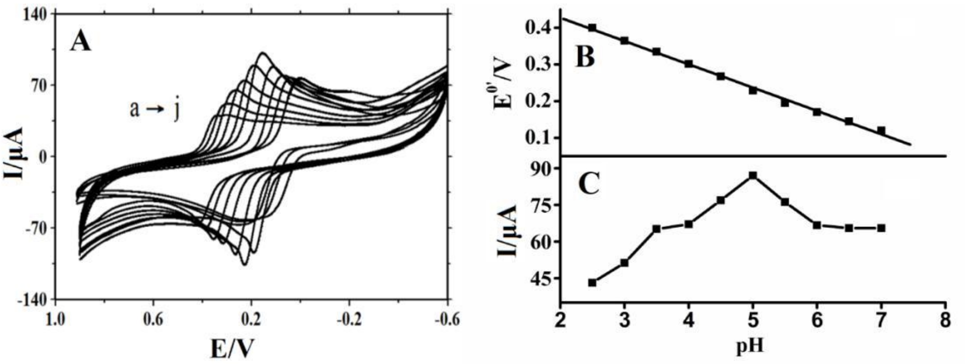

Figure 3. (A) Cyclic voltammograms of 5.0×10^{-4} mol L^{-1} metol on CTS-TiO_2/CILE with different pH values (from a to j are 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0) at the scan rate of 100 mV s^{-1}; (B) Relationship between the formal peak potential ($E^{0'}$) and buffer pH; (C) Relationship of the oxidation peak current (I_{pa}) with buffer pH.

3.4 Effect of scan rate on the electrochemical response

In a 5.0×10^{-4} mol L^{-1} metol solution, the effect of scan rate on the voltammetric response of metol at the CTS-TiO_2/CILE was investigated. As shown in Figure 4A, when the scan rate increased, the redox peak currents also increased correspondingly. The relationships of electrochemical responses with scan rate were further constructed. The redox peak currents exhibited a linear relationship with the square root of scan rate ($v^{1/2}$) in the range from 20 to 450 mV s^{-1} (Figure 4B), illustrating a diffusional-controlled redox process of metol on CTS-TiO_2/CILE. Therefore the diffusional coefficient (D) was further calculated by chronocoulometry. The relationship between the charge amount (Q) and $t^{1/2}$ was constructed and a linear regression equation of Q (mC)=116.46$t^{1/2}$+4.53 (γ=0.999) was got. In accordance with the integrated Anson's equation [33], the apparent diffusion coefficient (D) of metol was calculated as 8.95×10^{-5} cm^2 s^{-1}, which was larger than a previous reported value of 2.24×10^{-6} cm^2 s^{-1} [7].

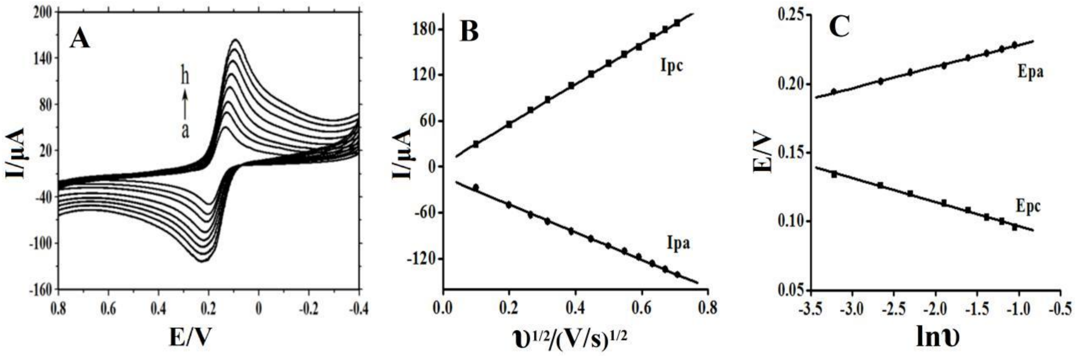

Figure 4. (A) Cyclic voltammograms of 5.0×10^{-4} mol L^{-1} metol on CTS-TiO_2/CILE with different scan rates (a–h: 40, 70, 100, 150, 200, 250, 300, 350 mV s^{-1}) in pH 5.0 B-R; (B) Linear relationship of I_{pc} and I_{pa} with $v^{1/2}$ in the range from 40 to 350 mV s^{-1}; (C) Linear relationship of E_{pa} and E_{pc} with ln$v$.

In the meantime, the oxidation peak potential shifted positively and the reduction peak potential moved negatively with the ΔE_p value enlarged as the scan rate increased, indicating a quasi-reversible process. Then the electron transfer kinetics of metol on CTS-TiO_2/CILE was calculated based on the relationship of the redox peak potentials and scan rate. In the scan range rate from 40 to 350 mV s^{-1}, the redox peak potentials of E_{pa} and E_{pc} had a linearships with ln$v$. The regression equations were got as E_{pc}(V)=-0.0155 ln$v$+0.086 (γ=0.999) and E_{pa}(V)=0.0132 ln$v$+0.236 (γ=0.999), respectively. According to the method demonstrated by Nicholson's model [34], the possible redox reaction mechanism could be calculated with the slopes of the lines expressed as $RT/(1-\alpha)nF$ for E_{pa} and $RT/\alpha nF$ for E_{pc}, where α and n were the symbols of charge transfer coefficient and number of electron transferred. Therefore, α, n and k_s (the electrode reaction standard rate constant) were calculated as 0.46, 1.8, 1.48 s^{-1}, respectively. The k_s value in this work was larger than 0.92 s^{-1} reported in a previous paper [35], which showed a fast electron transfer rate on CTS-TiO_2/CILE.

3.5 Calibration curve and reproducibility

Under the optimal experimental parameters, the relationship of oxidation peak current (I_{pa}) with metol concentration was studied by DPV for its better sensitivity than CV with the results shown in Figure 5. It could be seen that the linearity between I_{pa} value and metol concentrations covered the range of 0.08~80.0 μmol L^{-1} and 200.0~ 800.0 μmol L^{-1}. The equations could be expressed as I_{pa} (μA) = 0.142 C (μmol L^{-1})+0.638 (n=13, γ=0.997) and I_{pa} (μA) = 0.072 C (μmol L^{-1})+5.875 (n=4, γ=0.999), respectively. The detection limit was 0.0237 μmol L^{-1} (3σ), which was lower than previous report values of 5.0 μmol L^{-1} on a multiwall carbon nanotubes modified glassy carbon electrode [8] and 2.0 μmol L^{-1} on a 1-ethyl-3-methylimidazolium tetrafluoroborate based CILE [9]. The relative standard deviation (RSD) of 11 successive determinations of 2.0×10^{-5} mol L^{-1} metol had the results of 3.18 %, indicating that CTS-TiO_2/CILE exhibited good reproducibility for voltammetric detection. The stability of the electrode was further examined by repetitive scanning the modified electrode in a 5.0×10^{-4} mol L^{-1} metol solution, and the results indicated that 97.4 % of the initial response was remained after continuous 60 potential cycles. The CTS-TiO_2/CILE was stored at 4 °C refrigerator for 4 weeks, which gave the decrease of the response as 5.65 % with good stability.

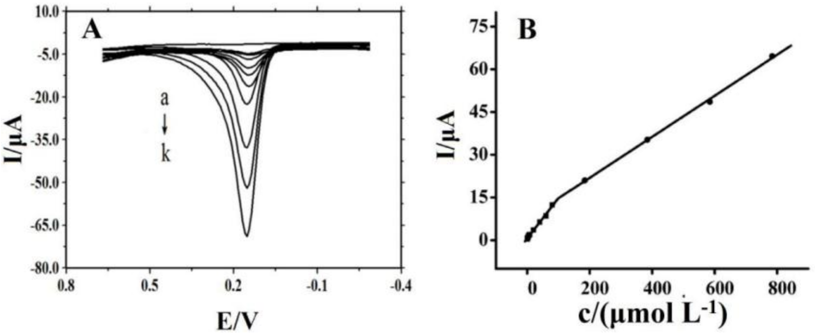

Figure 5. (A) DPV of metol with increasing concentration (a–k: 0.0, 6.0, 8.0, 20.0, 40.0, 60.0, 80.0, 200.0, 400.0, 600.0, 800.0 μmol L^{-1}); (B) The relationship of the oxidation peak current with metol concentration.

3.6 Interference

For evaluating the anti-interference ability of the present method for metol determination, the influences of common present substances including various ions, biomacromolecules and surfactants were investigated by the general procedure under optimum conditions with 1.0×10^{-4} mol L^{-1} metol and different amounts of possible interferents. The results were displayed in Table 1, and it can be seen that no significantly influences appeared for the detection of 1.0×10^{-4} mol L^{-1} metol at the selected concentration, which showed high anti-interference of the proposed method.

Table 1. Influences of coexisting substances on the determination of 1.0×10^{-4} mol/L metol (n=6)

Coexisting substance	Concentration (mg L^{-1})	Relative error (%)	Coexisting substance	Concentration (mol L^{-1})	Relative error (%)
Glucose	10.0	-1.69	Catechol	1.0×10^{-4}	-0.52
Deoxyribonucleic acid	10.0	-2.32	Cu^{2+}	1.0×10^{-4}	-1.93
L-arginine	10.0	0.34	Mg^{2+}	1.0×10^{-4}	2.46
Ribonucleic acid	10.0	3.09	Mn^{2+}	1.0×10^{-4}	-3.38
β-cyclodextrin	10.0	-1.59	Na^{+}	1.0×10^{-4}	-2.78
Glycine	10.0	-2.39	Ni^{2+}	1.0×10^{-4}	-2.23
Sodium dodecyl sulfate	10.0	1.89	Zn^{2+}	1.0×10^{-4}	-4.19
L-cysteine	10.0	-2.01	K^{+}	1.0×10^{-4}	2.04
Hydroquinone	17.8	1.96	NO_3^{-}	1.0×10^{-4}	-3.01
m-Nitrophenol	13.9	-2.03	Cl^{-}	1.0×10^{-4}	-2.24

3.7 Analytical applications

In order to ascertain the potential application, the proposed method based on CTS-TiO_2/CILE was used to analyze metol concentration in the artificial wastewater samples, which contained metol and metal ions. As shown in Table 2, metol in the water samples could be satisfactory detected with the recovery in the range from 98.6 to 104.0%, indicating the possible applications of the proposed electrode to metol detection. In order to prove the accuracy of this electrochemical method, a commonly used titration method for the metol determination [36] was also performed with the results shown in Table 2, it can be seen that the results were in agreement with those of electrochemical method. Therefore, the proposed method can be used for the routine analysis of metol.

Table 2. Determination results of metol in the artificial wastewater samples (n=5)

Sample	Specified (mol L^{-1})	Detected (mol L^{-1})	Added (mol L^{-1})	Total (mol L^{-1})	RSD (%)	Recovery (%)	Titration method (mol L^{-1})
1	1.0×10^{-4}	1.013×10^{-4}	1.0×10^{-5}	1.117×10^{-4}	1.85	104.0	1.02×10^{-4}
2	1.0×10^{-4}	1.020×10^{-4}	3.0×10^{-5}	1.329×10^{-4}	1.97	103.0	1.03×10^{-4}
3	1.0×10^{-4}	1.016×10^{-4}	5.0×10^{-5}	1.509×10^{-4}	2.38	98.6	1.03×10^{-4}
4	1.0×10^{-4}	1.021×10^{-4}	7.0×10^{-5}	1.718×10^{-4}	3.12	99.6	1.02×10^{-4}
5	1.0×10^{-4}	1.018×10^{-4}	9.0×10^{-5}	1.937×10^{-4}	2.64	102.1	1.03×10^{-4}

4. CONCLUSIONS

In this paper TiO_2 nanowire was synthesized and casted on the surface of CILE to get the modified electrode, which was further applied to the investigation on the electrochemical behaviors of metol. Due to the specific characteristics of TiO_2 nanowires with large surface area and certain conductivity, the electrochemical performance for metol detection was greatly enhanced. The parameters of the electrode reaction such as α, n, k_s and D of metol on CTS-TiO_2/CILE were calculated. Under the optimal experimental parameters, the linearity between I_{pa} value and metol concentrations covered the range from 0.08 to 800.0 μmol L^{-1} with a detection limit of 0.0237 μmol L^{-1} (3σ).

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References

1. R. Andreozzi, M. S. L. Casale, R. Marotta, G. Pinto and A. Pollio, *Water Res.*, 34 (2000) 4419
2. C. S. Prakasa Sastry, B. G. Rao and B. S. Reddy, *Fresenius J. Anal. Chem.*, 305 (1981) 415

3. Z. R. Meng, R. Zhao and X. R. Liu, *Fenxi Kexue Xuebao*, 16 (2000) 314
4. L Lunar, D Sicilia, S Rubio, D. Pérez-Bendito and U. NickelL, *Water Res.*, 34 (2000) 3400
5. J. Liao and P. Wang, *Analytical chemistry of photographic chemicals*, Chinese Film Press, Beijing, (1981)
6. E. P. Achterberg and C. Braungardt, *Anal. Chim. Acta*, 400 (1999) 381
7. S. F. Wang and D. Du, *Anal. Lett.*, 37 (2004) 361
8. J. Li, Y. Wang and Z. Liu, *Russian J. Electrochem.*, 42 (2006) 27
9. W. Sun, Q. Jiang, Y. Wang and K. Jiao, *Sensor Actuat. B Chem.*, 136 (2009) 419
10. W. Sun, Q. Jiang and K. Jiao, *J. Solid State Electrochem.*, 13 (2009) 1193
11. H. T. Liu, P. He, Z. Y. Li, C. Y. Sun, L. H. Shi, Y. Liu, G. Y. Zhu and J. H. Li, *Electrochem. Commun.*, 7 (2005) 1357
12. N. Maleki, A. Safavi and F. Tajabadi, *Anal. Chem.*, 78 (2006) 3820
13. C. X. Ruan, J. Lou, Y. Wang, Y. Q. Guo, W. M. Gao and Wei Sun, *J. Chin. Chem. Soc.*, 58 (2011) 930
14. H. W. Gao, M. Y. Xi, L. Xu and W. Sun, *Microchim. Acta*, 174 (2011) 115
15. W. Sun, J. H. Zhong, P. Qin and K. Jiao, *Anal. Biochem.*, 377 (2008) 115
16. W. Sun, Y. Z. Li, Y. Y. Duan and K. Jiao, *Biosens. Bioelectron.*, 24 (2008) 988
17. J. B. Zheng, Y. Zhang and P. P. Yang, *Talanta*, 73 (2007) 920
18. B. Haghighi and R. Nikzad, *Electroanal.*, 21 (2009) 1862
19. J. F. Bing, S. P. Ru, K. Fan, J. Wu and Y. B. Ying, *Microchim. Acta*, 171 (2010) 117
20. X. Y. Liu, X. D. Zeng, N. N. Mai, Y. Liu, B. Kong, Y. H. Li,W. Z. Wei and S. L. Luo, *Biosens. Bioelectron.*, 25 (2010) 2675
21. W. Sun, Y. X. Lu, Y. J. Wu, Y. Y. Zhang, P. Wang, Y. Chen and G. J. Li, *Sensor. Actuat. B-Chem.*, 202 (2014) 160
22. W. Sun, F. Hou, S. X. Gong, L. Han, W. C. Wang, F. Shi, J. W. Xi, X. L. Wang and G. J. Li, *Sensor. Actuat. B-Chem.*, 219 (2015) 331
23. F. Shi, W. Z. Zheng, W. C. Wang, F. Hou, B. X. Lei, Z. F. Sun and W. Sun, *Biosens. Bioelectron.*, 64 (2015) 131
24. W. Sun, X. L. Wang, Y. X. Lu, S. X. Gong, X. W. Qi, B. X. Lei, Z. F. Sun and G. J. Li, *Mater. Sci. Eng., C*, 49 (2015) 34
25. J. Bai and B. X. Zhou, *Chem. Rev.*, 114 (2014) 10131
26. S. M. Gupta and M. Tripathi, *Chin. Sci. Bull.*, 56 (2011) 1639
27. Y. Zhang, P. L. He and N. F. Hu, *Electrochim. Acta*, 49 (2004) 1981
28. S. J. Bao, C. M. Li, J. F. Zang, X. Q. Cui, Y. Qiao, and J. Guo, *Adv. Funct. Mater.*, 18 (2008) 591
29. X. L. Wang, G. J. Li, L. H. Liu, Y. Cheng, W. Zheng, S. M. Wu, F. Wu and W. Sun, *Anal. Methods*, 7 (2015) 2623
30. M. Song, X. H. Feng, H. Lu and X. M. Wang, *Electroanal.*, 22 (2010) 668
31. X. Zhang, J. H. Pan, A. J. Du, W. Fu, D. D. Sun and J. O. Leckie, *Water Res.*, 43(2009) 1179
32. W. Sun, Y.Y. Duan, Y.Z. Li, T.R. Zhan, K. Jiao, *Electroanalysis*, 21 (2009) 2667
33. F. C. Anson, *Anal. Chem.*, 36 (1964) 932
34. R. S. Nicholson, *Anal. Chem.*, 37 (1965) 1351
35. W. Sun, Y. Deng, J. Liu, W. M. Liu, ,Y. Cheng, L. Wang and Y. X. Gu, *Thin Solid Films*, 564 (2014) 379
36. C. Z. Zheng, *Manual of fine chemical product analysis*, Chemical Industry Press, Beijing, (2001) 273