

# Hydrazine Sensors Based on Nanostructured TiO<sub>2</sub> Films

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## Abstract

In this work, we describe the response of a selective hydrazine sensor based on a film of TiO<sub>2</sub> nanoparticles faceted predominantly in 101 and 001 sides. The sensor was fabricated depositing the nanoparticles plus 5% of nafion on a glassy carbon electrode. Chemical sensing for hydrazine was performed through simple and reliable current-voltage method. Hydrazine sensor exhibited a fast response and good selectivity. It also displayed an excellent sensitivity, very low detection limit, long-term stability and reproducibility. The sensor signal was found to depend linearly with the logarithm of concentration providing a linear calibration plot ( $r^2:0.997$ ) in an aqueous hydrazine solution ranging from 1.0 nM to 10.0 mM, with a sensitivity value of 35.04  $\mu\text{A cm}^{-2}$ . Out of this linear region an extremely low detection limit as 28.8 pM (S/N = 3). Analytical performance of TiO<sub>2</sub> nanoparticles in terms of chemical sensing are also discussed and analyses the real samples in detail in this work. This approach emerges as an effective technique in developing efficient chemical sensors for the detection of environmental pollutants in broad scales.

**Keywords:** Nanosensors; Titanium dioxide; Hydrazine sensor; Glassy carbon electrode; I-V method; Real sample

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**Introduction:**

Hydrazine ( $\text{N}_2\text{H}_4$ ) is a molecule with applications in many different industrial sectors that include photographic, dye, pharmaceutical, polymer, fuel (rockets, space craft's) explosive, agricultural (pesticides, and plant-growth regulators production), etc.<sup>1</sup> Its drawback is that it is a very toxic chemical and often considered as a cancer-causing, poisonous, hazardous, cyanogenetic and nephrotoxic substance.<sup>2</sup> 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.<sup>3</sup> 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.<sup>4,5</sup>

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. Developed hydrazine detection methods include spectrophotometric method, chromatography, titrimetric method, chemi-luminescence etc<sup>6-11</sup>. Due to low-cost, rapid response and higher sensitivity, electrochemical sensors are often more useful than any other methods for hydrazine detection and quantification.<sup>12, 13</sup> 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.<sup>14-17</sup> Different approaches such as the use of metal nanoparticles<sup>18, 19</sup>, metal oxides<sup>20</sup>, metal complexes, hexacyanoferrate salts or organic mediators<sup>10, 11</sup>, 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  $\text{TiO}_2$  (7% rutile 93% anatase) with average size 50 nm

in which anatase faces were mainly oriented in 101 and 001 planes. Titanium dioxide is a nontoxic and inexpensive material with very interesting applications, including its use as photocatalyst<sup>21, 22</sup> or electron selecting layer in solar cells.<sup>23, 24</sup> The use of this material is highly related with the structure and orientation of the crystalline planes,<sup>25</sup> for instance, in catalytic applications the interaction between the molecule and the surface of this material is essential to obtain the different selected properties.<sup>26</sup> The main crystalline forms of TiO<sub>2</sub> are rutile and anatase. Anatase (101) forms structures thermodynamically stable which are less reactive than (001).<sup>27</sup> For example, anatase (001) allows the dissociative adsorption of water, whereas (101) only accepts the adsorption.<sup>28</sup> In this scenario, TiO<sub>2</sub> faceted, which contains (001), is more reactive than normal TiO<sub>2</sub>.

In our approach a thin film of TiO<sub>2</sub> nanoparticles mixed with nafion conductive binders 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.

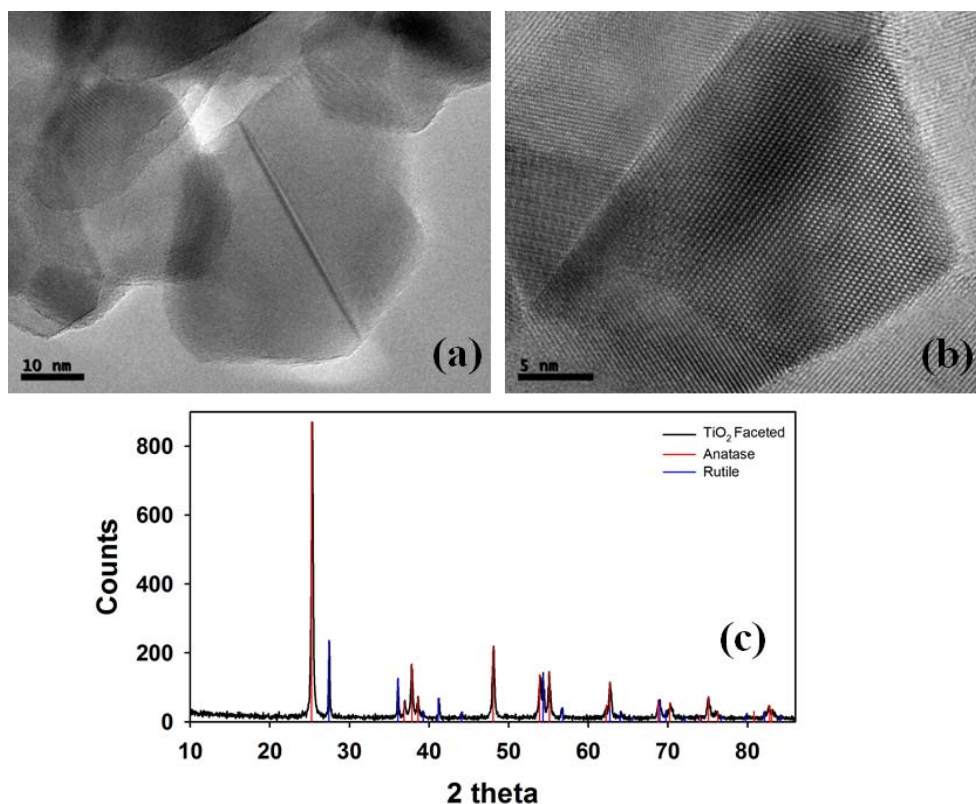
### **Experimental sections:**

Disodium phosphate, 2-nitrophenol (2-NP), monosodium phosphate, 3-methoxyphenol (3-MP), nafion (5% ethanolic solution), 4-aminophenol (4-AP), ammonium hydroxide (NH<sub>4</sub>OH), 4-methoxyphenol (4-MP), acetone (Act), benzaldehyde (BZD), chloroform (Chl), ethanol (EtOH), hydrazine, methanol (MeOH), and xanthine (Xan) used in this present work were used without any further purification and purchased from Sigma-Aldrich company. Crystallinity of TiO<sub>2</sub> nanoparticles was

measured with XRD. TEM images were obtained from 42TEK. Fabrication of GCE was carried out by mixing the faceted TiO<sub>2</sub> nanoparticles using 5% ethanolic nafion solution as conducting coating binder. It was then heated into an oven at 60.0 °C for 2 h to get the dry fabricated-film onto GCE. In the electrochemical cell, TiO<sub>2</sub> nanoparticles coated GCE was used as working electrode (WE), Pd-wire was the counter electrode (CE), and an aqueous 0.1 M phosphate solution (PBS, pH 7.0) used as electrolyte. To use as target analytes, aqueous hydrazine solution (0.1 M) was diluted to different concentrations (from 0.1 M to 0.1 nM) using deionized water. Electrical characterization of hydrazine sensor based on TiO<sub>2</sub> nanocrystals was carried out using current-voltage (I-V) measurements with a Keithley, 6517A electrometer. All I-V measurements were carried out missing the target element to 5.0 mL of PBS.

## **Results and Discussion**

Faceted TiO<sub>2</sub> nanoparticles, see Figure 1(a-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). The nanoparticles contained both rutile and anatase phases as plotted in Figure 1(c), with concentration ratio of 7%-93% given by provider.

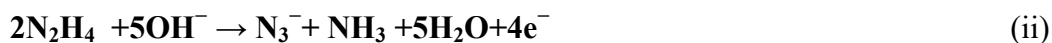


**Figure 1:** TEM images of (a) faceted TiO<sub>2</sub> nanoparticles, (b) showing the clear sharp edge of crystal, and (c) DRX of faceted TiO<sub>2</sub> nanoparticles.

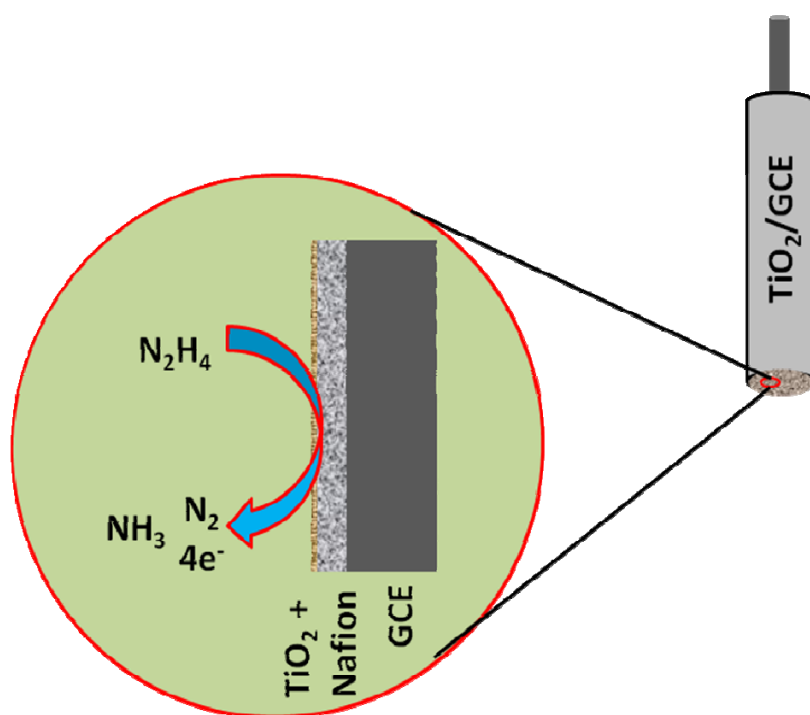
Toxic hydrazine in aqueous solution was detected and measured through current-voltage (I-V) measurements performed over nanostructured TiO<sub>2</sub> layers deposited on a substrate of GCE as depicted in Figure 2. Non-toxic nature, chemical stability and electrochemical activity make the TiO<sub>2</sub> nanoparticles one of the best material candidates for hydrazine sensing. Current response in I-V method during hydrazine detection largely depends on the dimensions, morphology, and porosity of the materials. Here we used 65.0 nm TiO<sub>2</sub> nanoparticles to obtain an electrode with high effective surface that optimizes sensor response. Upon contact with TiO<sub>2</sub> nanoparticles, hydrazine provides a remarkable response using this simple measurement method as shown in Figure 2.

Several reactions (i-iii) have been proposed for the oxidation of hydrazine onto TiO<sub>2</sub> nanoparticles<sup>29-31</sup>





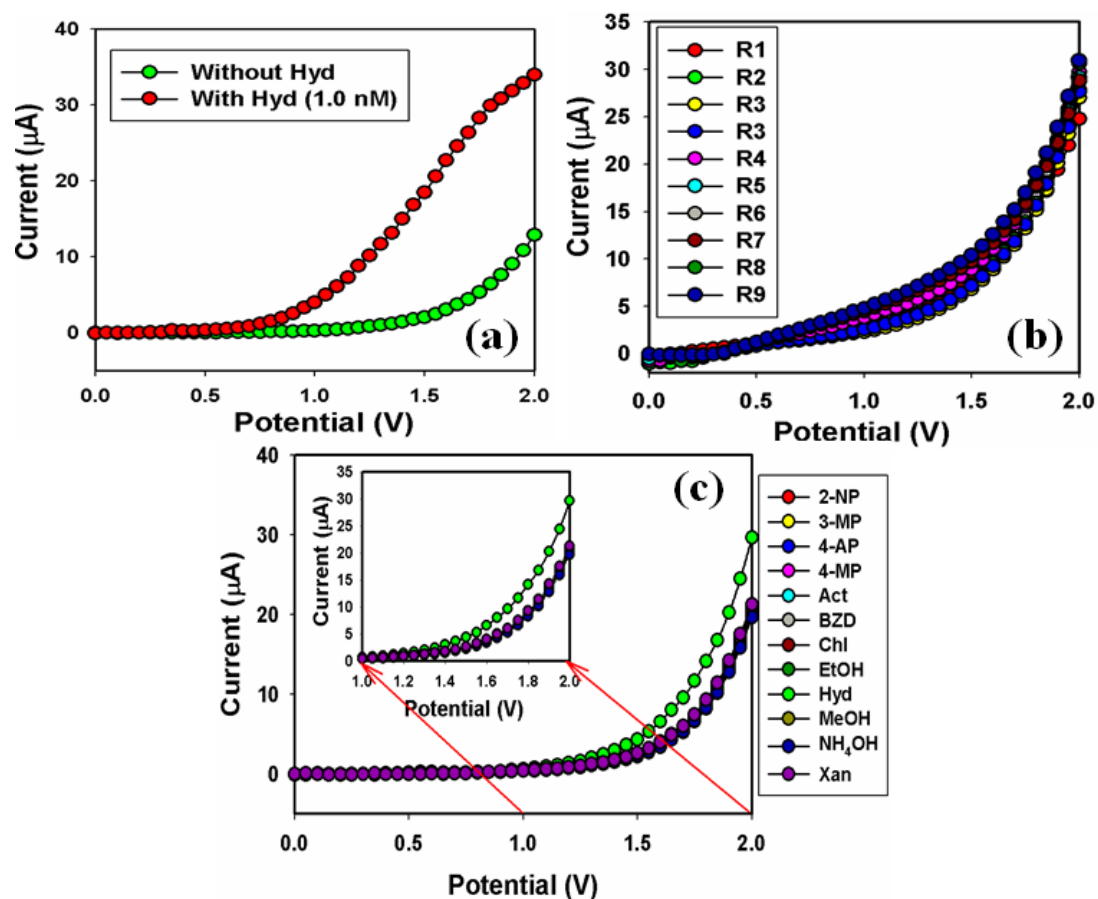
As a result, in contact with the  $\text{TiO}_2$  nanoparticles (np- $\text{TiO}_2$ ), hydrazine is oxidized releasing free electrons on the sensor surface which are collected during I-V measurement. In previous works, it has been demonstrated that in the presence of hydrazine, electrons are also released from reduced oxygen species adsorbed on the  $\text{TiO}_2$  nanoparticles surface, which increases the current intensity detected at room temperature.<sup>32, 33</sup>



**Figure 2:** Scheme of electrode the  $\text{TiO}_2$ -Nafion/GCE used for hydrazine sensing.

I-V response of the sensor in presence and absence of target hydrazine analyte, was measured at a delay time of 1.0 second in the electrometer. A significant amplification of current response with the increasing voltage is clearly demonstrated in Figure 3(a) for

this short response time. The mechanism proposed for hydrazine detection is as follows: when  $\text{TiO}_2$  surface is exposed to the hydrazine, a surface-mediated oxidation reaction takes place producing  $\text{N}_2\text{H}_4$  decomposition and the delivery of electrons to the electrode. At the same time, removal of  $\text{OH}^-$  adsorbed on  $\text{TiO}_2$  surface (or, alternatively, its protonation) lowers conduction band edge position in  $\text{TiO}_2$  what yields into a shift in the onset of the current in I-V curve.<sup>34</sup> 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.<sup>34, 35</sup> 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  $\text{TiO}_2$  conductance allows the fast response of the sensor that, for measurements at 2.0V, requires only 10 s to achieve a constant current.



**Figure 3:** (a) I-V response of TiO<sub>2</sub> NPs/GCE electrode in absence (green) and presence (red) of 1.0 nM hydrazine in the 0.1M PBS aqueous solution. Delay time between measurements was 1s. (b) Repeatability study. (c) Current-voltage curve indicating the selectivity of sensor. Inset: Magnified view of I-V response in 1.0~2.0V potential window.

Figure 3(b) represents repeatability of the I-V responses with the TiO<sub>2</sub> nanoparticles coated GCE for 0.1 nM hydrazine solutions using 9 different working electrodes (R1~R9) under identical conditions. Almost same current response was obtained for all electrodes after repeating the experiments 7 times, confirming the excellent repeatability of the sensor. This small change may be due to mass variation in TiO<sub>2</sub> nanoparticles



during the coating of GCE working electrode. At the same hydrazine concentration different electrodes show almost similar current responses.

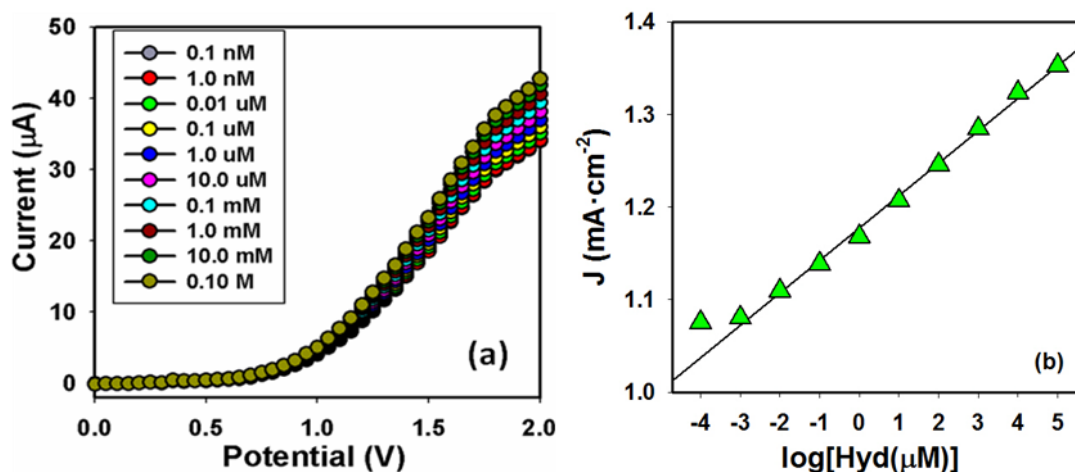
Selectivity of sensor to hydrazine was studied in presence of different chemicals like 2-NP, 3-MP, 4-AP, 4-MP, Act, BZD, Chl, EtOH, Hyd, MeOH, Xan, and NH<sub>4</sub>OH using the TiO<sub>2</sub> nanoparticles/GCE, which is presented in Figure 3(c). In this response comparison, the concentrations of all analytes were kept constant at 0.1 nM in PBS 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. Sensor is sensible to hydrazine while its response to different chemical is the same as for reference electrolyte.

Current-voltage response for the TiO<sub>2</sub> nanoparticles coated GCE was measured using aqueous hydrazine solution of different concentrations is shown in Figure 4(a). Calibration solution consisted on 5.0 mL of PBS 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 test the detection limits and sensibility of the proposed TiO<sub>2</sub> nanoparticles/GCE sensor. Measurements were taken in ambient conditions. Figure 4(a) shows that with the increasing amount of hydrazine the sensor response increases. The calibration plot, current (@ 2V) vs concentration for the full measured range is given in Figure 4(b). As can be observed, current does not follow a linear relation with hydrazine concentration. Instead it follows a law of the type

$$I = K \cdot \log[N_2H_4] + b \quad (1)$$

Very high sensitivity value  $K = 35.04 \mu A^{-1} cm^{-2}$  for hydrazine concentration given in micromol with  $b=1.177 \mu A \cdot cm^{-2}$  was calculated from the calibration plot. The linear dynamic range of the proposed sensor extends between 1.0 nM and 0.1 M with a linear

regression coefficient 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 pM ( $3 \times \text{Noise/Slope ratio}$ ).



**Figure 4.** I-V curves of the sensor under hydrazine concentration changing from 0.1 nM to 0.1 M (a) taken to build sensor calibration curve (b). Data of current were taken at 2.0V. Linear dynamic range in (b) extends from: 1.0 nM to 0.1 M

The TiO<sub>2</sub> nanoparticles/GCE sensor is more sensitive and has lower detection limit towards hydrazine than other materials already reported for hydrazine detection as given in the **Table 1**. The large effective surface area of the TiO<sub>2</sub> nanoparticles offers a positive nano-environment for the detection and quantification of hydrazine. It also yields to an enhanced reliability and stability of the measurements.

**Table 1:** Comparison of analytical performances of hydrazine detection using various nanomaterials or nanocomposites by electrochemical approaches.

Electrode materials	Anlytes	Sensitivity ( $\mu\text{A}\cdot\mu\text{M}^{-1}\cdot\text{cm}^{-2}$ )	Detection limit (nM)	Linear range ( $\mu\text{M}$ )	Ref
CNT powder microelectrode	Hyd	0.9944	---	----	36
Ag-ZnO Nanoellipsoids	Hyd	9.46	0.07	0.07-1.0	37
MWCNT/Chlorogenic acid	Hyd	0.0041	8	---	3
Hierarchical micro/nano architectures/ZnO	Hyd	0.51	0.25	0.8-200	38
Pristine ZnO NRs array	Hyd	4.48	0.2	---	39
ZnO-II/Au	Hyd	1.6	0.066	0.066-425	40
ZnO/SWCNT	Hyd	0.1	0.17	0.5-50	41
ZnO Nanoflowers	Hyd	3.49	0.18	---	42
Nano-Au ZnO-MWCNT	Hyd	0.0428	0.15	0.5–1800	43
PSS/Graphene/GCE	Hyd	---	1000.0	3.0-300	44
TiO <sub>2</sub> NPs/CGE	Hyd	<b>35.04*</b>	<b>0.0288</b>	<b>0.001-10000</b>	<b>This work</b>

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

The real samples (industrial effluent, PC bottle safe, PVC food packaging bag, sea and tape water) were analyzed in order to validate the proposed I-V method using TiO<sub>2</sub> nanoparticles/GCE. A standard addition method has been applied to determine the concentration of hydrazine in real samples. A fixed amount (~25.0  $\mu\text{L}$ ) of each sample was analyzed in PBS (10.0 mL, 0.1 M) using the fabricated TiO<sub>2</sub> 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 proposed I-V technique is satisfactory, reliable,

and suitable for analyzing real samples with assembled of TiO<sub>2</sub> nanoparticles/GCE (Table 2).

**Table 2:** Measured hydrazine concentration in different real samples.

Real samples	Calibrated concentration range	Measured current ( $\mu\text{A}$ )	Respective concentration (nM)
Industrial effluent		2.8	$\sim 0.038 \pm 0.01$
PC bottle Safa		2.5	$\sim 0.021 \pm 0.01$
PVC food packaging bag	0.1 nM ~ 1.0 mM	1.9	$\sim 0.017 \pm 0.01$
Sea water		1.2	$\sim 0.014 \pm 0.01$
Tap water		0.5	$\sim 0.009 \pm 0.01$

## Conclusions

Development of a chemical sensor for hydrazine based on a nanoporous film of faceted TiO<sub>2</sub> nanoparticles deposited on flat-GCE electrode with conducting coating binders is shown. The sensor displayed very high sensitivity and selectivity for hydrazine sensing among various interfering chemicals. 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 (<10s). 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.

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