

## Effect of Variable Nanogeometry of Titanium oxide-gold Nanocomposite: Application in Electrochemical Sensing of Hydrazine

Prem C Pandey\* and Arvind Prakash

Department of Chemistry, Indian Institute of Technology (BHU), Varanasi-221005, India

### Abstract

3-Aminopropyltrimethoxysilane (3-APTMS) and 3-glycidoxypropyltrimethoxy-silane (3-GPTMS) mediated synthesis of gold nanoparticles (AuNPs) of two different sizes [AuNP<sub>1</sub> (10 nm) and AuNP<sub>2</sub> (20 nm)] were made and used for nano-composite formation with TiO<sub>2</sub> nanoparticle suspension. The resulting TiO<sub>2</sub>-AuNP<sub>1</sub> and TiO<sub>2</sub>-AuNP<sub>2</sub> nanocomposites were used for making chemically modified electrodes to understand the role of nanogeometry in chemical sensing. TiO<sub>2</sub>-AuNP<sub>1</sub> and TiO<sub>2</sub>-AuNP<sub>2</sub> nanocomposites were characterized by transmission electron microscopy and UV-VIS spectroscopy. The analytical results revealed the average size of the nanocomposite in the range of 20-25nm. The nanocomposites were employed for modification of graphite paste electrodes and applied in electrochemical sensing of hydrazine. The results demonstrated that TiO<sub>2</sub>-AuNP<sub>1</sub> exhibit better electrocatalytic activity as compared to that of TiO<sub>2</sub>-AuNP<sub>2</sub> and only TiO<sub>2</sub> towards oxidation of hydrazine. Amperometric analysis of hydrazine on these electrodes at the applied potential of 0.4 V vs Ag/AgCl was made to quantify the sensing ability of modified electrodes. The sensitivity and lowest detection limit was found as 25, 57.2 and 145.7 μAmM<sup>-1</sup>cm<sup>-2</sup> and 50, 100, 20 nM for TiO<sub>2</sub>, TiO<sub>2</sub>-AuNP<sub>2</sub> and TiO<sub>2</sub>-AuNP<sub>1</sub> respectively.

**Keywords:** Electrocatalysis; TiO<sub>2</sub> nanocomposite; Gold nanoparticle; Hydrazine; Chemically modified electrode

### Introduction

In recent years, the chemical modification of electrode surfaces with nanocomposite has emerged as a vibrant area of research especially for electroanalysis not only because of the unusual property combinations but also because of unique design possibilities. A particularly interesting support platform, used for electrode modification, is metal oxide and its nanocomposites, which have many improved characteristics i.e., high surface area, nontoxicity, good biocompatibility, and chemical stability [1-5]. Among the metal oxides, TiO<sub>2</sub>, WO<sub>3</sub>, CeO<sub>2</sub>, ZnO, and ZrO<sub>2</sub> are easy to synthesize through solution-gel processes and also used as catalyst /photo catalyst for pollutant elimination and organic synthesis [6-10]. Furthermore, metal oxide composites with other metal nanoparticle's such as Au, Ag, Pd, Pt and Ru etc. provide good catalytic properties in addition to excellent selectivity towards particular analyte which allow a facile fabrication of electrochemical sensors [11-14]. Catalytic properties of metal nanoparticles (MNPs) have been vigorously investigated because of their specific properties and enormous potential applications as nanoelectronic, photovoltaic or electrochromic devices and sensors [15-18]. MNPs lost the reactivity due to precipitation or aggregation because of their high surface energies. Thus, the physical properties of the nanoparticles (quantum size effects) diminish the resulting materials are no longer homogeneous. Both facts have effects the final material properties. The concert of electrochemical sensor mainly depends on the morphology, size and surface area of MNPs on the modified electrodes. In order to enhance the electrocatalytic activity, the design of stable hybrid nanoparticles becomes one of the primary challenges for their applications [15]. Various stabilizing agents are used as carboxylic acid, sodium citrate, poly (vinyl-alcohol) polymer, Poly ethylene glycol, cetyltrimethylammonium bromide (CTBA) and 3-Aminopropyltrimethoxysilane (3-APTMS) [16-19]. We have reported the controlled synthesis of gold nanoparticles (AuNPs) having variable nanogeometry using active role of 3-APTMS and 3-Glycidoxypropyltrimethoxysilane (3-GPTMS) [19]. These nanoparticles are found to be dispersible in both aqueous and non-aqueous medium [20]. Accordingly it was planned to make

nanocomposite of titanium oxide suspension and different variable size of AuNPs, as such materials have shown promising practical applications in electrocatalysis because TiO<sub>2</sub> nanoparticles having high surface area to volume ratio, ion-changeable ability, optical transparency, biocompatible and photocatalytic ability, environmental safety [12,21]. The nanocomposites of TiO<sub>2</sub> with two sizes of AuNPs are reported herein.

Hydrazine is highly reactive and used as a fuel in rocket propulsion systems, also pesticides, blowing agents, pharmaceutical intermediates, and photographic chemicals [22]. Acute exposure of high level hydrazine shows symptoms like irritation of eyes, nose, and throat, temporary blindness, dizziness, pulmonary edema, and also damages the liver, kidneys, and central nervous system in humans [23]. All the above make their quantitative detection problems of considerable analytical interest. Among several techniques, electrochemical techniques offer the opportunity for low cost, highly sensitive and rapid methodologies for the determination of hydrazine [24]. We have demonstrated the role of AuNPs nanocomposite of nickel hexacyanoferrate for the analysis of hydrazine [25]. The present article reports on the use of TiO<sub>2</sub>-AuNPs nanocomposite for hydrazine sensing.

### Materials and Instrumentation

All the reagent used were analytical grade including Titanium isopropoxide, AuCl<sub>3</sub>, 3-Aminopropyltrimethoxysilane, 3-Glycidoxypropyltrimethoxysilane, isopropanol, HCl and hydrazine

\*Corresponding author: Prem C Pandey, Department of Chemistry, Indian Institute of Technology (BHU), Varanasi-221005, India, Tel: 91-22-2576-744, E-mail: [pcpandey.apc@iitbhu.ac.in](mailto:pcpandey.apc@iitbhu.ac.in)

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hydrate, graphite powder (particle size 1–2  $\mu\text{m}$ ) and Nujol oil (density 0.838) were obtained from Aldrich Chemical Co. The water used in experiments is double distilled-deionized water.

The absorption spectra were recorded by using a Hitachi U-2900 Spectrophotometer. Transmission electron microscopy (TEM) studies were performed using Hitachi 800 and 8100 electron microscopes (Tokyo, Japan) with an acceleration voltage of 200 kV. Cyclic voltammetry and amperometry were performed on an electrochemical workstation CHI 660B (CH Instruments, USA) in a three-electrode cell configuration with a working volume of 3 mL. An Ag/AgCl electrode (3 M KCl saturated with Ag/AgCl) and a platinum plate electrode served as reference and counter electrode respectively. All potentials given below were relative to the Ag/AgCl. The working electrode was a graphite paste electrode (GpE). All electrochemical experiment were conducted in 0.1 M phosphate buffer solution (pH 7.0) containing 0.5 M KCl.

### Synthesis of $\text{TiO}_2$ , $\text{TiO}_2\text{-AuNP}_1$ and $\text{TiO}_2\text{-AuNP}_2$ nanocomposite

The typical process of  $\text{TiO}_2$  nanoparticles synthesis involves the mixing of 700  $\mu\text{l}$  titanium isopropoxide in 10 ml isopropanol under stirred conditions over a vertex cyclo mixer, followed by drop wise addition of 20  $\mu\text{l}$  HCl (2M). The resulting mixtures were then subjected to peptization for 24 hours. Further, the semi-transparent solution was settled and the precipitate (titanic acid gel) was washed with double distilled-deionized water three times in order to eliminate any remaining acid content. The resulting gel was dried at 120°C followed by calcination at 500°C for 2 h. Two sizes gold nanoparticle were synthesized as previously described by our group [19]. The  $\text{TiO}_2\text{-AuNPs}$  nanocomposite systems were made by mixing 5 mg  $\text{TiO}_2$  nanoparticle dispersed in 1ml methanol and 50  $\mu\text{l}$  of AuNPred/AuNPviolet ( $\text{AuNP}_1/\text{AuNP}_2$ ) solution. The reaction mixtures ( $\text{TiO}_2\text{-AuNP}_1$  and  $\text{TiO}_2\text{-AuNP}_2$ ) were then subjected to ultra-sonication for 5 min. The resulting suspension was dried at 50°C for 12h.

### Fabrication of electrode

The electrode body used for the construction of the graphite paste electrode was obtained from Bioanalytical Systems (West Lafayette, IN; (MF 2010)). For modification of the electrode the well of electrode was filled with an active paste of composition as,  $\text{TiO}_2/\text{TiO}_2\text{-AuNP}_1/\text{TiO}_2\text{-AuNP}_2$  1% (w/w), graphite powder 69% (w/w) and nujol oil 30% (w/w). The desired amount of modifier was thoroughly mixed and stored into a stoppard glass vial at room temperature. The paste surface was manually smoothened on a clean butter paper.

### Results and Discussion

The absorbance spectra of the aqueous  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  solution are shown in Figure 1a, 1b and 1c respectively. Both nanocomposites show absorption in UV as well as in visible range except  $\text{TiO}_2$  suspension. The absorbance in visible range at 526 and 536 nm justify the presence of  $\text{AuNP}_1$  and  $\text{AuNP}_2$  of red and violet color. The inset to Figure 1 shows the photos of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  solution respectively.

The band gap of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  solution were calculated using the data of UV-Visible spectroscopy. In the parabolic band structure approximation, the band gap  $E_g$  and the absorption coefficient  $\alpha$  of an indirect band gap semiconductor are related through the following well known equation [26].

$$\alpha h\nu = A(h\nu - E_g)^2$$

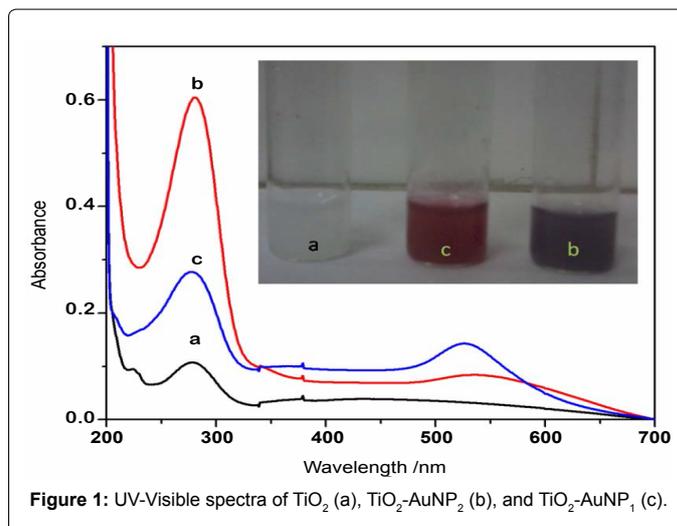


Figure 1: UV-Visible spectra of  $\text{TiO}_2$  (a),  $\text{TiO}_2\text{-AuNP}_2$  (b), and  $\text{TiO}_2\text{-AuNP}_1$  (c).

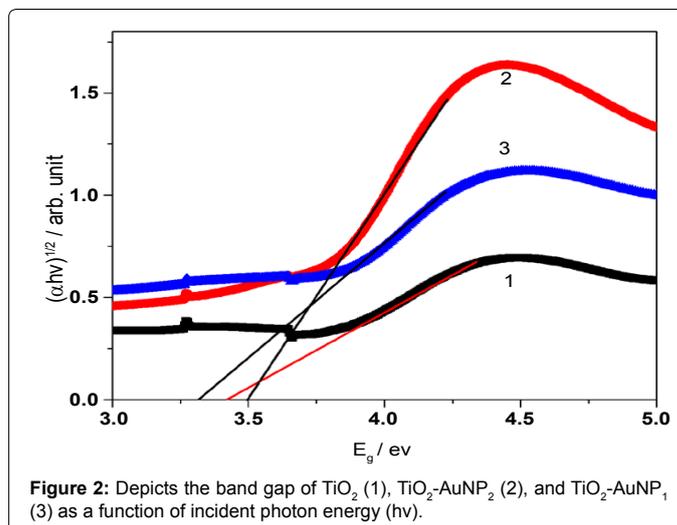


Figure 2: Depicts the band gap of  $\text{TiO}_2$  (1),  $\text{TiO}_2\text{-AuNP}_2$  (2), and  $\text{TiO}_2\text{-AuNP}_1$  (3) as a function of incident photon energy ( $h\nu$ ).

Where  $A$  is a constant of proportionality,  $h$  is Planck's constant and  $\nu$  is the frequency of incident photon. In our case, the band gap ( $E_g$ ) of the composite solution are calculated by plotting  $(\alpha h\nu)^{1/2}$  as a function of incident photon energy ( $h\nu$ ) and linearly regressing the linear portion of the  $(\alpha h\nu)^{1/2}$  to zero of the energy axis. The Figure 2a, 2b and 2c shows the value of  $E_g$  as 3.42, 3.49 and 3.31 for  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  solution respectively justifying enhancement in catalytic behaviour of nanocomposite. Figure 3A and 3B shows the transmission electron microscopy (TEM) images of  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  nanocomposite. It is cleared from images that  $\text{TiO}_2\text{-AuNP}_2$  nanoparticles are agglomerated and  $\text{TiO}_2\text{-AuNP}_1$  nanoparticles are in a chain like network. The average particle sizes of the  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  nanoparticles are found in the range of 20-25 nm. The network like morphology of  $\text{TiO}_2\text{-AuNP}_1$  nanoparticles enhances particular performance of large surface-to-volume ratio also confirmed from TEM image.

The modified electrodes of these  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  nanocomposite are made to evaluate the electrochemical performances for practical applications. Figure 4a, 4b and 4c depicts the cyclic voltammetry obtained for  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  modified GP electrodes in absence (curve A), and presence of 1 mM  $\text{N}_2\text{H}_4$  (curve B). The results illustrates that the oxidation potential of

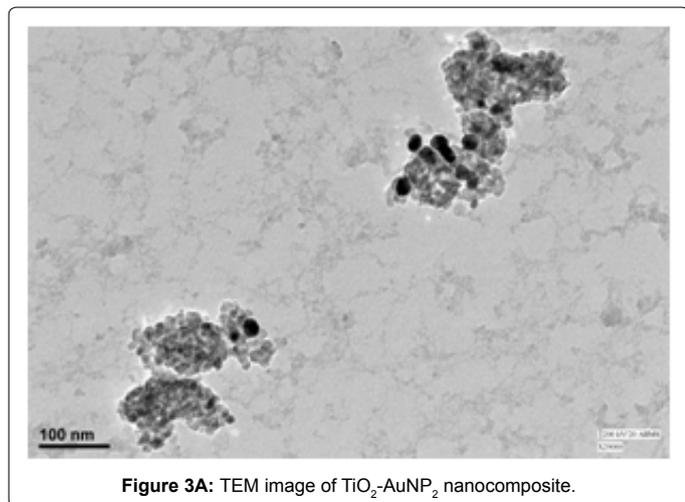


Figure 3A: TEM image of  $\text{TiO}_2\text{-AuNP}_2$  nanocomposite.

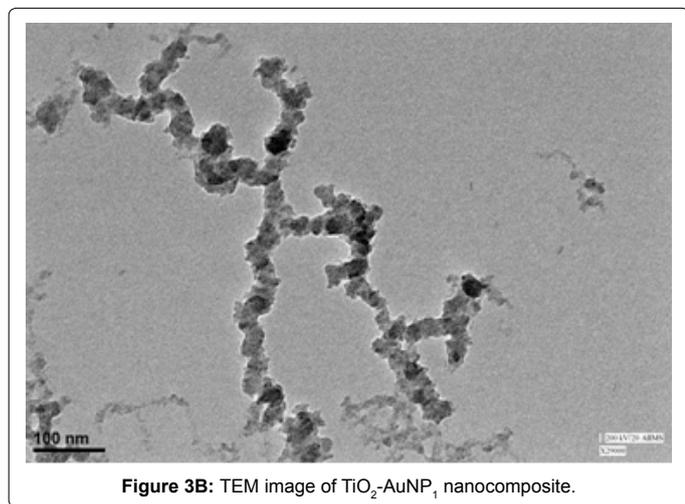


Figure 3B: TEM image of  $\text{TiO}_2\text{-AuNP}_1$  nanocomposite.

$\text{N}_2\text{H}_4$  occurs at 0.56, 0.41 and 0.48 V and the corresponding to  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  modified GP electrodes. The resulting anodic current for the same are found to be 3.24, 9.93 and 17.34  $\mu\text{A}$  with respect to  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  modified GP electrodes justifying the role of AuNPs of different nanogeometry in the  $\text{TiO}_2$  matrix. Quantitative analysis of hydrazine was made by conducting amperometric measurements. Figure 5a, 5b and 5c represents the typical results of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  modified GP electrodes recorded at 0.4 V vs Ag/AgCl. The corresponding calibration curves are shown in inset to Figure 5. The electrochemical data were used to calculate the sensitivity which are found to be 25, 57.2 and 145.7  $\mu\text{AmM}^{-1}\text{cm}^{-2}$  for  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-AuNP}_2$  and  $\text{TiO}_2\text{-AuNP}_1$  modified GP electrodes with the lowest detection limit of 50, 100, 20 nm for the same. A comparison on the electrocatalytic performance of the present systems on electro-catalytic oxidation of Hydrazine is made with those of earlier reported ones as given in Table 1. The data (table 1) reveal advantages of the present system as compared to that of other system.

### Interference study

The influence of various species on the determination of hydrazine (0.1 mmol/L) was studied under optimum conditions by  $\text{TiO}_2\text{-AuNP}_1$  modified GP electrode. No interference was observed with common cations and anions (500-fold quantities of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{PO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{Ca}^{2+}$  and 100-fold  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  ions)

and found to be less than 3.8% deviation with 10-fold quantities of interfering species (l-cysteine, l-tryptophan, ascorbic acid (AA), uric acid (UA), dopamine (DA), glucose (GO), and hydroxylamine ( $\text{NH}_2\text{OH}$ )), indicating the present electrode has good selectivity.

### Stability and reproducibility

The reproducibility and repeatability of hydrazine sensing on  $\text{TiO}_2\text{-AuNP}_1$  was determined. In a series of 10 sensors prepared in the same way, a relative standard deviation (R.S.D.) of 5.6% was obtained towards 0.1 mmol/L hydrazine, indicating the reliability of the method. A set of 10 different amperometric measurements for 0.1 mmol/L hydrazine with a single sensor yield a R.S.D. of 5.9%. The stability of the hydrazine sensor was explored. The proposed sensor was stored at 4°C. The response to 0.1 mmol/L hydrazine was tested each week within a month of storage, the response of the sensor only decreased by 6.3% compared to the initial response, which shows the long-term stability [27-36].

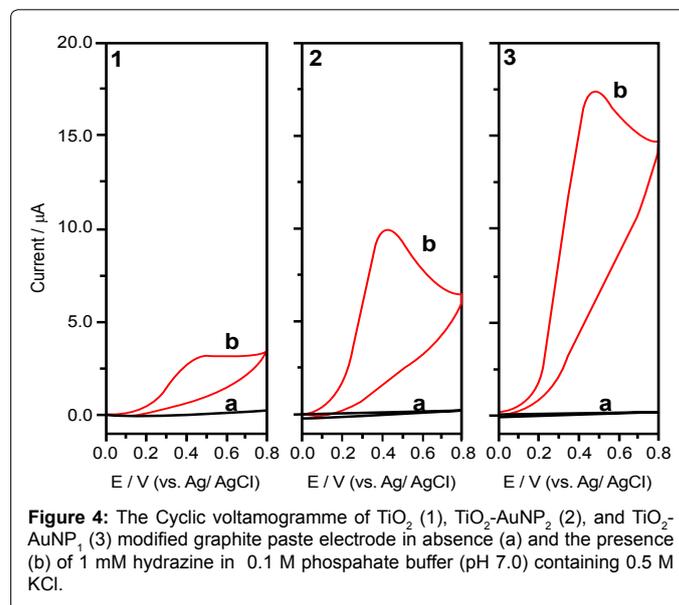


Figure 4: The Cyclic voltammogram of  $\text{TiO}_2$  (1),  $\text{TiO}_2\text{-AuNP}_2$  (2), and  $\text{TiO}_2\text{-AuNP}_1$  (3) modified graphite paste electrode in absence (a) and the presence (b) of 1 mM hydrazine in 0.1 M phosphate buffer (pH 7.0) containing 0.5 M KCl.

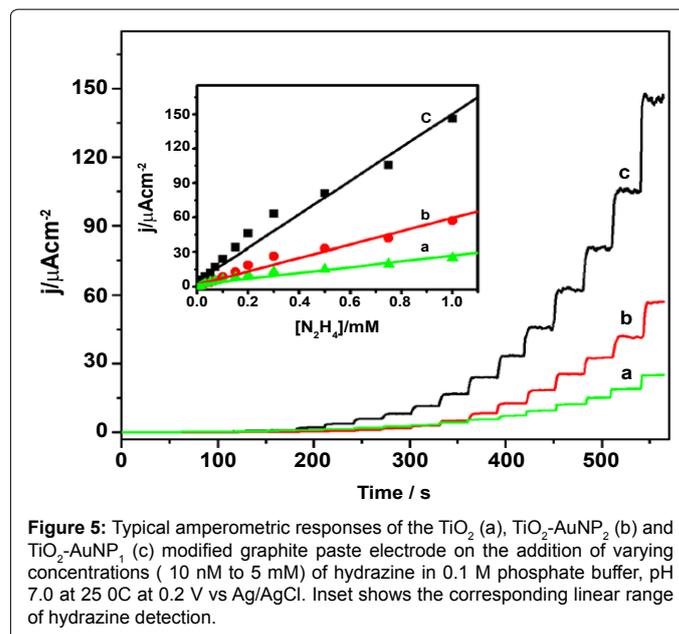


Figure 5: Typical amperometric responses of the  $\text{TiO}_2$  (a),  $\text{TiO}_2\text{-AuNP}_2$  (b) and  $\text{TiO}_2\text{-AuNP}_1$  (c) modified graphite paste electrode on the addition of varying concentrations (10 nM to 5 mM) of hydrazine in 0.1 M phosphate buffer, pH 7.0 at 25 °C at 0.2 V vs Ag/AgCl. Inset shows the corresponding linear range of hydrazine detection.

Electrode materials	Response time (s)	Detection limit ( $\mu\text{M}$ )	Linear range ( $\mu\text{M}$ )	Ref.
Au/PPy/GCE	-	0.2	1–500	27
Nano-Au/Ti	-	42	500–4000	28
Hematoxylin multi-wall carbon nanotubes	<2	0.68	2.0–122.8	29
Copper oxide nanoarray	<5	0.17	-	30
BiHCF-modified CCE	-	3	7.0–1010	31
Curcumin multi-wall carbon nanotubes	<3	1.4	2–44	32
Carbon nanotubes and catechol derivatives	<2	0.050	0.50–6.5	33
Nano-Au/Porous-TiO <sub>2</sub> /GCE	<3	0.5	2.5–500	34
PVP–a GNCs	<2	1.1	5 to 460	35
Ni <sub>0.95</sub> -La <sub>0.05</sub> -RVC	-	140	50–5000	36
TiO <sub>2</sub> -AuNP <sub>1</sub>	<2	0.020	0.010-1000	This work
TiO <sub>2</sub> -AuNP <sub>2</sub>	<5	0.100	0.100-1000	This work

**Table 1:** A comparison of electrocatalytic detection of hydrazine using various type of modified electrode systems.

## Conclusions

The studies conducted in the present investigation demonstrate the synthesis of TiO<sub>2</sub> nanocomposite using two sizes of gold nanoparticles. AuNP<sub>1</sub> and AuNP<sub>2</sub> being in increasing nanogeometry are used for the fabrication of TiO<sub>2</sub>-nanocomposite. The as prepared nanocomposites e.g. TiO<sub>2</sub>-AuNP<sub>2</sub> and TiO<sub>2</sub>-AuNP<sub>1</sub> are used to make modified graphite paste electrode for sensitive sensing of hydrazine. The results clearly indicate that incorporation of two different size of gold nanoparticle in TiO<sub>2</sub> matrix lead to significant enhancement in the oxidation response of hydrazine. In addition the contribution of TiO<sub>2</sub>-AuNP<sub>1</sub> towards the amplification of hydrazine oxidation was found much better as compared to that of TiO<sub>2</sub>-AuNP<sub>2</sub> and TiO<sub>2</sub>. The TiO<sub>2</sub>-AuNP<sub>1</sub> nanocomposite act as an active material justifying excellent electrocatalytic activity, fast response, highly sensitivity, better lowest detection limit and promising application potential in electrochemical sensing.

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