Iron-Doped Titanium Dioxide Nanoparticles As Potential Scaffold for Hydrazine Chemical Sensor Applications

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Abstract: Herein, we report the fabrication of a modified glassy carbon electrode (GCE) with high-performance hydrazine sensor based on Fe-doped TiO2 nanoparticles prepared via a facile and low-cost hydrothermal method. The structural morphology, crystalline, crystallite size, vibrational and scattering properties were examined through different characterization techniques, including FESEM, XRD, FTIR, UV–Vis, Raman and photoluminescence spectroscopy. FESEM analysis revealed the high-density synthesis of Fe-doped TiO2 nanoparticles with the average diameter of 25 ± 5 nm. The average crystallite size of the synthesized nanoparticles was found to be around 14 nm. As-fabricated hydrazine chemical sensors exhibited 1.44 μA μM−1 cm−2 and 0.236 μM sensitivity and limit of detection (LOD), respectively. Linear dynamic ranged from 0.2 to 30 μM concentrations. Furthermore, the Fe-doped TiO2 modified GCE showed a negligible inference behavior towards ascorbic acid, uric acid, glucose, SO42−, NO3−, Pb2+ and Ca2+ ions on the hydrazine sensing performance. Thus, Fe-doped TiO2 modified GCE can be efficiently used as an economical, easy to fabricate and selective sensing of hydrazine and its derivatives.

Keywords: Fe-doped TiO2; hydrothermal; GCE; hydrazine; chemical sensor; amperometry

1. Introduction

Hydrazine is extensively used in rocket propellants, pesticides, explosives, photography chemicals, antioxidants and plant growth regulators in various related industries and laboratories [1,2]. Effluents released from these industries and laboratories are the foremost environmental source of hydrazine. It is considered one of the poisonous chemicals even at low concentration and is very hazardous to living organisms. The potential symptoms of hydrazine exposure range from eye and nose irritation, pulmonary edema, skin dermatitis, temporary blindness and serious damage to many human organs such as the kidney and liver [3–5]. Due to its mutagenic and carcinogenic behavior, it has been cited in the Environmental Protection Agency (EPA) list. It is therefore mandatory to trace the presence of minor amounts of hydrazine in the aqueous medium.
Previously reported techniques for the detection of hydrazine include spectrophotometry [6], fluorimetry [7,8], chemiluminescence [9] and potentiometry [10,11]. However, all these methods are accompanied by several disadvantages like low sensitivity, and they require expensive instrumentation followed by complicated procedures. Electrochemical determination is considered to be the promising alternative for the determination of hydrazine in terms of selectivity, sensitivity and portability, with an economical and simple operating procedure [12,13]. Unfortunately, hydrazine undergoes direct oxidation at the bare electrode surface, thus resulting in sluggish electrode kinetics and high over potentials [14,15]. Therefore, chemically modified electrodes have been used to detect hydrazine, which significantly reduce the overpotential, as well as accelerate redox reactions and hence the oxidation current responses [16,17].

Recently, there is a big interest in the utilization of new materials in scientific societies due to improved processibility, applicability and vast applications in various fields of sciences. In the past few years, tremendous work has been done on metal oxide based nanomaterials or composites, especially ZnO [18], CuO [19,20], TiO$_2$ [21,22] and MnO$_2$ [23], which are considered an ideal platform for material preparation used in pharmaceuticals and cosmetics industries, for the treatment of wastewater and in other fields [24]. TiO$_2$ is one of the most extensively used semiconductor materials owing to its non-toxicity, high performance, great stability and low preparation cost. Due to its good conductivity, high electrocatalytic activity and electron transport properties, TiO$_2$ is the most suitable material for devising the electrodes for various electrochemical and biosensing applications. Khodari et al. [25] used an electrochemical sensor, prepared by casting TiO$_2$ nanoparticles (NPs) onto a carbon electrode surface, for the determination of resorcinol. The TiO$_2$ NPs were demonstrated to be competent in boosting the electron transfer between resorcinol and the electrode surface as well as transport of resorcinol molecules to the surface of the sensor. Guo and coworkers [26,27] synthesized TiO$_2$ nanofibers for the bio-sensing of glucose. The fabricated TiO$_2$ nanofibers exhibited good direct electrochemistry as well as magnificent sensitivity along with fast response time for the detection of glucose. In order to further increase the electron transfer rate between the working modified electrode and the analyte solution and, hence, rapid and sensitive current response, doping of metal oxides has been reported as one of the best ways. Among the various dopants, Fe$^{3+}$ ions are most suitable owing to their similar ionic radii to that of Ti$^{4+}$ ions. Fe$^{3+}$ ions (63 pm) can easily replace the Ti$^{4+}$ ions (68 pm) from the TiO$_2$ crystal lattice. Further, Fe$^{3+}$ ions prevent electron–hole (e$^–$–h$^+$) recombination, better charge separation and incorporation of oxygen vacancies in the crystal lattice and surface of the TiO$_2$ [28,29]. Additionally, the choice of Fe$^{3+}$ ions as dopant has also been confirmed for some other semiconductor metal oxides. Hexamethylenediamine (HMDA) grafted and Fe nanoparticles incorporation into SnO$_2$ nanostructures exhibited strong surface affinity of 8.5 $\mu$mol/m$^2$ for H$_2$ as an important aspect of green energy storage applications at ambient temperature and pressure conditions [30]. ZnO powders doped with Fe nanoparticles through an in situ dispersion method showed improved conductivity and capacitance as compared to undoped ZnO nanoparticles [31]. HMDA grafted and Fe nanoparticles doped ZnO nanoparticles showed excellent conductivity which was attributed to the formation of effective proton-conductivity on the surface of the ZnO as well as proton transfer between Fe nanoparticles [32]. Fe-doped TiO$_2$ nanoparticles displayed superior photocatalytic degradation of methylene blue dye, phenol and toxic organic compounds as compared to undoped TiO$_2$ under UV and visible light illumination [33–35].

Herein, Fe-doped TiO$_2$ nanoparticles were prepared through a facile hydrothermal technique and subsequently analyzed using different characterization techniques for their various characteristics and to affirm the formation of the doped TiO$_2$ nanoparticles. Modified glassy carbon electrode (GCE) was fabricated by coating a thin film of Fe-doped TiO$_2$ nanoparticles onto it. As-fabricated hydrazine chemical sensors exhibited excellent hydrazine chemical sensing parameters.

2. Experimental Details

2.1. Synthesis of Fe-Doped TiO$_2$ Nanoparticles
For the preparation of Fe-doped TiO$_2$ nanoparticle, a facile hydrothermal method was adopted (2% doping of Fe ion was performed in the Fe-doped TiO$_2$ nanoparticle). Tetrabutyl titanate (Ti(BuO)$_4$) and ferric nitrate (Fe(NO$_3$)$_3$) were used as TiO$_2$ precursor and Fe dopant, respectively. Twenty milliliters of 0.5 M Ti(BuO)$_4$ solution was poured drop-wise to 5 M aqueous NaOH solution followed by the addition of 20 mL of 0.1 M Fe(NO$_3$)$_3$ solution dropwise. A Teflon lined stainless steel autoclave containing above solution was then heated at 200 °C for 10 h. The following reaction mechanisms have been proposed for the synthesis of Fe-doped TiO$_2$ nanoparticles (Equations (1)–(3)).

\[
\text{Ti(BuO)$_4$} + 4 \text{NaOH} \rightarrow \text{Ti(OH)$_4$} + 4 \text{BuONa}
\]  

\[
\text{Fe(NO}_3)_3 + 3 \text{NaOH} \rightarrow \text{Fe(OH)$_3$} + 3 \text{NaNO}_3
\]  

\[
\text{Ti(OH)$_4$} \xrightarrow{\text{Calcination}} \text{TiO}_2 + 2 \text{H}_2\text{O}
\]

During the hydrothermal process, tetrabutyl titanate was hydrolyzed to titanium hydroxide (Ti(OH)$_4$) and sodium butoxide. Ferric nitrate used as dopant was also hydrolyzed to its hydroxide, i.e., ferric hydroxide (Fe(OH)$_3$). BuONa and NaNO$_3$ were removed by washing with ethanol and deionized (DI) water. These washings also eliminated any unreacted Fe(NO$_3$)$_3$. Thoroughly washed Ti(OH)$_4$ and Fe(OH)$_3$ were dried for 6 h in an electric oven at 70 ºC. During calcination, titanium hydroxide was converted into TiO$_2$ with Fe$^{3+}$ ions occupying the lattice sites in the TiO$_2$ crystal lattice. The calcination was carried out in oxygen atmosphere at 450 ºC for 2 h. The calculated synthesis yield of the synthesized Fe-doped TiO$_2$ nanoparticles were found to be 0.8 g.

2.2. Characterizations of Fe-Doped TiO$_2$: Nanoparticles

X-ray diffraction (XRD; PAN analytical Xpert Pro. Cambridge, UK) with Cu–Kα radiation was performed for the analysis of crystal phase and crystallite size. The optical characteristics were estimated by using UV–Vis Spectrophotometer (Perkin Elmer-Lamda 950, Waltham, MA, USA) within the wavelength range of 200–800 nm by dispersing and sonicating the Fe-doped TiO$_2$ in distilled water for 30 min. Scattering properties of the doped TiO$_2$ material were analyzed by Raman spectrum and examined using Raman spectrometer (Perkin Elmer-FTIR Spectrum-100, Waltham, MA, USA) from 100 to 900 cm$^{-1}$. FTIR spectrum of the Fe-doped TiO$_2$ was collected by FTIR spectrophotometer (Perkin Elmer-FTIR Spectrum-100, Waltham, MA, USA) through KBr pelletization from 500 to 4000 cm$^{-1}$. The photoelectronic properties of the Fe-doped TiO$_2$ nanoparticles were analyzed through photoluminescence spectral measurement.

2.3. Hydrazine Chemical Sensor Fabrication

Prior to electrode coating with Fe-doped TiO$_2$ nanoparticles, the GCE with surface area of 0.071 cm$^2$ (Bio-Logic SAS, Seyssinet-Pariset, France) was polished with a 1 μm polishing diamond. After this, the surface of the GCE was further polished with 0.05 μm alumina slurry and finally washed with distilled water. The modified GCEs with active materials (Fe-doped TiO$_2$) were fabricated as follows: The GCE surface was smoothly coated by the Fe-doped TiO$_2$ using ethyl acetate and conducting binder–butyl carbitol acetate followed by drying at 60 ºC for 3 h. A three electrode electrochemical cell was connected to electrochemical workstation, Zahner Zennium, Germany, with a Pt wire as a counter electrode, and Fe-doped TiO$_2$ nanoparticle modified GCE as working electrode and an Ag/AgCl (saturated KCl) as a reference electrode were used during the electrochemical measurements. Different concentrations of hydrazine (0.2 μM–30 μM) were electrochemically tested. All the electroanalytical experiments were performed in 0.1 M phosphate buffer solution (PBS) of pH 7.4 at room temperature.

3. Results and Discussion
3.1. Characterizations and Properties of Fe-Doped TiO$_2$ Nanoparticles

Figure 1 depicts the XRD diffraction patterns of Fe-doped TiO$_2$ nanoparticles. The XRD studies clearly demonstrated the presence of both anatase and rutile phases with anatase as the major phase. The presence of main diffraction peaks in the XRD pattern of Fe-doped TiO$_2$ nanoparticles at $2\theta = 25.28, 37.8, 48.07, 54.25$ and $62.63, 68.9, 70.28$ and $75.13$ were consistent with (101), (103), (004), (200), (105), (211), (204), (116), (220) and (107) lattice planes of anatase phase (JCPDS No. 21-1272) [24].

The XRD peaks corresponding to rutile phase also emerged at $2\theta = 27.50$ and $41.54$ diffraction angles corresponding to (121) and (111) diffraction planes (JCPDS No. 21-1276). The synthesized samples did not exhibit any diffraction peaks for Fe, which suggests that the Fe$^{3+}$ content in the Fe-doped TiO$_2$ was below the detection limit, and due to almost similar ionic radii, the Fe$^{3+}$ ions could substitute Ti$^{4+}$ from some of the lattice sites of TiO$_2$ as discussed earlier. This further indicates that Fe$^{3+}$ ions were successfully integrated into TiO$_2$ matrix homogeneously without the development of iron oxide on the TiO$_2$ surface. This homogeneous distribution of Fe$^{3+}$ ions in TiO$_2$ matrix and low concentration, responsible for the absence of any Fe$^{3+}$ peaks in the XRD patterns, have also been reported earlier in the literature [36,37]. The average crystallite size of the synthesized nanoparticles was estimated using the Scherrer formula (Equation (4)) and was found to be around 14 nm.

$$d = \frac{0.89\lambda}{\beta \cos \theta}$$

where $\lambda = 1.542$ Å, $\theta =$ Bragg angle of diffraction, $\beta =$ full width at half maximum.

The detailed structural and morphological properties of Fe-doped TiO$_2$ were examined by FESEM analysis. The corresponding low and high magnification FESEM images are depicted in Figure 2a–d. A large number of spherical shaped and highly agglomerated Fe-doped TiO$_2$ particles with an average diameter of about 20 nm can be seen. In addition to spherical shapes, some Fe-doped TiO$_2$ with cubic, pentagonal, oval and other irregular geometries can also be seen from high magnification FESEM images (Figure 2c,d).

To observe the optical properties of the Fe-doped TiO$_2$ nanoparticles, a UV–Vis absorption spectroscopic study was performed. It can be examined from Figure 3a that Fe-doped TiO$_2$ nanoparticles exhibited a wide absorption peak below 400 nm, which is the typical absorption of TiO$_2$. This peak can be attributed to the electronic excitation from lower energy level to higher energy level in the anatase phase of the TiO$_2$. Furthermore, the change in color of the sample from white (pure TiO$_2$) to creamish yellow (Fe-doped TiO$_2$) depicted the increase in absorption towards visible light due to the incorporation of dopant metal [38].
Figure 2. (a) and (b) Low magnification and (c) and (d) high magnification FESEM images for Fe-doped TiO$_2$ nanoparticles.

Figure 3b illustrates the Raman spectra of Fe-doped TiO$_2$ nanoparticles. Five main bands—144.2, 195, 396.4, 513.2 and 634.8 cm$^{-1}$, corresponding to the six Raman active modes—were illustrated for the anatase phase of TiO$_2$ (3E$_g$, 2B$_{1g}$ and 1A$_{2g}$) [39]. The spectra indicated the crystalline nature of the synthesized nanoparticles. Furthermore, no additional peak related to the iron oxide was seen, which corroborates the results of XRD.

Figure 3c shows the FTIR spectra of Fe-doped TiO$_2$ nanoparticles. The spectrum reflects that doping had no effect on the bonding environment of the TiO$_2$ host nanoparticles. The broadband at 3433 cm$^{-1}$ was assigned to the symmetric and asymmetric stretching vibrations of O–H bonds of the adsorbed water molecules during sample formation. An additional peak at 1628 cm$^{-1}$ was attributed to the bending vibration related to the hydroxyl group of the adsorbed water. The band centered at ~520 cm$^{-1}$ was due to metal–oxygen, i.e., Ti–O and Fe–O, bonds [40].

The photoelectronic properties of Fe-doped TiO$_2$ nanoparticles were studied from the photoluminescence spectrum (Figure 3d). The UV region peak at around 375 nm is likely related to the near-band-edge (NBE) excitonic emission. Interestingly, the energy corresponding to above NBE peak is close to the energy gap of 3.17 eV of anatase TiO$_2$ as reported earlier [40]. The NBE transition originated from the electrons–holes recombination. The incorporation of dopant Fe did not cause any significant alteration in the PL spectrum.
3.2. Electrochemical Sensing Properties of Hydrazine Using Fe-Doped TiO$_2$: Nanoparticles

The electrochemical sensing capability of Fe-doped TiO$_2$ nanostructure was examined using cyclic voltammetry. Figure 4a,b shows typical cyclic voltammogram (CV) of bare GCE, undoped TiO$_2$: modified GCE and Fe-doped TiO$_2$: modified GCE in absence and presence, respectively, of 0.5 mM hydrazine in 0.1 M PBS (pH 7.4) at 50 mVs$^{-1}$ scan rate. As can be observed from Figure 4a, in blank PBS solution bare GCE, undoped TiO$_2$: modified GCE, and Fe-doped TiO$_2$: modified GCE did not generate any characteristic peak in the selected voltage range. However, with the addition of 0.5 mM hydrazine, no significant peak was observed by bare electrode, but a significant oxidation peak at 0.45 V vs. Ag/AgCl was detected in the case of both undoped TiO$_2$: modified GCE and Fe-doped TiO$_2$: modified electrode (Figure 4b), which clearly illustrated the efficient electrocatalytic activity of the modified GCE. The current response at Fe-doped TiO$_2$: modified electrode was much larger than the undoped TiO$_2$: modified GCE, ~137% larger, which indicates the enhanced electrocatalytic activity of coated GCE after the addition of Fe.
3.3. Amperometric Studies

The amperometric (i–t) response was also carried out with the purpose to detect the hydrazine analyte using Fe-doped TiO$_2$ nanoparticle modified GCE. Amperometric studies were performed, and the constant potential was set at a value of 0.45 V with successive addition of hydrazine (0.2–30 μM) into a continuously stirred 0.1 M PBS (pH 7.4). As revealed in Figure 5a, Fe-doped TiO$_2$ modified GCE fabricated sensor illustrated a significant and steep rise in the current value after each successive addition of hydrazine. The measured current increased rapidly with a response time of ~20 s during the amperometric measurements. The corresponding calibration curve for amperometric hydrazine sensing showed a linear response in the concentration range 0.2 to 30 μM (Figure 5b). The correlation coefficient of the line $R^2$ was found to be 0.998, and the linear equation was $y = 0.1019x + 0.0157$. The linearity in the plot also confirmed that the hydrazine oxidation process was diffusion-controlled and indicated the fast electron transfer rate, which led to the sharper and well-defined peaks.

It has been proposed that hydrazine in slightly basic medium (pH = 7.4) is oxidized onto the surface of the Fe-doped TiO$_2$ to release electrons (Equation (5)) [41,42].
\[ \text{N}_2 \text{H}_4 + 8 \text{HO}^- \rightarrow 2 \text{NO} + 6 \text{H}_2 \text{O} + 8 \text{e}^- \]  

(5)

The schematic proposed hydrazine sensing by Fe-doped TiO$_2$ is shown in Figure 6.

![Figure 6. Proposed mechanism for the hydrazine sensing by Fe-doped TiO$_2$ nanoparticles.](image)

The redox behavior of the Fe$^{3+}$ ions facilitate the transfer of electrons released from the oxidation of the hydrazine to the conduction band of the TiO$_2$ or migrate the electrons to reduce the Ti$^{4+}$ to Ti$^{3+}$ ions. Li et al. [43] proposed that Fe$^{3+}$ can act as a hole as well as an electron trap, which further enhances the electron transfer process. Furthermore, Zhu et al. [44] proposed the following reactions to depict the redox nature of Fe$^{3+}$ ions ((Equations (6)–(9)).

\[ \text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \]  

(6)

\[ \text{Fe}^{3+} + \text{h}^+ \rightarrow \text{Fe}^{4+} \text{ (Hole trap)} \]  

(7)

\[ \text{Fe}^{3+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{2+} + \text{Ti}^{3+} \text{ (Electron migration)} \]  

(8)

\[ \text{Fe}^{3+} + \text{Ti}^{3+} \rightarrow \text{Fe}^{2+} + \text{Ti}^{4+} \text{ (Recombination)} \]  

(9)

Therefore, when hydrazine comes in contact with Fe-doped TiO$_2$, the electron density in the conduction band increases, which leads to the increase in electrical conductivity and, thus, increase in the current potential. The higher the concentration of the hydrazine, the greater is the electron density in the conduction band and, hence, the current potential is higher.

The sensitivity of the synthesized sensor was calculated from the slope of the calibration curve divided by the electrode area [45,46]. The limit of detection (LOD) of the fabricated hydrazine sensor was accordingly estimated via the following equation (Equation (10)):

\[ \text{LOD} = 3.0^* \sigma_n/b \]  

(10)

where $\sigma_n$ is the standard deviation of the population of the blank signals (0.008 $\mu$A) and $b$ is the slope of the regression line. It is possible to replace $\sigma_n$ by the residual standard deviation of the regression, $s_{y/x}$, also known as standard error of the regression [47]. The sensitivity and LOD were found to be 1.44 $\mu$A $\mu$M$^{-1}$ cm$^{-2}$ and 0.236 $\mu$M, respectively. These obtained results demonstrated the potential of the Fe-doped TiO$_2$ nanostructure modified electrode as a suitable electrochemical sensor for sensitive and selective determination of hydrazine. The synthesized hydrazine electrochemical sensor was reliable and depicted fantastic reproducibility. It was ascertained that no significant decrease in
sensitivity was observed when tested for more than three weeks while being stored at room temperature in a closed container.

In order to assess the analytical potential of the fabricated sensor for real sample analysis, the selectivity of Fe-doped TiO2 nanostructures to hydrazine was evaluated. The selectivity test of the sensor was conducted to check the influence of some interfering electro-active chemical species on the sensing property of Fe-doped TiO2 by measuring the i–t response. Figure 7 demonstrates the amperometric responses of Fe-doped TiO2 modified GCE for the successive addition of different concentrations of hydrazine and 100 μM of ascorbic acid (AA), uric acid (UA), glucose, SO42−, NO3−, Pb2+ and Ca2+ at a regular interval of 100 s in 0.1 M PBS at an applied potential value of +0.45 V. The negligible change in the observed current, even if the various co-existing interfering species were present, undoubtedly revealed the excellent selectivity of the fabricated sensor.

The sensor parameters of Fe-doped TiO2 nanoparticle modified GCE and other recently reported sensors are compared in Table 1. Detailed comparison shows that the fabricated sensor had excellent electrocatalytic performance for selective detection and sensing of hydrazine.

![Figure 7. Amperometric (i–t) measurement showing the interference behavior of the Fe-doped TiO2 coated GCE upon the successive injections of 10 or 5 μM hydrazine and each 100 μM of AA, glucose, UA, SO42−, NO3−, Pb2+ and Ca2+ into a continuously stirred 0.1 M PBS (pH 7.4) solution operating at +0.45 V vs. Ag/AgCl.](image)

| Sensor Electrode                        | Sensitivity   | LOD       | Ref. |
|-----------------------------------------|---------------|-----------|------|
| Leaf shape CuO/OMC/GCE                 | 0.00487 μA.μM$^{-1}$.cm$^{-2}$ | 0.887 μM  | [4]  |
| NiCoSi sphere/GCE                      | 179.1 μA.mM$^{-1}$.cm$^{-2}$  | 0.6 μM    | [5]  |
| WO3 NPs/Au electrode                   | 0.185 μA.μM$^{-1}$.cm$^{-2}$  | 144.73 μM | [32] |
| Polythiophene/ZnO/GCE                  | 1.22 μA.μM$^{-1}$.cm$^{-2}$  | 0.207 μM  | [48] |
| Ag@FeO nanosphere/GCE                  | 270.0 μA.mM$^{-1}$.cm$^{-2}$ | 0.06 μM   | [49] |
| CdO/CNT nanocomposites/GCE             | 25.79 μA.μM$^{-1}$.cm$^{-2}$ | 4.0 pM    | [50] |
| Pd/Co-NCNTs                            | 343.9 μA.mM$^{-1}$.cm$^{-2}$ | 0.007 μM  | [51] |
| Pd (CNT-Pd)/GCE                        | 0.3 μA.mM$^{-1}$.cm$^{-2}$   | 8.0 μM    | [52] |
| Nanoporous gold/ITO                    | 0.161 μA.μM$^{-1}$.cm$^{-2}$ | 0.0043 μM | [53] |
| α-Fe2O3/polyaniline nanocomposite      | 1.93 mA.μM$^{-1}$.cm$^{-2}$  | 0.153 μM  | [54] |
| Chrysanthemum-like CoO/GCE             | 107.9 μA.mM$^{-1}$.cm$^{-2}$ | 3.7 μM    | [55] |
| AuNPs/CNTs-rGO/GCE                     | 9.73 μA.μM$^{-1}$.cm$^{-2}$  | 0.065 μM  | [56] |
4. Conclusions

In summary, highly crystalline Fe-doped TiO$_2$ nanoparticles were synthesized through hydrothermal synthesis and subsequently characterized by different characterization techniques. Finally, Fe-doped TiO$_2$ nanoparticles were applied as an efficient electron mediator for the fabrication of hydrazine chemical sensor using GCE. As-fabricated modified GCE showed sensitivity, LOD and LDR of 1.44 μA μM$^{-1}$ cm$^{-2}$, 0.236 μM and 0.2–30 μM, respectively, through an amperometric sensing approach. It was proposed that redox behavior of the Fe$^{3+}$ ions facilitates the transfer of electrons released from the oxidation of the hydrazine to the conduction band of the TiO$_2$, which leads to the increase in electrical conductivity. The negligible change in the observed current in the presence of various co-existing interfering chemical species further confirms the excellent selectivity of the fabricated sensor towards hydrazine.

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