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ORIGINAL PAPER

Hydrazine sensors development based on a glassy carbon electrode modified with a nanostructured TiO$_2$ films by electrochemical approach

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Abstract The authors describe a selective hydrazine sensor that is based on the use of a film of TiO$_2$ nanoparticles faceted predominantly at the 101 and 001 sides. The hydrazine (Hyd) sensor was fabricated by depositing the nanoparticles in 5% concentration in a nafion matrix on a glassy carbon electrode (GCE). The sensor exhibits a fast response, excellent sensitivity and good selectivity over 1.0 nM to 10.0 mM. The sensor responds linearly to the logarithm of the concentration of dissolved hydrazine in the range from 1.0 nM to 10.0 mM, with a sensitivity of 35.04 μA.mM^{-1}.cm^{-2}. The detection limit is 28.8 ± 0.2 pM (at an S/N ratio of 3) is extremely low. In our perception, this approach emerges as an effective technique for developing efficient chemical sensors for environmental pollutants.

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Introduction

Hydrazine (N$_2$H$_4$) is a molecule with applications in many different industrial sectors that includes photographic, dye, pharmaceutical, polymer, fuel (rockets, space craft's) explosive, agricultural (pesticides, and plant-growth regulators production), etc. [1]. Its drawback is that it is a very toxic chemical and often considered as a cancer-causing, poisonous, hazardous, cyanogenetic, and nephrotoxic substance [2]. Symptoms for severe exposure of hydrazine includes: burning in eyes and nose, short-term loss of sight, faintness, vomiting, respiratory edema, and unconsciousness. Liver and kidney functions may also be badly affected by long time exposure of hydrazine as well [3]. Central nervous system is also affected by hydrazine that sometimes leads to unconsciousness. When absorbed through skin, it produces caustic-like burn and also interrupts the production of blood [4, 5].

Extreme toxicity and serious effects on health and environment requires the immediate detection of hydrazine with a reliable method that may be easily adapted to such wide industrial environments. Hydrazine detection methods include spectrophotometric method, chromatography, titrimetric method, chemi-luminescence etc. [6–11]. Due to low-cost, rapid response, higher sensitivity, electrochemical sensors are often more useful than any other methods for hydrazine detection and quantification [12, 13]. However, electrochemical oxidation of hydrazine at a bare electrode is kinetically slow and associated with high over potential. Consequently, searching for new materials for the modification of electrodes towards enhancing the rate of electron transfer and reducing the over potential of the hydrazine oxidation is necessary [14–17]. Different approaches such as the use of metal nanoparticles [18, 19], metal oxides [20], metal complexes, hexacyanoferrate salts or organic mediators [10, 11], have been tested up to now with different levels of success.

In this work, we have analyzed sensitivity and specificity of a hydrazine sensor fabricated with nanoparticles of TiO₂ (7% rutile 93% anatase) with average size 50 nm in which anatase faces were mainly oriented in 101 and 001 planes. Titanium oxide has been widely studied and utilized in many applications, owing to its strong oxidization utility, high chemical inertness, low cost, and non-toxicity. Titanium dioxide is a non-toxic and inexpensive material with very interesting applications, including its use as photocatalyst [21, 22] or electron selecting layer in solar cells [23, 24]. The use of this material is highly related with the structure and orientation of the crystalline planes [25], for instance, in catalytic applications the interaction between the molecule and the surface of this material is essential to obtain the different selected properties [26]. The main crystalline forms of TiO₂ are rutile and anatase. Anatase (101) forms structures thermodynamically stable which are less reactive than (001) [27]. For example, anatase (001) allows the dissociative adsorption of water, whereas (101) only accepts the adsorption [28]. In this scenario, TiO₂ faceted, which contains (001), is more reactive than normal TiO₂. Various TiO₂ modified sensors such as CdO-TiO₂ nanocomposite thin films for resistive hydrogen sensing [29], hybrid material consisting of bulk-reduced TiO₂-GO-polyaniline for resistance based sensing of gaseous ammonia [30] and gold nanoparticle–doped mesoporous TiO₂ for conductometric sensor towards ammonia and ethanol [31] was used for the detection of different hazardous substances at room conditions. Determination of hydrazine based on electrochemical sensing by using a nanostructured TiO₂ photoanode has been extensively used in energy harvesting and environmental decontamination, but recently it has been proposed as a promising analytical tool. Indeed this technique has been successfully applied for the determination of environmental pollutants and biomolecules [32]. In electrochemical oxidation of hydrazine, TiO₂ is more frequently used as a supporting material than an electrocatalyst, due to its low electrical conductivity. Reusable hydrazine amperometric sensor was also developed with nafion-coated TiO₂-carbon nanotube modified electrode for selective stable sensor at room conditions [33].

In our approach, a thin film of TiO₂ nanoparticles mixed with nafion conductive binder was deposited onto glassy carbon electrode (GCE) to build a hydrazine chemical sensor. Detection of this carcinogenic agent was done using the simple and reliable current-voltage (I-V) method at ambient conditions. We show that this hydrazine sensor displays unique and excellent properties in terms of wide range of target concentration, ultra-sensitive recognition and short response-time.

Experimental sections

Disodium phosphate, 2-nitrophenol (2-NP), monosodium phosphate, 3-methoxyphenol (3-MP), nafion (5% ethanolic solution), 4-aminophenol (4-AP), ammonium hydroxide (NH₄OH), 4-methoxyphenol (4-MP), acetone (Act), benzaldehyde (BZD), chloroform (Chl), ethanol (EtOH), hydrazine (Hyd), methanol (MeOH), and xanthine (Xan) used in this present work were used without any further purification and purchased from Sigma-Aldrich company (https://www.sigmaaldrich.com). For sensor investigation, the stock solution was made at 0.1 nM for all chemicals such as 2-NP, 3-MP, 4-AP, 4-MP, Act, BZD, Chl, EtOH, Hyd, MeOH, Xan, and NH₄OH. Crystallinity of TiO₂ nanoparticles was measured with XRD. TEM images were obtained from 42 TEK. AFM measurements were taken using a scanning probe microscope JSPM-5200 (from JEOL; www.jeol.co.jp) working in AFM AC mode. Faceted TiO₂ samples were grinded in a mortar, suspended in ethanol solution, deposited over a glass substrate and dried at 60°C during 30 min.

Fabrication of GCE (0.0316 cm²) was carried out by 1:1 mixing of the faceted TiO₂ nanoparticles (5.0 mg) and 5% ethanolic nafion (10.0 μL) solution as conducting coating binder. It was then heated into an oven at 60.0°C for 2 h to get the dry thin-fabricated-film (0.5 μm) onto GCE. In the electrochemical cell, TiO₂ nanoparticles coated GCE was used as working electrode (WE), Pd-wire (dia, 5 μm) was the counter electrode (CE), and an aqueous 0.1 M phosphate solution (PB, pH 7.0) used as electrolyte. To use as target analytes, aqueous hyd solution (0.1 M) was diluted to different concentrations (from 0.1 M to 0.1 nM) using deionized water. The geometry of Hyd-sensor electrode is round-disc of glassy-carbon tips connected with rod-like electrode. The thickness of fabricated film is 1.0 mm. Electrical characterization of hydrazine sensor based on TiO₂ nanocrystals was carried out at room conditions using current-voltage (I-V) measurements with a Keithley, 6517A electrometer (www.tek.com/keithley). In this investigation, current-voltage (I-V) method was used throughout the sensor investigation in terms of all analytical parameters measurement. In this system, two electrodes (working and counter) are used to measure the resultant current in respect of potential like as sensors available in the market, where no reference electrode is required at all. All I-V measurements were carried out with hydrazine as the target analyte into 5.0 mL of PB.
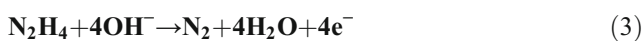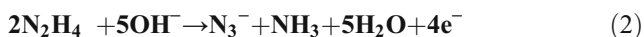
Results and discussion

Faceted TiO₂ nanoparticles (Fig. S1a-b), with average particle size 65.0 nm determined by TEM images were obtained from 42TEK. Exposed sides of anatase nanoparticles are mainly (101) and (001) indices. The nanoparticles are contained both rutile and anatase phases as presented in Fig. S1(c), with concentration ratio of 7%–93% given by provider. Image in Fig. S2(a) presents phase signal of AFM measurement of a single particle showing two exposed planes with edge size

42.0 nm. Note the similarity of this image with the crystal in in TEM measurement. Single particles tend to agregate in small clusters as shown in Fig. S2(b) are presented, where the well defined crystal structure is observed. In Fig. S2, two nanoclusters with several well defined nanocrystals with edge ~62.0 nm can be observed. Eventually large crystals are also observed in the dispersion (Fig. S3).

Toxic hydrazine in aqueous solution was detected and measured through current-voltage (I-V) measurements performed over nanostructured TiO_2 layers deposited on a substrate of GCE as depicted in Fig. 1. Non-toxic nature, chemical stability and electrochemical activity make the TiO_2 nanoparticles one of the best material candidates for hydrazine sensing. Current response in I-V method during hydrazine detection is largely depended on the dimensions, morphology, and porosity of the materials. Here it was used 65.0 nm TiO_2 nanoparticles to obtain the fabricated-electrode with high effective surface that optimized sensor responses. Upon contact with TiO_2 nanoparticles, hydrazine provides a remarkable response using this simple measurement method as shown in Fig. 1.

Several reactions (1–3) have been suggested for the oxidation of hydrazine onto TiO_2 nanoparticles [34–36].

$$N_2H_4 + H^+ \rightarrow N_2 + 5H^+ + 4e^- \tag{1}$$

$$2N_2H_4 + 5OH^- \rightarrow N_3^- + NH_3 + 5H_2O + 4e^- \tag{2}$$

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \tag{3}$$

As a result, in contact with the TiO_2 nanoparticles (np-TiO_2), hydrazine is oxidized by releasing free electrons on the sensor surface which is measured during I-V measurement. In previous reports, it has been demonstrated that in the presence of hydrazine, electrons are also released from reduced oxygen species adsorbed on the TiO_2 nanoparticles
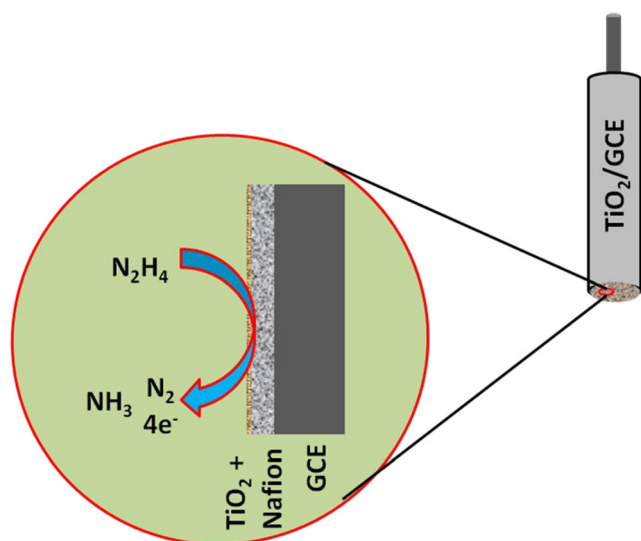
surface, which increases the current intensity detected at room temperature [37, 38].

I-V response of the sensor in presence and absence of target hydrazine analyte was measured at a delay time of 1.0 s in the electrometer. A significant amplification of current response with the increasing voltage is clearly demonstrated in Fig. 2a for this short response time. The suggested mechanism for hydrazine detection is as follows: when TiO_2 surface is exposed to the hydrazine, a surface-mediated oxidation reaction takes place producing N_2H_4 decomposition and the delivery of electrons to the electrode. At the same time, removal of OH^- adsorbed on TiO_2 surface (or, alternatively, its protonation) lowers conduction band edge position in TiO_2 what yields into a shift in the onset of the current in I-V curve [39]. This effect, together with the electrons injected from hydrazine oxidation, produces an increase of the number of electrons in the conduction-band at any fixed potential, enhancing the conductance of the electrode at this potential [39, 40]. As a consequence of these effects, current signal is observed at lower potentials and intensifies with the increasing potential and hydrazine concentration. The increase of TiO_2 conductance allows the fast response of the sensor that, for measurements at +2.0 V, requires only 10 s to achieve a constant current.

Figure 2b represents repeatability of the I-V responses with the TiO_2 nanoparticles coated GCE for 0.1 nM hydrazine solutions using 9 different working electrodes (Run, R1 ~ R9) under identical conditions. Almost similar current response were obtained for all electrodes after repeating the experiments 7 times, confirming the excellent repeatability of the sensor. A comparative histo-gram is also drawn based on the response at +2.0 V and presented in Fig. 2c. This small change may be due to mass variation in TiO_2 nanoparticles during the coating of GCE working electrode. At the same hydrazine concentration with different electrodes were exhibited almost similar current responses.

Selectivity of sensor to hydrazine was studied in presence of different chemicals like 2-NP, 3-MP, 4-AP, 4-MP, Act, BZD, Chl, EtOH, Hyd, MeOH, Xan, and NH_4OH using the TiO_2 nanoparticles/GCE, which presented in Fig. 2d. In this comparison of I-V responses, the concentrations of all analytes were kept constant at 0.1 nM in PB under identical condition and the same fresh electrode was used in every observation. In presence of hydrazine, the fabricated electrode shows higher current compared to all other interferon's, which demonstrated by the measurement of I-V technique in identical conditions. It is clearly visible the magnified images in the inset of Fig. 2(d). In selectivity study during I-V process, electrons are released in presence of hydrazine with hydroxides in aqueous system with the surface of TiO_2/GCE, which improved and enhanced the current responses against potential during at room conditions. In presence of other chemical interferences, hydroxide ions are not active as hydrazine.

Fig. 1 Schematic diagram for the hydrazine sensor based on TiO_2-Nafion/GCE electrodes

Fig. 2 a I-V response of TiO$_2$ NPs/GCE electrode in absence (green) and presence (red) of 1.0 nM hydrazine in the 0.1 M PB (pH 7.0) aqueous solution, **b** Repeatability study, **c** Histo-gram of repeatability responses (Data taken at 2.0 V), and **d** Current-voltage curve indicating the selectivity of sensor. Inset: Magnified view of I-V response in 1.0 ~ 2.0 V potential window. Delay time between measurements is 1 s
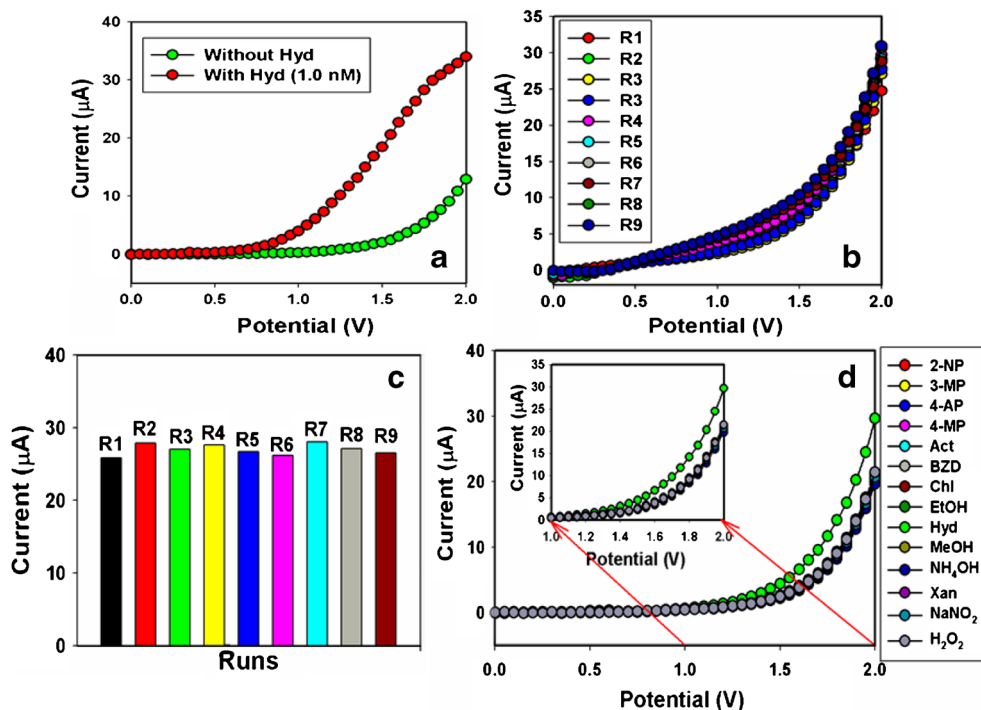
Therefore, hydrazine is selective in this approach and demonstrated by experimental evidences. Sensor is sensible to hydrazine while its response to different chemical is the same as for reference electrolyte. Interference study was also performed in presence of 0.1 nM concentration of each analytes (Hyd, NH$_4$OH, Ethanol, KNO$_2$, and H$_2$O$_2$) and included in the supporting information section (Fig. S4).

Current-voltage response for the TiO$_2$ nanoparticles coated GCE was measured using aqueous hydrazine solution of different concentrations is shown in Fig. 3(a). Calibration solution consisted on 5.0 mL of PB to which (25.0 μL) hydrazine aqueous solution was subsequently added from stock solution. Aqueous solutions of hydrazine from 0.1 nM to 0.1 M were taken to investigate the detection limits and sensitivity of the TiO$_2$ nanoparticles/ GCE sensor. Measurements were taken in ambient

conditions. Figure 3(a) shows that with the increasing amount of hydrazine the sensor response increases. The calibration plot, current (at +2.0 V) vs concentration for the full measured range is given in Fig. 3(b). As can be observed, current does not follow a linear relation with hydrazine concentration. Instead it follows a law of the type (Eq. 4)

$$I = K \cdot \log[N_2H_4] + b \qquad (4)$$

Very high sensitivity value K = 35.04 μA.mM^{-1}.cm^{-2} for hydrazine concentration given in micromol with b = 1.177 μA·cm^{-2} was calculated from the calibration plot. The linear dynamic range of the suggested sensor extends between 1.0 nM and 0.1 M with a linear regression coefficient

Fig. 3 I-V curves of the sensor under (**a**) hydrazine concentration changing from 0.1 nM to 0.1 M and (**b**) calibration curve of the sensor. Data of current where taken at +2.0 V. Linear dynamic range in (**b**) extends from 1.0 nM to 0.1 M
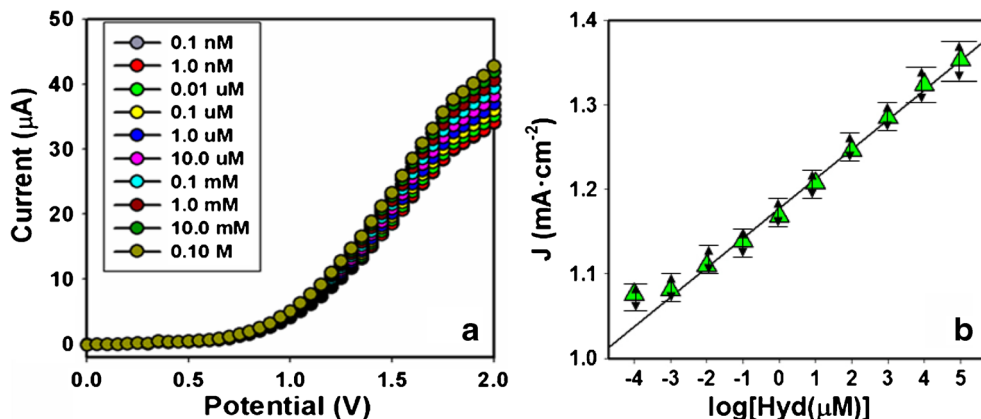
Table 1 Comparison of analytical performances of hydrazine detection using various nanomaterials or nanocomposites by electrochemical approaches

Electrode materials	Methods	Sensitivity ($\mu A \cdot \mu M^{-1} \cdot cm^{-2}$)	Detection limit (nM)	Ref
MWCNT/Chlorogenic acid	CV	0.0041	8	3
CNT powder microelectrode	CV	0.9944	---	41
Ag-ZnO Nanoellipsoids	CV	9.46	0.07	42
Hierarchical micro/nano architectures/ZnO	CV	0.51	0.25	43
Pristine ZnO NRs array	CV	4.48	0.2	44
ZnO-II/Au	CV	1.6	0.066	45
ZnO/SWCNT	CV	0.1	0.17	46
ZnO Nanoflowers	CV	3.49	0.18	47
Nano-Au-ZnO-MWCNT	CV	0.0428	0.15	48
PSS/Graphene/GCE	CV	---	1000.0	49
TiO2 NPs/CGE	I-V	35.04*	0.0288 ± 0.0002	This work

* in $\mu A \cdot mM^{-1} \cdot cm^{-2}$

of 0.997. Below 1.0 nM, the sensor departed from behavior described in Eq. (4), but good response was still attained allowing a limit of detection as low as 28.8 ± 0.2 pM (3 × Noise/Slope ratio).

The TiO$_2$ nanoparticles/GCE sensor is more sensitive as well as lower detection limit towards hydrazine than other materials already reported [3, 41–49] for hydrazine detection as given in the Table 1. The large effective surface area of the TiO$_2$ nanoparticles offers a positive nano-environment for the detection and quantification of hydrazine. The higher sensitivity of the modified TiO$_2$ nanoparticles/GCE sensor assembly can be attributed to the outstanding absorption (porous surfaces) and adsorption ability, high catalytic-activity, and good biocompatibility of the TiO$_2$ nanoparticles/GCE sensor. The anticipated sensitivity of TiO$_2$ nanoparticles/GCE sensor is comparatively higher and detection limit is reasonably lower than earlier reported hydrazine sensors based on other nanomaterials/nanocomposites modified electrodes dignified by I-V systems [50, 51]. Because of high specific surface area, TiO$_2$ nanoparticles/Nafion/GCE provides a conventional nano-environment for the hydrazine determination with favorable quantity. The high sensitivity of TiO$_2$ nanoparticles/GCE delivers high electron communication features which enhanced the direct electron transfer between the active sites of TiO$_2$ nanoparticles/GCE sensor and analytes (Hyd). It also yields to an enhanced reliability and stability of the measurements. The TiO$_2$ nanoparticles/Nafion/GCE system is demonstrated a simple and reliable route for the detection of hydrazine using Nafion/GCE-electrodes. It is also revealed that the significant access to a large group of chemicals for wide-range of environmental applications in environmental and healthcare fields respectively.

The real samples (industrial effluent, PC bottle, PVC food packaging bag, sea water, and tape water) were analyzed in order to validate the I-V method using TiO$_2$ nanoparticles/GCE. A standard addition method has been applied to determine the concentration of hydrazine in real samples. A fixed amount (~25.0 μL) of each sample was analyzed in PB (10.0 mL, 0.1 M) using the fabricated TiO$_2$ nanoparticles/GCE. The results have been included regarding the quantity of hydrazine in industrial effluent, PC bottle from SAFA Company, PVC food packaging bag, sea and tape water samples, which apparently entrenched that the I-V technique is satisfactory, reliable, and suitable for analyzing real samples with assembled of TiO$_2$ nanoparticles/GCE (Table S1).

Conclusions

Development of a selective chemical sensor for hydrazine based on a nanoporous film of faceted TiO$_2$ nanoparticles deposited on flat-GCE electrode with conducting nafion binders is presented in this approach. The sensor displayed very high sensitivity and selectivity for hydrazine sensing among various interfering chemicals at identical conditions. The sensor has demonstrated very good linear behavior for a 9 orders of magnitude variation in hydrazine concentration, ultra-low detection limit and very short response time (<10 s; Fig. S5). The employed procedure for the measurement emerges as an effective technique in developing efficient hazardous chemical sensors for the detection of environmental pollutants in broad scales.

Compliance with ethical standards   The author(s) declare that they have no competing interests.

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