

A New and Simple Electrochemically Assisted Photocatalysis Sensor of Hydrazine using a Ti/TiO₂ Electrode

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Eletrodo de folha de Ti modificado com filme de TiO₂ (Ti/TiO₂) é descrito pela primeira vez como tendo uma atividade fotoeletrocatalítica eficiente frente a oxidação de hidrazina em solução tampão de fosfato. O eletrodo Ti/TiO₂ foi preparado por anodização da folha de Ti em solução aquosa e aplicado na medição fotoamperométrica hidrodinâmica da hidrazina em condições ideais (pH 7,0, potencial bias de 0,8 V vs. eletrodo de referência). A fotocorrente da oxidação fotoeletrocatalítica mostrou-se linear para o intervalo de concentração de hidrazina de $1,00 \times 10^{-5}$ a $2,00 \times 10^{-4}$ mol L⁻¹. O limite de detecção encontrado foi $8,54 \times 10^{-6}$ mol L⁻¹.

TiO₂ film modified Ti foil electrode (Ti/TiO₂) is described for the first time as having an efficient photoelectrocatalytic activity towards hydrazine oxidation in phosphate buffer solution. Ti/TiO₂ electrode was prepared by anodizing Ti foil in aqueous solution, and applied for the hydrodynamic photoamperometry measurement of hydrazine in optimum conditions (pH 7.0, bias potential of 0.8 V vs. reference electrode). The photoelectrocatalytic oxidation photocurrent of the photoelectrode determined by photoamperometry method was linearly dependent on the hydrazine concentration and the linearity range obtained was 1.00×10^{-5} - 2.00×10^{-4} mol L⁻¹. The limit of detection was found to be 8.54×10^{-6} mol L⁻¹.

Keywords: photoelectrocatalysis, determination, hydrazine, modified titanium foil, titanium dioxide

Introduction

Many research reports about TiO₂ are related to its application for degradation of most kinds of organic pollutants, such as detergents, dyes, pesticides, herbicides, etc., under UV light irradiation.¹⁻⁵ Only in a few articles, photoelectrocatalytic determination of some materials with electrodes has been investigated. Recently, tin oxide nanoparticle electrode for selective photoelectrochemical detection of DNA⁶ and TiO₂/CdS hybrid modified ITO (indium tin oxide) for α -fetoprotein detection⁷ have been applied. Also, the modified carbon paste electrode was prepared by adsorption of methylene blue (MB) on zirconiumphosphate⁸ and muscovite.⁹ These modified electrodes were successfully used for the photoelectrocatalytic oxidation of the ascorbic acid in a flow injection analysis (FIA) system. Moreover, Xu and co-workers¹⁰ reported that the dopamine coordinated nanoporous TiO₂ film electrode covered on an ITO

electrode showed to be a new photoelectrochemical methodology for sensitive NADH determination. Also, other research groups have been interested in the photoelectrocatalytic oxidation of NADH using a new polymeric phenothiazine modified graphite electrode,¹¹ poly(toluidine blue O) modified glassy carbon electrode,¹² poly-hematoxylin modified glassy carbon electrode,¹³ electropolymerized methylene blue modified glassy carbon electrode¹⁴ and poly(neutral red) modified glassy carbon electrode¹⁵ since the photoelectrocatalytic method has better sensitivity than the electrocatalytic method for the determination of NADH. Zhang and co-workers¹⁶ developed a photoelectrochemical detector for determination of glucose and sucrose using FIA and high performance liquid chromatography (HPLC) based on the oxidation power of nanostructured TiO₂ coated onto the ITO substrate.

On the other hand, hydrazine and its derivatives are excellent reducing agents. These families of agents are widely used in different industries and agriculture as emulsifiers, catalysts, corrosion inhibitors, explosives and

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rocket propellants.¹⁷ Hydrazine that can be absorbed through skin has carcinogenic and hepatotoxic effect. It affects liver, kidney and brain and is very important in pharmacology.¹⁸ There are reports regarding the electrocatalytic determination of hydrazine.¹⁹⁻²⁴ Therefore, for the first time in this context, the present work aimed towards the photoelectrocatalytic determination of hydrazine using Ti/TiO₂ foil electrode as a novel and simple method.

Experimental

Materials

The solvent for electrochemical studies was doubly distilled water. The hydrazine from Merck was used as received. Titanium foil (thickness 0.25 mm, assay 99.7%) was purchased from Sigma-Aldrich. Buffer solutions were prepared from NaOH, H₃PO₄ and their salts for pH range of 3.0 to 11.0. Graphite electrodes were cut from a graphite plate.

Preparation of working electrode

A piece of raw Ti foil was cut into small rectangular pieces (3.0 × 3.0 cm²) which were then polished with different abrasive papers, rinsed in an ultrasonic bath containing cold distilled water, chemically etched by immersion in HF/HNO₃/H₂O (1:4:5 v/v/v) mixed solution²⁵ and finally rinsed with acetone and deionized water. The treated Ti sheet served as anode and a platinum rod served as cathode, and both were placed in a solution of 0.2 vol.% hydrofluoric acid. Anodization was performed at a constant voltage of 20 V for 20 min. The freshly generated TiO₂ film electrode was then rinsed with distilled water and air dried. Finally, it was calcined in a muffle oven at 500 °C for 2 h.

Instrumentation

Photoelectrocatalytic degradation experiments were carried out as shown in Figure 1 in a single photoreactor that consists of a quartz cylindrical cell (3.0 cm diameter × 8.0 cm height, 1.8 mm thick). The reactor and the UV lamp were placed in a black box in order to avoid extraneous illumination. A platinum rod as a counter electrode and Ag|AgCl|KCl (3 mol L⁻¹) as reference electrode were used. Photoelectrochemical experiments were carried out using a potentiostat/galvanostat (μAutolab Type III). A collimated light beam from a 4 W medium pressure mercury lamp with a maximum UV irradiation peak was used for excitation of the photoelectrode.

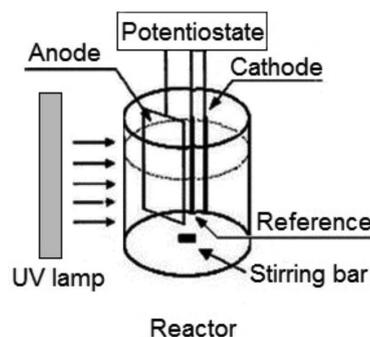


Figure 1. Schematic diagram of the reactor system.

Results and Discussions

Scanning electron microscopy (SEM) of Ti/TiO₂ electrode

Figure 2 shows typical SEM images of the unmodified and TiO₂ modified Ti electrodes. It can be seen from the micrograph that TiO₂ film was formed on the surface of titanium. The film coverage is almost uniform, although some ups and downs were occasionally seen on the surface.

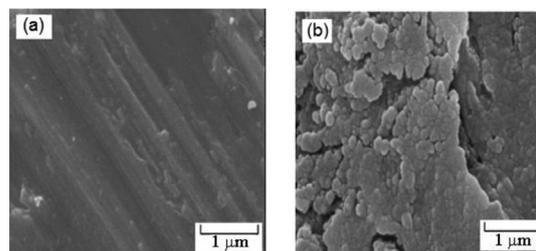


Figure 2. SEM micrograph of (a) Ti and (b) Ti/TiO₂ electrodes.

Photoelectrochemical properties of Ti/TiO₂ electrode

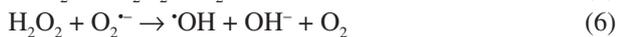
In photocatalysis process, when the TiO₂ nanoparticles in colloidal suspensions or deposited as a thin film on a solid carrier are illuminated with UV light, a great number of electrons can be excited from the valence band (VB) to the conduction band (CB) by absorbing UV light quanta, leaving highly oxidative holes in VB (h_{VB}⁺) and forming negative sites in CB (e_{CB}⁻), as shown in Figure 3a route 1 and reaction 1:²⁶



Organic compounds can then be directly oxidized by the hole or by heterogeneous hydroxyl radicals formed from the following reaction between the photogenerated vacancy and adsorbed water:



In addition, other weaker oxidizers (superoxide radical ion $O_2^{\cdot-}$, HO_2^{\cdot} and H_2O_2) and more $\cdot OH$ can be produced from the photoinjected electron by the following reactions:²⁶



The major loss in efficiency of photocatalysis is due to the recombination of electrons promoted to the valence band either with unreacted holes or with adsorbed hydroxyl radicals as observed in Figure 3a route 2 and the following reactions:²⁷



The electrochemical technology can provide much higher efficiency for organic material oxidation by means of photoelectrocatalysis. The efficiency of this process was improved by applying a suitable anodic potential to the circuit owing to the conducting graphite substrate. The application of an anodic bias to the Ti/TiO₂ electrode further provides a potential gradient within the film to efficiently drive away the photogenerated holes and electrons in different directions. The photogenerated holes could oxidize the organic compounds at the anode surface (Figure 3a route 3), while the photogenerated electrons were transferred to the acceptor at the metallic cathode through the external electrical circuit (Figure 3a route 4). The whole reaction process viewed on both macroscopic and microscopic scales, is shown in Figure 3.

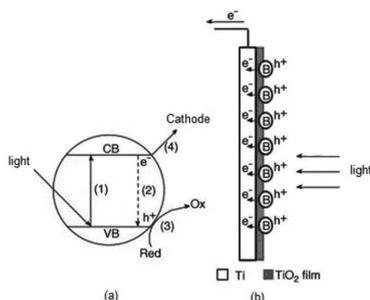


Figure 3. Schematic representation of photocurrent generation from the microscopic (a) and macroscopic (b) views.

In order to evaluate the photoelectrochemical activity of the Ti/TiO₂ electrode and to confirm its ability to oxidize hydrazine by photoelectrocatalysis, cyclic voltammetry experiments in the dark and under UV light irradiation were performed in the absence and presence of hydrazine (Figure 4). The tests were conducted in phosphate

buffer solution (pH 7.0). As can be seen in Figure 4, the electrochemical oxidation current value of the Ti/TiO₂ electrode in the dark and in the absence of hydrazine is very small (curve a). However, the value of this current under irradiation increases very much (curve c). This indicates that photogenerated electrons on the Ti/TiO₂ electrode could be effectively driven to the counter electrode by the application of positive potential, which would be beneficial to electron-hole separation.

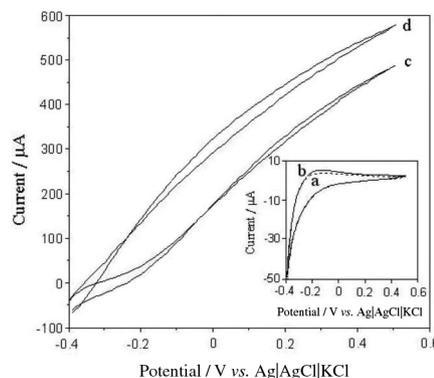


Figure 4. Cyclic voltammograms of the Ti/TiO₂ electrode in the dark (a,b) or under UV irradiation (c,d), in the presence (a,c) or absence (b,d) of 4.60 mmol L⁻¹ hydrazine, at a scan rate 10 mV s⁻¹.

Using the same conditions, the photoelectrochemical behavior of the Ti/TiO₂ electrode in the presence of hydrazine (curves b and d, respectively) was studied. In the dark, almost no difference between currents was observed in the absence and presence of hydrazine, which means that no electrochemical oxidation of hydrazine at the surface of the Ti/TiO₂ electrode occurred. But under UV illumination, a significant increase can be observed in the presence of hydrazine with respect to the absence of this material. The cause of these observations is that in buffer solution, the photogenerated holes in the Ti/TiO₂ electrode oxidize either adsorbed water molecules or hydroxyl groups, while the presence of hydrazine provides a much more facile pathway for the transfer of holes across the film/electrolyte interface, which results in a higher photocurrent.

Hydrodynamic amperometry was used to study photoelectrochemical response of the Ti/TiO₂ electrode in buffer solution with or without hydrazine solution under UV irradiation. The results are shown in Figure 5. It can be seen that the rise and fall of the photocurrent corresponded well to the illumination being switched on and off. The generation of photocurrent consisted of two steps. The first step of the photocurrent appears promptly after the illumination, and the second step of the photocurrent reaches a steady state. This pattern of photocurrent is highly reproducible for several on-off cycles of illumination. The results of hydrodynamic

amperometry were consistent with observations of cyclic voltammetry. The current response on the Ti/TiO₂ electrode in the dark is insignificant in the absence and presence of hydrazine which means that no electrochemical oxidation occurred. Under illumination, a significant increase in the photocurrent is observed, the value of this increase is smaller in the absence of hydrazine than that one in the presence of hydrazine (curves a and b, respectively).

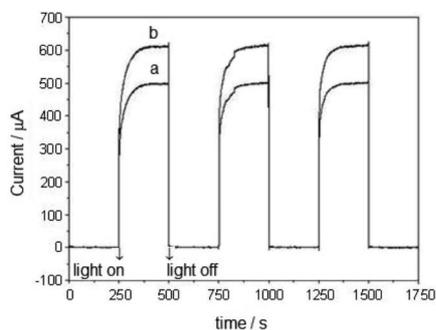


Figure 5. Photocurrent of the Ti/TiO₂ electrode for several on-off cycles of illumination at an applied potential of 0.6 V vs. reference electrode in (a) phosphate buffer solution (pH 7.0) and (b) containing 0.15 mmol L⁻¹ hydrazine.

Influence of solution pH on photoelectrocatalytic oxidation of hydrazine

The pH value is a key factor that influences the photoelectrocatalytic oxidation of materials. Therefore, in this study, the relationship between pH value and photocurrent difference of the Ti/TiO₂ electrode in the absence and presence of hydrazine (ΔI) was investigated (Figure 6). As shown in this figure, hydrazine photoelectrocatalytic oxidation kinetics are optimal at pH 7.0 when compared with other pHs. The pH value influences the photoelectrocatalytic oxidation process in many ways, such as TiO₂ flat-band potential variation and changes in adsorption ability of the target compound on the TiO₂ film.²⁸

Influence of bias potential on photoelectrocatalytic oxidation of hydrazine

The bias potential is an important factor in the process of photoelectrocatalytic oxidation of hydrazine. The difference between photocurrents of the Ti/TiO₂ electrode in the absence and presence of hydrazine was considered as a criterion for studying effect of bias potentials ranged between 0.2 and 1.4 on this process (Figure 7). The results showed that the potential of 0.8 V was the optimal bias potential. The application of a positive potential across the Ti/TiO₂ photoelectrode could produce a potential gradient inside the film that forced the photogenerated holes to move

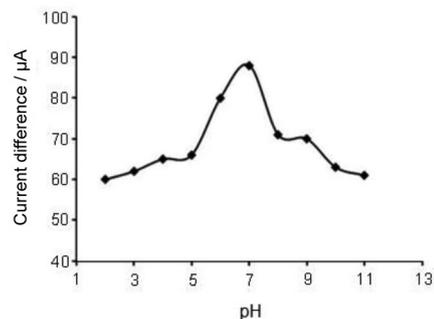


Figure 6. Effect of solution pH on the difference between photocurrents of the Ti/TiO₂ electrode in the absence and the presence of 0.15 mmol L⁻¹ hydrazine at bias potential of 0.6 V vs. reference electrode.

in opposite directions. Subsequently, the concentration of photogenerated holes (or hydroxyl radicals formed by subsequent oxidation of water) on the surface increased which in turn led to an increase in the amount of oxidized hydrazine. Therefore, the increase of bias potential results in the increase of the photocurrent of Ti/TiO₂ photoelectrode both in the absence and presence of hydrazine. Of course, further increasing the applied potential beyond 0.8 V leads to a slight decrease in the hydrazine oxidation. This can be explained by more water being oxidized by photogenerated holes.²⁹ However, what matters is the difference between these photocurrents.

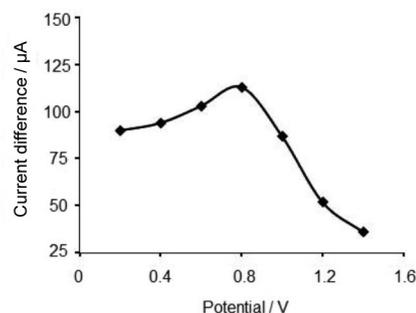


Figure 7. Effect of bias potential on the difference between photocurrents of the Ti/TiO₂ electrode in the absence and the presence of 0.15 mmol L⁻¹ hydrazine in phosphate buffer solution (pH 7.0).

Reproducibility and stability of Ti/TiO₂ electrode

To prove the reproducibility of the Ti/TiO₂ electrode, hydrodynamic amperometry experiments were repeatedly performed (six times) with this electrode in phosphate buffer solution (pH 7.0) (Figure 8). As can be seen, the Ti/TiO₂ electrode has good reproducibility. The stability of this electrode was also investigated. After storage of the electrode for one, two, three and four weeks, only a small decrease of current sensitivity (about 4.2, 6.0, 8.5 and 10.6%, respectively) was observed, which can be attributed to the good stability of the Ti/TiO₂ electrode.

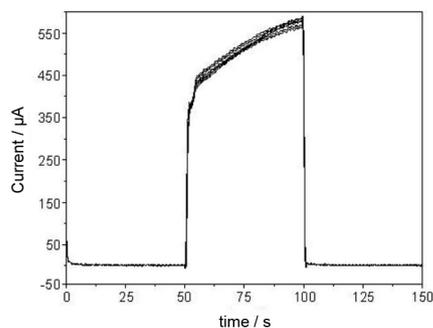


Figure 8. Six successive hydrodynamic amperograms of the Ti/TiO₂ electrode in the phosphate buffer solution (pH 7.0) at bias potential of 0.6 V vs. reference electrode.

Interference studies

Interference studies were carried out with several chemical substances prior to the application of the proposed method to determine hydrazine. The potentially interfering substances were chosen from those substances commonly found with hydrazine. The tolerance limit is defined as the maximum concentration of the interfering substance that causes relative error less than 5% for the determination of 0.15 mmol L⁻¹ hydrazine. The results showed that 20 fold quantities of glucose, fructose and sucrose and 40 fold quantities of K⁺, Na⁺, Mg²⁺, Ca²⁺, Cl⁻, F⁻, HCO₃⁻ and SO₄²⁻ had no interference on hydrazine determination. However, ascorbic acid had major interference in the determination of hydrazine at the surface of the Ti/TiO₂ electrode. The interference from ascorbic acid can be minimized by using the ascorbic oxidase enzyme which exhibits high selectivity to the oxidation of ascorbic acid, if necessary.

Photoelectrocatalytic determination and recovery of hydrazine

Photoelectrocatalytic oxidation current of hydrazine at the surface of Ti/TiO₂ was linearly dependent on the hydrazine concentration. The calibration plot was linear in the range of 1.00×10^{-5} – 2.00×10^{-4} mol L⁻¹ with correlation coefficient of 0.9967. The limit of detection was as 8.54×10^{-6} mol L⁻¹ (Figures 9A and 9B). Thus, the photoelectrocatalytic oxidation of hydrazine can be readily applied for the

determination of hydrazine. The comparison of several parameters of hydrazine at some modified electrodes is listed in Table 1. It can be seen that these parameters are comparable with values reported by other research groups for electrocatalytic oxidation of hydrazine by the surface of chemically modified electrodes by other mediators.³⁰⁻³²

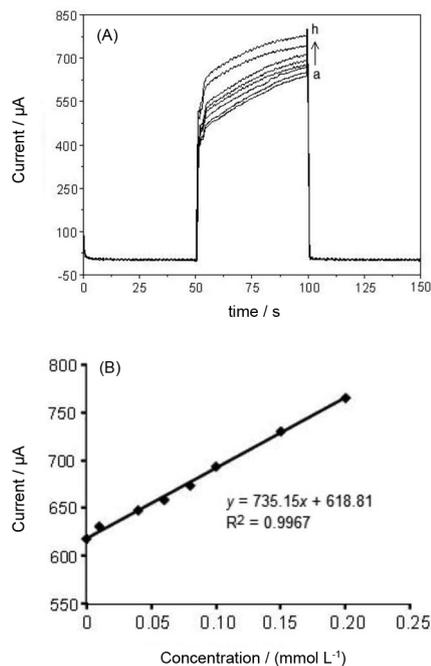


Figure 9. (A) Hydrodynamic amperometry of the Ti/TiO₂ electrode in the phosphate buffer solution (pH 7.00) and at bias potential of 0.8 V vs. reference electrode in the presence of various hydrazine concentrations: (a) 0.00, (b) 0.01, (c) 0.04, (d) 0.06, (e) 0.08, (f) 0.10, (g) 0.15 and (h) 0.20 mmol L⁻¹. (B) Plot of photocurrent as a function of hydrazine concentration.

In order to demonstrate the capability of the Ti/TiO₂ electrode towards the catalytic oxidation of hydrazine, this ability to determinate amperometrically hydrazine by recovery of added hydrazine in solution was examined. The determination of added hydrazine was carried out by the standard addition method. The data obtained for the hydrazine analysis by this method is illustrated for three replicates in Table 2. Also, in order to investigate the proposed method, the same sample was analyzed using redox titration method with potassium dichromate

Table 1. Comparison of some of the analytical parameters of the different modified electrodes for hydrazine determination

Electrode	Method	LDR / (µmol L ⁻¹)	LOD / (µmol L ⁻¹)	Reference
NPHMGC ^a	electrocatalysis, cyclic voltammetry	20-2000	8	30
PCVMGC ^b	electrocatalysis, amperometry	5-500	4.2	31
NHCFMGC ^c	electrocatalysis, amperometry	400-4000	90.6	32
Ti/TiO ₂	photoelectrocatalysis, amperometry	10-200	8.54	this work

^aNickel hexacyanoferrate nanoparticles modified carbon ceramic electrode; ^bpyrocatechol violet modified glassy carbon electrode; ^cNi-hexacyanoferrate modified paraffin impregnated graphite electrode. LDR: Linear dynamic range. LOD: Limit of detection.

Table 2. Photoelectrocatalytic determination of hydrazine in the phosphate buffer (pH 7.0) with Ti/TiO₂ electrode

Added ^a / (μmol L ⁻¹)	Proposed method		Official method		<i>t</i> _{exp}	<i>F</i> _{exp}
	Found ^a / (μmol L ⁻¹)	Recovery / %	Found ^a / (μmol L ⁻¹)	Recovery / %		
32.26	30.97 ± 2.87	96.00	33.37 ± 2.98	103.44	1.07	2.49

^aAverage of three replicate determinations.

in acidic solution as an official method.³³ The results are summarized in Table 2. As can be seen, the results obtained from the two methods are in good agreement and confirm the reliability of the proposed method. A statistical test (*F*-test) was used to confirm the precision of the proposed method. As can be seen, the *F*-test results bear a noticeable difference from the critical value (19.00) in four degrees of freedom and 95% of confidence. Moreover, a statistical *t*-test was performed to evaluate the accuracy of the proposed method. The results suggested that there is no evidence of systematic difference between the results obtained by either of the methods. Four degrees of freedom and 95% of confidence as well as the critical *t*-value (2.78) were used to support the conclusions of this test.

Conclusions

In this work, for the first time a new and simple hydrazine sensor based on photoelectrocatalytic determination using Ti/TiO₂ electrode prepared by anodizing Ti foil in aqueous solution was developed. The sensor showed promising determination of hydrazine with good limit of detection. The Ti/TiO₂ electrode can be simply prepared and was successfully used as an amperometric sensor for hydrazine determination with suitable precision and accuracy.

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