Journal of

NANOSTRUCTURES



Synthesis of TiO₂ Nanoparticle and its Application to Graphite Composite Electrode for Hydroxylamine Oxidation

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Article history: Received 16/7/2013 Accepted 21/11/2013 Published online 1/12/2013

Keywords: Titanium dioxid Nanoparticles Carbon paste electrode Electrocatalysis

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1. Introduction

Nanostructured materials have aroused dramatic interests and have become an intensive research area for the past decade due to their finite small size, high specific surface area, high porosity, and unique physical/chemical properties. The fascinating properties and functions related to the size effect incur intriguing applications in many fields [1, 2]. Metal and metal oxide nanoparticles are the most widely employed nanomaterials owing to excellent physical and catalytic properties

Abstract

In this work, sol-gel method was used tosynthesize titanium dioxide nanoparticles (TiO₂). The TiO₂nanoparticles was characterized by Scanning Electron Microscopy (SEM), x-ray diffraction (XRD) and BET technique.The TiO₂ and coumarin derivative (7-(1,3-dithiolan-2-yl)-9, 10-dihydroxy-6H-benzofuro [3,2-c] chromen-6-on) were incorporated in a graphite composite electrode. The resulting modified electrode displayed a good electrocatalytic activity for the oxidation of hydroxylamine, which leads to a reduction in its overpotential by more than 520 mV. Differential pulse voltammetry (DPV) of hydroxylamine at the modified electrode exhibited a linear dynamic range (between 0.5 and 500.0 μ M) with a detection limit (3 σ) of 0.133 μ M. The high sensitivity, ease of fabrication and low cost of this modified electrode for the detection of hydroxylamine demonstrate its potential sensing applications.

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of these materials. Therefore, there is a requirement for the development of these nanoparticles with tuned properties [1]. TiO_2 are widely used in cosmetics, solar cells, batteries, additives in toothpaste and white paint, and others. Recently, there is a considerable interest in using TiO₂ nanoparticles as a film-forming material since they have high surface area, optical transparency, good biocompatibility, and relatively good conductivity. Various TiO₂ films used to immobilize proteins or enzymes on electrode surface for either mechanistic study of the proteins or fabricating electrochemical biosensors. The fabrication of modified electrodes with nanoparticles has been the focus of recent attention owing to enhancement of the response signal, increased sensitivity and better reproducibility [2-5]. There are four principle enhancement techniques for voltammetric and amperometric modified electrodes, namely selective permselectivity, preconcentration, selective and recognition electrocatalysis [6]. Electrocatalysis at chemically modified electrodes is widely utilized for the determination of many drugs and bio-substrates. Various inorganic and organic materials have been used to fabricate modified electrodes which can enhance the electron transfer rate and reduce the overpotential for the oxidation of substrates [7, 8].

Hydroxylamine (HX) is an intermediate in two important microbial processes of the nitrogen cycle: it is formed during nitrification as well as during anaerobic ammonium oxidation [9, 10]. Furthermore, hydroxylamine is a precursor of nitrous oxide as a side product during nitrification [9]. Oceanic nitrification is a major formation pathway of dissolved nitrous oxide in the ocean [11]. Since oceanic nitrous oxide emissions are of significant importance for the climate of earth [12], deciphering the distribution of potential precursors such as; hydroxylamine is important to understand formation pathways of nitrous oxide. the Hydroxylamine is an important industrial raw material. It has also been identified as an intermediate in many biological processes. Government regulations have been called for the waste stream levels of hydroxylamine to be under low ppm level to ensure that the local marine species are not endangered. Therefore, the determination of hydroxylamine low in

concentrations is very important in both of the industrial and biological samples.

In this work, we describe synthesis and application of TiO₂ nanoparticles as an electrocatalyst and coumarin derivative as a mediator in carbon paste matrix for voltammetric determination of hydroxylamine. The experimental results indicated that thismodified electrode offers several advantages such as high repeatability, good stability and high apparent charge transfer rate constant. In addition, electrocatalytic effect of modified electrode was investigated for electro oxidation of hydroxylamine. DPV was also used to evaluate the analytical performance of hydroxylamine and good limit of detection was obtained by this sensor.

2. Experimental procedure 2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, Netherlands). The experimental conditions were controlled with general purpose electrochemical system (GPES) software. A conventional three electrode cell was used. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the modified carbon paste electrode were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 691 pH/Ion used for Meter was pН measurement.Specific surface area was measured on TiO₂ nanoparticles determined by the Brunauer-Emmett-Teller analysis (BET) method from the N₂ isotherms collected with a Belsorp mini II BEL system on degassed samples.The TiO₂ nanoparticles were characterized by Scanning Electron Microscopy (SEM, Hitachi S-4160).

All solutions were freshly prepared with double distilled water. Hydroxylamine and other reagents

were analytical grade (Merck). Graphite powder and paraffin oil (DC 350, density = 0.88 g cm-3) as the binding agent (both from Merck, Darmstadt, Germany) were used for preparing the pastes. DC was synthesized in laboratory.

2.2. Synthesis of 7-(1, 3-dithiolan-2-yl)-9, 10dihydroxy-6H-benzofuro [3, 2-c] chromen-6-one (DC)

DC was by electrosynthesis method and the manner described in our previous work [13]. Briefly, 80 mL of 0.15 M phosphate buffer (pH 7.0) in water/acetonitrile (85/15 volume ratio), containing 0.7 mmol of 4-(1, 3-dithiolan-2-yl) benzene-1, 2-diol and 0.7 mmol 4hydroxycoumarin was electrolyzed at controlledpotential (0.35 vs. SCE) in a divided cell. The electrolysis was terminated when the current decayed to 5% of its original value. The precipitated solid was collected by filtration and was washed several times with water.

2.3.Synthesis of TiO₂ nanoparticles

The TiO₂ nanoparticles were prepared according to the procedure described in the literature [14, 15]. Briefly, titanium tetra isopropoxide (TTIP) was used as a precursor and was mixed with triethanolamine (TEOA: N (CH₂CH₂OH)₃) at a molar ratio of TTIPO: TEOA = 1 : 2 and stirred for half an hour. Followed, same volume of doubly distilled water was added to the above mixture and stirred for 2 hours at room temperature. The final solution was placed in a screw-capped pyrex bottle and aged at 100°C for 24 h for gelation. Finally, the resulting highly viscous gel was transferred to a Teflon autoclave and aged at 140°C for 72 h to nucleate and grow titania particles.

2.4. Preparation of the electrode

To obtain the best conditions in the preparation of the DC-CTPEs, we optimized the ratio of DC and TiO₂. The results of our studied showed that maximum peak current intensity of the hydroxylamine could be obtained t the surface of DC-CTPE with optimum ratio of DC and TiO₂. The DC-CTPEs were prepared by dissolving 0.01 g DC in 2 mL chloromethane and then added in 0.900 g graphite powder and 0.090 g TiO₂ with a mortar and pestle. Then, 0.8 mL of paraffin were added to the above mixture and mixed for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube. A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, DC modified CPE electrode (DC-CPE) without TiO_2 , TiO_2 paste electrode (CTPE) without DC, and unmodified CPE in the absence of DC and TiO_2 were also prepared in the same way.

3. Results and discussion

3.1. Characterization of TiO₂ nanoparticles

The obtained values for the specific surface area and pore volume of the synthesized TiO_2 nanoparticles are summarized in table 1. Average particle sizes are presented in table 1. As shown, the nano particle titanium dioxide has been successfully synthesized, with average particle size equal to 50nm. TiO_2 nanoparticles were analyzed by XRD analyses. The XRD pattern of TiO_2 nanoparticles, in the 20 range of 10–80°, is shown in Fig. 1. In this range, nine diffraction peaks of the anatase phase of titania phase can be observed.

Table 1. Crystalline phase (CP), specific surface areas (SS), pore volume (PV), average particle sizes (APS) and pore diameter (PD) of the TiO_2

СР	SS	PV	APS	PD	
Ana	49.9	0.179	50	14.3	
tase	m ² /g	cm ³ /g	nm	nm	

Figure 2 shows a SEM image of solid products. As shown in Fig. 2, SEM images of the TiO_2 nanoparticles in the anatase phase demonstrated an almost spherical shape. The average TiO_2 nanoparticles sizes were in the range of 40–60 nm at calcination temperature 400 °C.





Fig.2. SEM image of TiO₂ nanoparticles

3.2. The surface morphologies of electrodes

Fig. 3 displays a typical morphology of DC-CTPE characterized by SEM. It seems the morphology of the electrode surface has changed due to the presence of the TiO_2 nanoparticles, which has caused a more compact morphology.



Fig.3. SEM images of (A) CPE and (B) DC-CTPE

3.3. Electrochemical impedance spectroscopic study

The interfacial characteristic of the different modified electrodes were studied by electrochemical impedance spectroscopy (EIS). Fig. 4 shows the impedance spectra as Nyquist plots for bare CPE (curve a) and DC-CTPE (curve b) electrodes in 0.5 mM K₄Fe(CN)₆ and 0.5 mM K₃Fe(CN)₆ containing 0.1 M KCl solution. The semicircle diameters of Nyquist plot reflect the

electron transfer resistance (R_{ct}), which is related to the electron transfer kinetics of the redox probe at the surface of the electrode. It could be seen that on the CPE electrode the value of R_{ct} was obtained at 6 k Ω (curve a), which was due to the presence of non-conductive liquid paraffin in the carbon paste. After TiO₂ nanoparticles were added into the carbon paste to get a CTPE, the value of R_{ct} was decreased to 3.3 k Ω (curve b), which was smaller than that of CPE electrode and was due to the unique properties of TiO₂ nanoparticles such as huge surface area, increasing the electron transfer kinetics and catalytic ability.



Fig.4. Nyquist plots of CPE (a) and CTNPE (b) in a 0.1 M KCl solution containing the redox couples of 0.5 mM K_4 Fe(CN)₆ and 0.5 mM K_3 Fe(CN)₆

3.4. Electrocatalytic oxidation of hydroxylamine at a DC-CTPE

Fig. 5 shows typical cyclic voltammograms of 0.5 mM hydroxylamine at unmodified CPE (curve b), DC-CPE (curve d) and DC-CTPE (curve e).As can be seen, the anodic peak potential for hydroxylamine oxidation at the bare CPE is about 700 mV (curve b), while the corresponding potential at DC-CTPE is 180 mV (curve e). The comparison of these two curves (curves b and e of Fig. 5) shows the peak potential of hydroxylamine oxidation at the surface of modified electrode shifts by about 520 mV toward negative values compared

with that at the bare electrode. The comparison of the oxidation of hydroxylamine at DC-CPE (curve d) and DC-CTPE (curve e) shows an enhancement of the anodic peak current at DC-CTPE relative to the value obtained at DC-CPE, which indicated that the presence of TiO_2 nanoparticles in the electrode could enhance the peak currents.



Fig. 5. CVs of (a) unmodified CPE in 0.1 M phosphate buffer solution (pH 7.0) at scan rate of 20 mV s⁻¹; (b) as (a) + 0.50 mM hydroxylamine; (c) as (a) at the surface of DC-CTPE; (d) as (b) at the surface of DC-CPE; (e) as (b) at the surface of DC-CTPE.

The results indicated that the presence of TiO_2 on CPE surface had great improvement on the electrochemical response, which was partly due to excellent characteristics of TiO_2 such as high surface area, optical transparency, good biocompatibility, and relatively good conductivity. Comparison of curve (c) and (e) shows the anodic peak current at the surface of DC-CTPE is greatly enhanced by addition of hydroxylamine to the solution while, the cathodic peak current disappears. From these results, an electrocatalytic behavior is observed for solution oxidation at the surface of DC-CTPE via an EC' catalytic mechanism. This mechanism is shown in scheme 1. In this scheme, hydroxylamine is oxidized in the catalytic chemical reaction (C') by the oxidized form of DC (DC_{ox}) which produced via an electrochemical reaction (E).



Scheme 1. Electrocatalytic reaction mechanism for hydroxylamineat the surface of DC-CTPE

Therefore, when the DC is oxidized at the potential of 180 mV, the hydroxylamine can be oxidized too in this potential. Thus the hydroxylamine is oxidized at the potential of 180 mV at the DC-CTPE while it is oxidized at 700 mV at the bare electrode.

3.5. Calibration plot and limit of detection

Differential pulse voltammetry (DPV) has the advantage of an increase in sensitivity and better characteristics analytical for applications. Therefore DPV was used to obtain the linear concentration range and detection limit of hydroxylamine at the DC-CTPE electrode. The results show that the electrocatalytic peak currents of hydroxylamine oxidation at the surface of the DC-CTPE electrode consist of two linear segments with different slopes; a slope of 0.338 μ A μ M⁻¹ for the first linear segment $(0.5-50.0 \ \mu\text{M})$ and a slope of 0.043 μ A μ M⁻¹ for the second linear segment (50.0-500.0 µM). The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitation [15]. The detection limit (3σ)

was calculated from the first linear segment of the calibration plot as 0.133μ M.

3.6. Application of DC-CTPE for recovery and determination of hydroxylamine in real samples

To evaluate the applicability of the proposed method, the method was employed to determine hydroxylamine in drinking water and river water sample.



Fig. 6. DPVs of DC-CTPE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of hydroxylamine. The numbers of 1–8 correspond to: 0.5, 3.0, 10.0, 20.0, 35.0, 50.0, 100.0, 200.0, 300.0, 400.0 and 500.0 μ M of hydroxylamine. Insets show the plot of the electrocatalytic peak current as a function of hydroxylamine concentration in the ranges of (A) 0.50–50.0 μ M, (B) 50.0–500.0 μ M.

The samples were analyzed by DPV after adjusting pH using phosphate buffer (pH= 7.0). The samples tested were found to be free from hydroxylamine and thus, synthetic samples were prepared by adding known amounts of hydroxylamine to water samples. The recovery percent obtained by the method reveal the capability of the method for determination of hydroxylamine in drinking andriver water samples. The results are shown in Table 2.

Table 2. Determination of hydroxylamine in water sample (n = 5)

1	,			
 Sample	HX	HX	Recovery	R.S.D.
	$added \left(\mu M \right)$	found (μM)	(%)	(%)
Drinking	-	< DL	-	-
Water	25	25.5	102.0	1.3
	60	59.3	98.8	1.6
River	-	< DL	-	-
Water	25	25.8	103.2	2.2
	60	59.4	99.0	1.8

4. Conclusions

In the present study, carbon-paste electrode modified with TiO₂ nanoparticles and DC was used for the determination of hydroxylamine. Compared with its response at CPE, the electrochemical sensitivity of hydroxylamine at the proposed electrode was improved dramatically, revealing some advantages of DC-CTPE over CPE such as high conductivity and electron transfer. High sensitivity and fast reproducibility of the voltammetric responses, and low detection limit (0.133 µM), together with the ease of preparation and surface regeneration, makes the proposed modified electrode very useful for accurate determination of hydroxylamine in real samples.

Acknowledgment

The authors would like to thank Yazd University Research Council, IUT Research Council and Excellence in Sensors for financial support of this research.

References

[1] F. Mirkhalaf, J. Paprotny, DJ. Schiffrin, J. American Chem. Soc. 128 (2006) 7400.

[2] M. Mazloum-Ardakani, A. Khoshroo, Anal. Chim.Acta.798 (2013) 25. [3] A. Lando, K. Lauwaet, P. Lievens, Phy. Chem. Chem. Phys. 11 (2009) 1521.

[4] G. Lai, H. Zhang, D. Han Anal. Lett.41 (2008) 3088.

[5] M. Mazloum-Ardakani, A. Khoshroo, Electrochimica. Acta.103 (2013) 77.

[6] M. Mazloum-Ardakani, Z. Taleat, A. Khoshroo, H.Beitollahi, H. Dehghani, Biosens. Bioelectron.35 (2012) 75.

[7] M. Mazloum-Ardakani, Z. Taleat, H. Beitollahi, J. Electroana. Chem. 624 (2008) 73.

[8] M. Mazloum-Ardakani, H. Kholghi, M.A. Sheikh-Mohseni, A. Benvidi, H. Naeimi, J. NanoStructure. 2 (2012) 145.

[9] D. J. Arp, L.Y. Stein, Crit. Rev. Biochem. Mol. Biol. 38 (2003) 471.

[10] M. S. M. Jetten, Plant. Soil. 230 (2001) 9-19

[11] H. W. Bange, M. O. Andreae, Global Biogeochem. Cycle.13 (1999) 1127.

[12] S. A. Montzka, P. J. Fraser, J. H. Butler, P. S. Connell and et. al. Controlled substances and other source Gases, in Scientific assessment of ozone depletion:, Global ozone research and monitoring project-report, World Meteorological Organization (WMO), Geneva,no. 47, 2002. pp. 1.1–1.83.

[13] M. Mazloum-Ardakani, A. Khoshroo, D. Nematollahi, B.-F.Mirjalili, J. Electrochem. Soc. 159 (2012) H912.

[14] T. Sugimoto, X. Zhou, A. Muramatsu, J. Colloid Interface Sci. 259 (2003) 43.

[15] M. MalekshahiByranvand, A. NematiKharat, L.Fatholahi, Z. MalekshahiBeiranvand, J.NanoStructure. 3 (2013) 1.

[16] A. J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., Wiley, 2000.