

## Synthesis of TiO<sub>2</sub> Nanoparticle and its Application to Graphite Composite Electrode for Hydroxylamine Oxidation

M. Mazloun-Ardakani\*, A. R. Khoshroo

Department of Chemistry, Faculty of Science, Yazd University, Yazd, 89195-741, I.R. Iran

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### \*Corresponding author:

E-mail address:

mazloun@yazduni.ac.ir

Phone: +98 3518211670

Fax: +98 983518210644

### Abstract

In this work, sol-gel method was used to synthesize titanium dioxide nanoparticles (TiO<sub>2</sub>). The TiO<sub>2</sub> nanoparticles were characterized by Scanning Electron Microscopy (SEM), x-ray diffraction (XRD) and BET technique. The TiO<sub>2</sub> 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 μM) with a detection limit (3σ) of 0.133 μM. 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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## 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

of these materials. Therefore, there is a requirement for the development of these nanoparticles with tuned properties [1]. TiO<sub>2</sub> are widely used in cosmetics, solar cells, batteries, additives in toothpaste and white paint, and others. Recently, there is a considerable interest in using TiO<sub>2</sub> nanoparticles as a film-forming material since they have high surface area, optical transparency, good biocompatibility, and relatively good conductivity. Various TiO<sub>2</sub> 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 preconcentration, permselectivity, selective recognition and 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 the formation pathways of nitrous oxide. 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 in low

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

In this work, we describe synthesis and application of  $\text{TiO}_2$  nanoparticles as an electrocatalyst and coumarin derivative as a mediator in carbon paste matrix for voltammetric determination of hydroxylamine. The experimental results indicated that this modified 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 Meter was used for pH measurement. Specific surface area was measured on  $\text{TiO}_2$  nanoparticles determined by the Brunauer-Emmett-Teller analysis (BET) method from the  $\text{N}_2$  isotherms collected with a Belsorp mini II BEL system on degassed samples. The  $\text{TiO}_2$  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<sup>-3</sup>) 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, 10-dihydroxy-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 4-hydroxycoumarin was electrolyzed at controlled-potential (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 TiO<sub>2</sub> nanoparticles

The TiO<sub>2</sub> 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 (CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>) at a molar ratio of TTIP: 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 TiO<sub>2</sub>. The results of our studied showed that the maximum peak current intensity of hydroxylamine could be obtained at the surface of DC-CTPE with optimum ratio of DC and TiO<sub>2</sub>. 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 TiO<sub>2</sub> 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<sub>2</sub>, TiO<sub>2</sub> paste electrode (CTPE) without DC, and unmodified CPE in the absence of DC and TiO<sub>2</sub> were also prepared in the same way.

## 3. Results and discussion

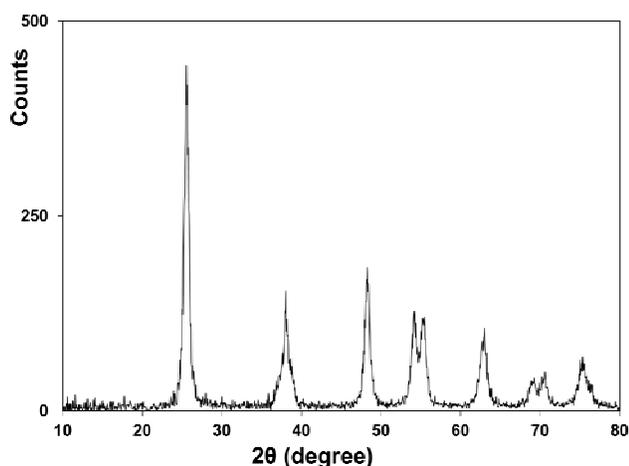
### 3.1. Characterization of TiO<sub>2</sub> nanoparticles

The obtained values for the specific surface area and pore volume of the synthesized TiO<sub>2</sub> 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<sub>2</sub> nanoparticles were analyzed by XRD analyses. The XRD pattern of TiO<sub>2</sub> nanoparticles, in the 2θ 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.

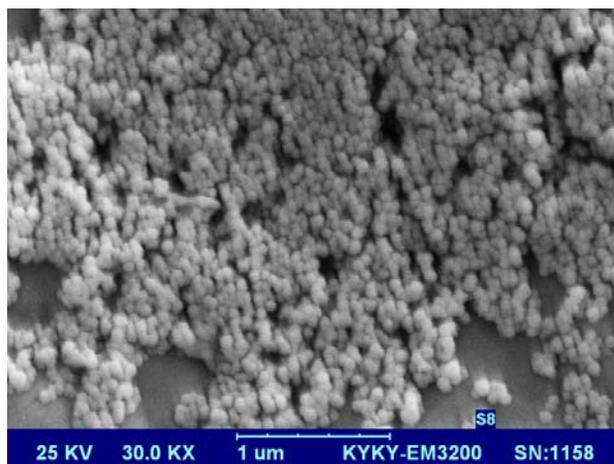
**Table 1.** Crystalline phase (CP), specific surface areas (SS), pore volume (PV), average particle sizes (APS) and pore diameter (PD) of the TiO<sub>2</sub>

CP	SS	PV	APS	PD
Ana	49.9	0.179	50	14.3
tase	m <sup>2</sup> /g	cm <sup>3</sup> /g	nm	nm

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



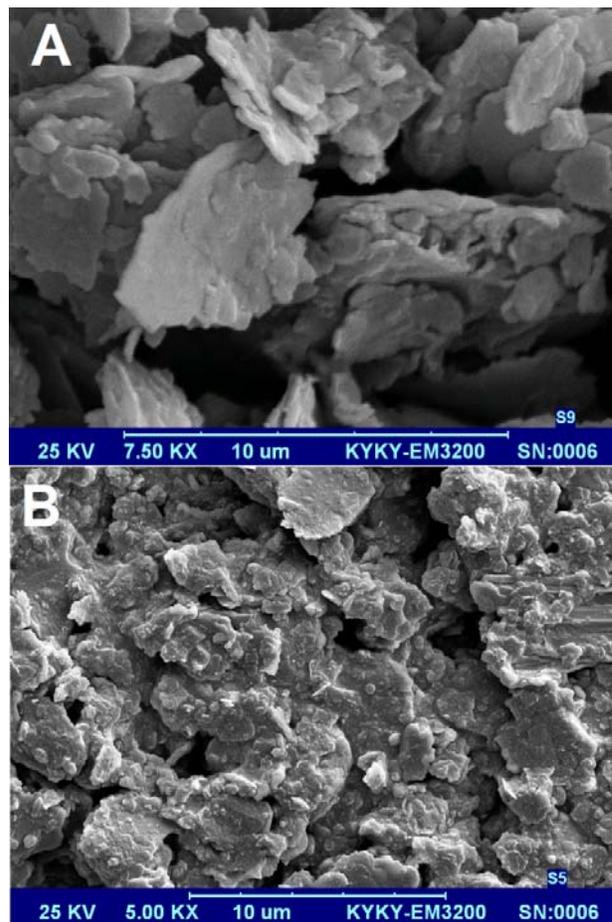
**Fig.1.** XRD patterns of TiO<sub>2</sub> nanoparticles



**Fig.2.** SEM image of TiO<sub>2</sub> 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<sub>2</sub> nanoparticles, which has caused a more compact morphology.

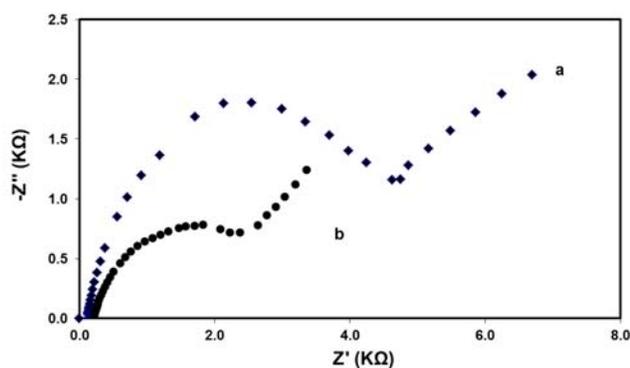


**Fig.3.** SEM images of (A) CPE and (B) DC-CTPE

### 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 K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.5 mM K<sub>3</sub>Fe(CN)<sub>6</sub> 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 $\Omega$  (curve a), which was due to the presence of non-conductive liquid paraffin in the carbon paste. After TiO<sub>2</sub> nanoparticles were added into the carbon paste to get a CTPE, the value of  $R_{ct}$  was decreased to 3.3 k $\Omega$  (curve b), which was smaller than that of CPE electrode and was due to the unique properties of TiO<sub>2</sub> nanoparticles such as huge surface area, increasing the electron transfer kinetics and catalytic ability.

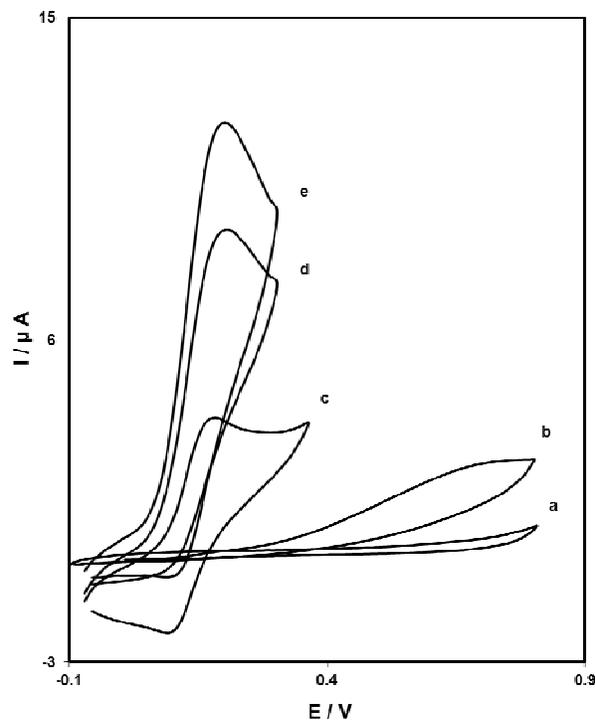


**Fig. 4.** Nyquist plots of CPE (a) and CTNPE (b) in a 0.1 M KCl solution containing the redox couples of 0.5 mM K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.5 mM K<sub>3</sub>Fe(CN)<sub>6</sub>

### 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

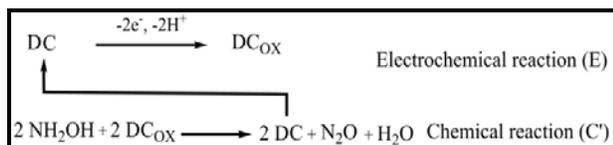
with that at the bare electrode. The comparison of the oxidation of hydroxylamine at DC-CPE (curve d) and DC-CTPE (curve e) shows an enhancement of the anodic peak current at DC-CTPE relative to the value obtained at DC-CPE, which indicated that the presence of TiO<sub>2</sub> nanoparticles in the electrode 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<sup>-1</sup>; (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<sub>2</sub> on CPE surface had great improvement on the electrochemical response, which was partly due to excellent characteristics of TiO<sub>2</sub> 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 hydroxylamine at 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.

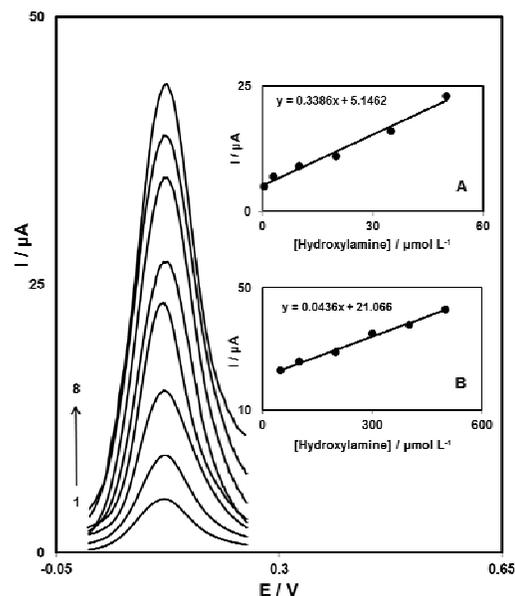
### 3.5. Calibration plot and limit of detection

Differential pulse voltammetry (DPV) has the advantage of an increase in sensitivity and better characteristics for analytical 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  $0.338 \mu A \mu M^{-1}$  for the first linear segment (0.5-50.0  $\mu M$ ) and a slope of  $0.043 \mu A \mu M^{-1}$  for the second linear segment (50.0-500.0  $\mu M$ ). The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitation [15]. The detection limit ( $3\sigma$ )

was calculated from the first linear segment of the calibration plot as  $0.133 \mu M$ .

### 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  $\mu M$  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  $\mu M$ , (B) 50.0–500.0  $\mu M$ .

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 and river water samples. The results are shown in Table 2.

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

Sample	HX added ( $\mu\text{M}$ )	HX found ( $\mu\text{M}$ )	Recovery (%)	R.S.D. (%)
Drinking Water	-	< DL	-	-
	25	25.5	102.0	1.3
	60	59.3	98.8	1.6
River Water	-	< DL	-	-
	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  $\text{TiO}_2$  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 fast electron transfer. High sensitivity and reproducibility of the voltammetric responses, and low detection limit ( $0.133 \mu\text{M}$ ), together with the ease of preparation and surface regeneration, makes the proposed modified electrode very useful for accurate determination of hydroxylamine in real samples.

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