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## An electrochemical synthesis strategy of composite based ZnO microspheres-Au nanoparticles on reduced graphene oxide for the sensitive detection of hydrazine in water samples

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An electrochemical synthesis strategy has been approached to prepare the novel composite *viz.* reduced graphene oxide nanosheets/ZnO microspheres (~0.6  $\mu$ m)–Au nanoparticles (~50 nm) modified glassy carbon electrode (GCE/RGO/ZnO-Au) for the trace level detection of hydrazine. The as-prepared composite is characterized by using Scanning Electron Microscopy (SEM) along with Energy Dispersive X-ray (EDX) analysis confirm the presence of Au nanoparticles along with globular ZnO microspheres embedded over the entire surface of graphene nanosheets. The electrochemical detection of hydrazine is performed by using cyclic voltammetry and chronoamperometry methods. Fascinatingly, the oxidation peak current of hydrazine at RGO/ZnO-Au modified GCE is 4.1 fold higher than that of RGO-Au modified GCE and 2.4 fold higher than ZnO/Au-modified GCE along with favorable lower overpotential at 0.1 V. The chronoamperometric hydrazine sensor shows a very lower detection limit of 18 nM with higher sensitivity of 5.54  $\mu$ A  $\mu$ M<sup>-1</sup> cm<sup>-2</sup>. The excellent analytical parameters of the RGO/ZnO-Au modified for the various related modified electrodes suggests that the electrode can be widely used for the trace level detection of hydrazine for several industrial applications with low cost, ease of preparation, repeatability and long-term stability.

#### 1. Introduction

Hydrazine is widely used in many industrial and pharmaceutical applications. It is being used as a powerful reducing agent in chemical reactions and as a fuel in direct fuel cell systems. It also finds application in the preparation of catalysts, antioxidants, emulsifiers, pesticides, dyes and explosives.<sup>1,2</sup> Hydrazine is a small inorganic molecule, which is very harmful to human life. Because it is highly poisonous and can easily absorb by oral, skin and breathing routes. Moreover, it affects the lungs, kidney, and central nervous system of living organisms and mutagenic effects.<sup>3</sup> Hence, it is

imperative for the sensitive determination of hydrazine. Aforetime, several analytical methods were available viz. Ion chromatography,<sup>4</sup> flow injection analysis,5 chemiluminescence<sup>6</sup> and spectrophotometry<sup>7</sup> for the hydrazine determination. However, these methods are rather time-consuming and are not suitable for field measurements. In this context, electrochemical analysis has evolved as a viable alternative providing the opportunity for rapid and reliable detection of hydrazine with advantages of high selectivity, sensitivity, low cost and simplicity.8 However, the electrochemical oxidation of hydrazine at a conventional glassy carbon electrode is kinetically sluggish requiring a high overpotential.<sup>9</sup> Therefore chemically modified electrodes are often employed for the electrochemical determination of hydrazine. Though, numerous chemically modified electrodes were developed in the past,<sup>10-12</sup> still a

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thirst to explore better modified electrodes exists aiming towards a highly sensitive and selective electrochemical determination of hydrazine.

Graphene has been one of the most investigated materials in electrochemistry owing to its interesting electronic and electrocatalytic properties.<sup>13-17</sup> These properties can be further tailored by making graphene as a composite with metal and metal oxide nanoparticles. Moreover, a great number of graphene based nanocomposites have been prepared and used in electrochemical sensors and biosensor applications.<sup>18-20</sup> Especially, graphene-Au nanocomposites have been reported to exhibit pronounced electrocatalytic properties due to the excellent synergetic effect operating between graphene and Au nanoparticles.<sup>21-23</sup> Graphenezinc oxide composites are considered to be advanced electrode materials for dye sensitized solar cells,<sup>24</sup> energy storage,<sup>25</sup> electrochemical sensors<sup>24</sup> and biosensors.<sup>27-30</sup> Recently, the application of some graphene nanocomposites for the electrochemical detection of hydrazine has been demonstrated in literature. For instance, poly(sodium styrenesulfonate) (PSS)graphene nanocomposite film,<sup>31</sup> prussian blue on graphene matrix,<sup>32</sup> hierarchical flower-like cobalt on petalage-like graphene hybrid microstructures,<sup>33</sup> polyaniline/graphene composite,<sup>34</sup> Au/graphene and bismuth/graphene,35,36 copper sulfide/reduced graphene oxide nanocomposite<sup>37</sup> and AuPd/graphene<sup>38</sup> have been effectively used for the detection of hydrazine.

Herein, we report the application of a new nanocomposite *viz.* reduced graphene oxide/zinc oxide–Au nanocomposite (RGO/ZnO-Au) towards the electrochemical detection of hydrazine at nanomolar level. The preparation of RGO/ZnO-Au nanocomposite is accomplished by a two-step electrochemical approach. The new RGO/ZnO-Au nanocomposite modified electrode is found to show a very good response to hydrazine. A highly sensitive chronoamperometry sensor has been developed for the detection of hydrazine and it is found that the nanocomposite shows exemplary performance in terms of lower detection limit and higher current sensitivity compared to many of the reported hydrazine sensors based on graphene nanocomposites.

#### 2. Experimental

#### 2.1 Reagents and solutions

Graphite powder and hydrazine monohydrate (NH<sub>2</sub>NH<sub>2</sub>.H<sub>2</sub>O) were purchased from Alfa Aesar. Zinc nitrate hexahydrate, (Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O), chloroauric acid (HAuCl<sub>4</sub>.3H<sub>2</sub>O) and all other chemicals were purchased from Sigma-Aldrich. All the chemicals were of analytical grade and used as received. 0.1 M phosphate buffer solution (PBS) served as electrolyte which was prepared using K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>. Ultra-pure double distilled water (conductivity  $\geq$ 18 M $\Omega$  cm) was used for all the experiments. Prior to each electrochemical experiment, the electrolyte was deoxygenated by passing high purity nitrogen for 10 minutes.

#### 2.2 Apparatus

The electrochemical measurements were carried out using an electrochemical workstation (CH Instruments, Model 680) with a conventional three electrode cell using glassy carbon electrode (GCE) (CH instruments) as working electrode (area 0.07 cm<sup>2</sup>), saturated calomel electrode (SCE) as reference electrode and Pt wire as counter electrode. Amperometric measurements were performed by an analytical rotator AFMSRX (PINE instruments) with a rotating disc electrode (RDE) having a geometrical area of 0.24 cm<sup>2</sup>. Morphology studies were carried out using a scanning electron microscope (SEM) (JEOL JSM 6390). Energy-dispersive X-ray (EDX) spectra were recorded using HORIBA EMAX X-ACT (Model 51-ADD0009).

# 2.3 Preparation of RGO/ZnO-Au nanocomposite modified GCE (GCE/RGO/ZnO-Au)

GO was prepared by Staudenmaier method.<sup>39</sup> About 5  $\mu$ L of the GO dispersion (2 mg in 1 ml H<sub>2</sub>O) was drop coated onto a pre-cleaned GCE and dried at ambient conditions. The GO modified GCE was placed in an electrochemical cell containing an aqueous solution of 5  $\times$  10<sup>-2</sup> M Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and 5  $\times$  10<sup>-2</sup> M KNO<sub>3</sub>. The simultaneous reduction of GO to reduced graphene oxide (RGO) and electrodeposition of ZnO have been achieved by performing 15 consecutive cycles in the potential range between +0.2 and -1.5 V at a scan rate of 50 mV s<sup>-1</sup> (Fig. 1A)<sup>24</sup>. The RGO/ZnO modified GCE (GCE/RGO/ZnO) after rinsing with water was transferred to another electrochemical cell containing 2 mM HAuCl<sub>4</sub>.3H<sub>2</sub>O in 0.1 M KCl. Au nanoparticles were deposited by doing cyclic voltammetry in the potential range from +0.2 V to -1.0 V at 50 mV s<sup>-1</sup> for 6 cycles to obtain GCE/RGO/ZnO-Au (Fig. 1B).<sup>40</sup> The process pathway of the electrochemical synthesis of RGO/ZnO-Au as illustrated in scheme

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1. The optimum loading of Au nanoparticles into the RGO/ZnO electrode matrix has been established through varying the number of electrodeposition cycles and evaluating its electrocatalytic activity towards the oxidation of 0.5 mM of hydrazine in PBS (pH 7.4) at a scan rate of 50 mV s<sup>-1</sup>. A plot of hydrazine oxidation peak current against the number of cycles used in Au deposition (Inset to Fig. 1B) clearly shows that maximum electrocatalysis can be achieved for an electrode prepared with six electrodeposition cycles and hence this optimum condition has been used for Au nanoparticles deposition onto GCE/RGO/ZnO to obtain GCE/RGO/ZnO-Au. Control of the number of cycles of Au electrodeposition can be expected to have a profound effect on the Au particle size and content, both of which are important factors in determining the catalytic efficiency. For parallel comparative experiments, GCE/ZnO-Au and GCE/RGO-Au modified electrodes were prepared by adopting appropriate steps in the above described procedure.



Scheme 1 Schematic illustrations of the chemical and electrochemical synthesis strategy of RGO/ZnO-Au composite.

#### 3. Results and discussion

# 3.1 Investigation of simultaneous reduction of GO and formation of ZnO on GCE

Electrochemical reduction of pristine GO for 15 consecutive cyclic voltammograms (Inset to Fig 1A) exhibited a large cathodic peak at about -1.37 V, corresponding to the reduction of abundant oxygen functionalities (carboxyl, hydroxyl and epoxy) residing on the edge and basal plane of GO [41]. The current magnitude was drastically

reduced in the subsequent cycles and the peak disappeared after 15 cycles, showing the completion of reduction. Fig.1A shows the simultaneous electrochemical reduction of GO and electrodeposition of ZnO. It can be observed that in the first cycle, a large cathodic peak appeared at -1.1 V corresponding to the reduction of oxygen functionalities of GO as in the case of pristine GO [42]. The peak potential is lowered by about 0.25 V and the current magnitude is also enhanced considerably compared to the values obtained in inset to Fig 1A. The current magnitude at -1.1 V reduced drastically in the second cycle. After 15 cycles the cathodic peak disappeared suggest that the maximum amount of the electrochemical reduction of GO to RGO is achieved. In the course of electrochemical experiment, at the first cycle a new anodic peak appeared at -0.58 V, whose current magnitude increased gradually with subsequent cycles. The peak at -0.58 V could be associated with the formation of ZnO [43].



Fig. 1 (A) 15 Consecutive cyclic voltammograms recorded at GO/GCE in an aqueous solution containing  $0.05 \text{ M} (\text{ZnNO}_3)_2.6\text{H}_2\text{O}$ 

and 0.05 M KNO<sub>3</sub> at 50 mV s<sup>-1</sup>. Inset: 15 Consecutive cyclic voltammograms recorded at GCE/GO in 0.05 M KNO<sub>3</sub> at 50 mV s<sup>-1</sup>. (B) Electrochemical deposition of Au on GCE/RGO-ZnO. Electrolyte: 0.05 M (ZnNO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and 0.05 M KNO<sub>3</sub>. Sweep rate: 50 mV s<sup>-1</sup>. Inset: Plot of hydrazine oxidation peak current versus number of cycles used for Au electrodeposition.

It is known in literature that the nitrate ion in the electrolyte can assist the formation of oxide by the following reaction (Eq. 1) [44]. As reported previously, electrochemical deposition of ZnO could possibly occur by adopting the following mechanistic pathway.

$$\operatorname{Zn}^{2^+} + \operatorname{NO}_3^- + 2e^- \longrightarrow \operatorname{ZnO} + \operatorname{NO}_2^-$$
 (Eq. 1)

#### 3.2 Morphology and elemental characterization

As can be seen from the SEM images shown in Fig. 2A, the morphology of RGO portrays the typical thin, wrinkled sheet-like 2D graphene structure.



Fig. 2 SEM images of (A) RGO (B) RGO-ZnO (C) RGO/ZnO-Au and EDX spectra of (D) RGO/ZnO and (E) RGO/ZnO-Au.

Fig. 2B,C shows the SEM images of RGO/ZnO and RGO/ZnO-Au films along with their EDX spectra (Fig. 2D and E). The SEM image of RGO/ZnO shows the presence of ZnO microspheres interspersed over the graphene matrix, whereas that of

RGO/ZnO-Au nanocomposite shows the random distribution of Au nanoparticles onto the RGO/ZnO modified surface. The EDX spectrum of RGO/ZnO shows the signals for C, O and Zn elements confirming thus the formation of ZnO. Furthermore, the EDX spectrum of RGO/ZnO-Au exhibits an additional signal for Au confirming its presence in the composite film.



**Fig. 3** a) XPS spectra of RGO/ZnO-Au and, b) enlarged view of XPS spectra covering the Au  $4t^{5/2}$  and Au  $4t^{5/2}$  and, c) Zn  $2p^{1/2}$ , and Zn  $2p^{3/2}$ .

In addition, the formation of RGO/ZnO-Au composite and their surface properties were studied by X-ray photoelectron spectroscopy (XPS). Fig. 3a shows the XPS result which clearly showed the presence of predominant species *viz*. C, O,  $Zn^{2+}$ , Au<sup>+</sup> at 285.7, 530.6, 1021.6, 1046.3, 86.3, and 89.7 eV are corresponding to C 1s, O 1s, Zn 2p<sub>3/2</sub>, Zn 2p<sub>1/2</sub>, Au 4f7/2, and Au 4f5/2, respectively. The observed binding energies for these peaks are more consistent with the reported literature values (Fig. 3b).<sup>45,46</sup> Consequently, it is indicative that the Zn and Au species are in the RGO/ZnO-Au composite materials prepared by the electrochemical deposition are predominantly Zn<sup>2+</sup>, and Au<sup>+</sup>.

#### 3.3 Electrochemical impedance spectroscopy (EIS) studies

EIS is an efficient tool to monitor the interfacial properties of the modified electrodes. Fig. 4 shows the Nyquist plots (–Z" vs Z') of the

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three modified electrodes *viz*. GCE/ZnO-Au, GCE/RGO-Au and GCE/RGO/ZnO-Au in comparison to bare GCE in 0.1 M KCl containing  $5 \times 10^{-3}$  M equimolar [Fe (CN)<sub>6</sub>]<sup>3-/4-</sup>. All the plots show the presence of two distinct regions *viz*. a semicircle at high frequency region and a linear part at low frequency region.



**Fig. 4** Nyquist plots of (a) bare GCE (b) GCE/ZnO-Au (c) GCE /RGO-Au (d) GCE/RGO/ZnO-Au obtained in 0.1 M KCl solution containing 5 mM  $Fe(CN)_6^{3./4-}$ .

The semicircle corresponds to the electron transfer process, and its diameter is equivalent to the charge transfer resistance  $(R_{ct})$ . The linear part at lower frequencies corresponds to a diffusion-limited process. Significant differences in the  $R_{ct}$  values of the modified electrodes with respect to the bare GCE clearly indicate the surface modification. The  $R_{ct}$  value of bare GCE is about 706  $\Omega$ (Fig. 4a). After the GCE is modified with ZnO/Au,  $R_{ct}$  increases markedly to 1406  $\Omega$  which can be attributed to the semiconducting nature of ZnO film (Fig. 4b). The R<sub>ct</sub> value of GCE/RGO-Au is about 160  $\Omega$  (Fig. 3c) which is much lower than bare GCE indicating a facile electron transfer process attributable to the highly conducting gold nanoparticle impregnated reduced graphene oxide surface layer. When the RGO/ZnO-Au (Fig. 4d) nanocomposite is applied to modify the GCE,  $R_{ct}$  is moderately increased to 212  $\Omega$ . These results show that the RGO/ZnO-Au nanocomposite film is successfully prepared on the GCE surface.

#### 3.4 Electrocatalytic oxidation of hydrazine

Fig. 5A shows the cyclic voltammograms for the oxidation of 0.5 mM hydrazine at bare GCE, GCE/RGO/ZnO, GCE/ZnO-Au, GCE/RGO-Au, and GCE/RGO/ZnO-Au in PBS (pH 7.4) at a scan rate of 50 mV s<sup>-1</sup>. The cyclic voltammogram for the oxidation of hydrazine at bare GCE shows a small anodic current which increases with increasing potential with a featureless anodic peak observed, indicating that the electron transfer requires a high overpotential (curve a). The GCE/RGO/ZnO voltammetry curve shows a very low irreversible oxidation peak current with higher oxidation potential.





**Fig. 5** (A) Cyclic voltammograms for the oxidation of 0.5 mM of hydrazine in 0.1 M PBS (pH 7.4) at 50 mV s<sup>-1</sup> (a) bare GCE (b) GCE/RGO/ZnO (c) GCE/ZnO-Au (d) GCE/RGO-Au (e) GCE/RGO/ZnO-Au. (B) Cyclic voltammograms of GCE/RGO/ZnO-Au at 50 mV s<sup>-1</sup> in 0.1 M PBS (pH 7.4) at various concentrations of hydrazine in mM (a) 0.5 (b) 0.99 (c) 1.46 (d) 1.92 (e) 2.37 (f) 2.81 and (g) 3.24. Inset: plot of log (peak current) *vs.* log (hydrazine concentration).

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irreversible anodic peak responsible for the hydrazine oxidation at 0.37 V with a peak current ( $I_{pa}$ ) of 45.2  $\mu$ A. On the other hand, the cyclic voltammogram of GCE/RGO-Au exhibits hydrazine oxidation peak at about 0.09 V with  $I_{pa}$  of 26.2  $\mu$ A. Fascinatingly, cyclic voltammogram of GCE/RGO/ZnO-Au exhibits a well-defined and greatly enhanced hydrazine oxidation peak at 0.10 V, with  $I_{pa}$  of 107.6 µA. This proves that the RGO/ZnO-Au nanocomposite film on the GCE has a strong catalytic effect on the oxidation of hydrazine. It is notable that the I<sub>pa</sub> of hydrazine oxidation at GCE/RGO/ZnO-Au is 4.1 fold higher than that observed at GCE/RGO-Au and 2.4 fold higher than that observed at GCE/ZnO-Au modified electrodes. The large decrease in the overpotential by about 0.27 V associated with a significant increase in the peak current at the GCE/RGO/ZnO-Au compared to GCE/ZnO-Au reflects a faster electron transfer kinetics for hydrazine oxidation onto the former owing to the better conductivity and higher surface area of RGO. The results demonstrate the good electrocatalytic ability of the prepared RGO/ZnO-Au modified GCE, owing to the high synergy operating between RGO, ZnO and Au. In addition, from the above results it is concluded that Au nanoparticles play a main role in the hydrazine oxidation. The high surface area graphene greatly helps to reduce the overpotential for hydrazine oxidation. The composite RGO/ZnO is provides more active sites and large surface area for distribution of Au nanoparticles.

The cyclic voltammogram at GCE/ZnO-Au shows an

Fig. 5B shows the cyclic voltammograms of GCE/RGO/ZnO-Au in 0.1 M PBS (pH 7.4) with increasing concentration of hydrazine ranging from 0.5 to 3.24 mM (a to g). The oxidation peak current is found to increase linearly with increasing hydrazine concentration which indicates the efficient electrocatalytic ability of the modified electrode without any fouling effect. A plot of the logarithm of peak current against logarithm of hydrazine concentration is linear (Inset in Fig. 5B) with a slope of nearly 1, indicating that the catalytic reaction obeys first order kinetics with respect to hydrazine concentration in solution.<sup>9</sup>

Fig. 6A shows the effect of scan rate on GCE/RGO/ZnO-Au in the presence of 0.5 mM hydrazine in PBS (pH 7.4). A well defined anodic peak appears at 0.1 V whose peak current magnitude increases linearly with increase of scan rate (0.01-0.1 V s<sup>-1</sup>) and moreover the anodic peak potential has a tendency to shift to more positive values (0.02-0.10 V) with increasing scan rate. The shift in peak potential indicates the irreversible nature of the hydrazine oxidation process. The  $I_{pa}$  is found to be proportional to scan rate (Inset in Fig. 6A) indicating that the hydrazine oxidation process at GCE/RGO/ZnO-Au is a surface-controlled electro catalytic reaction.

#### 3.5 Effect of pH

The electrochemical oxidation of hydrazine has been established to be a 4e reaction as shown in Eq. 1 and the reaction is sensitive to pH of the electrolyte.<sup>11</sup>





**Fig. 6** (A) Cyclic voltammograms of 0.5 mM hydrazine in 0.1 M PBS (pH 7.4) at different scan rates (a) 10 (b) 20 (c) 30 (d) 40 (e) 60 (f) 70 and (g) 100 mV s<sup>-1</sup>. Inset: Plot of  $I_{pa}$  versus scan rate (B) Cyclic voltammograms of 0.3 mM hydrazine at GCE/RGO/ZnO-Au modified electrode in 0.1 M PBS of pH (a) 4 (b) 7 (c) 7.4 (d) 8 and (e) pH 9. Scan rate: 50 mV s<sup>-1</sup>.

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The effect of pH has been investigated by cyclic voltammetry in 0.1 M PBS at pH values varying from 4 to 9 and the data are presented in Fig. 6B. The results show that the hydrazine oxidation peak potentials are favorably shifted to less positive potentials with increasing pH. The oxidation peak current shows a remarkable increase with pH varying from 4 to 7.4 and thereafter it decreases. These results can be explained by the fact that the pKa of hydrazine is 7.9 which means that at pH < pKa, hydrazine will be present in its protonated form and is more likely to experience a repulsive effect from the anodically polarized electrode surface, resulting in a higher overpotential and lower peak current values. However, when the pH is close to pk<sub>a</sub>, hydrazine remains in its neutral form resulting in its facile oxidation. At  $pH > pK_a$ , the peak currents decrease with increasing pH which can be ascribed to the deprotonation of hydrazine. The observed effects of pH on the oxidation of hydrazine are similar to those reported for several other modified electrodes.36,47,48 Considering the present results, the optimum pH for obtaining maximum current sensitivity is inferred to be pH 7.4.

#### 3.6 Amperometric determination of hydrazine

The amperometric current-time response was recorded to construct the calibration curve and determine the limit of detection (LOD) of hydrazine. Fig. 7A shows a typical amperometric response of the GCE/RGO/ZnO-Au upon successive additions of 50 nM of hydrazine at a regular interval of 25 s into a continuously stirred 0.1 M PBS (pH = 7.4) at an applied potential of 0.1 V and an electrode rotation speed of 3000 rpm. For clarity, the lower concentration range of the amperogram is shown as an inset in Fig. 7A. The amperometric sensor exhibits a rapid and sensitive response to the change of hydrazine concentration from 0.05 to 5  $\mu$ M with increase in the steady state current upon successive addition of hydrazine. For every addition of hydrazine, the steady state current is reached very quickly i.e. within 3 s, indicating that the nanocomposite electrode has a short response time for hydrazine.

The corresponding calibration curve of the fabricated amperometric hydrazine sensor (Fig. 7B) exhibits a linear response with a correlation coefficient of 0.997 and the linear equation (Eq.2) is

$$I (\mu A) = 1.344 [Hydrazine] (\mu M) + 0.060 (Eq.2)$$

Based on a signal to noise ratio (S/N) of 3, the limit of detection (LOD) was estimated using the formula (Eq. 3)<sup>49</sup>

$$LOD = 3 S_b/m \quad (Eq.3)$$



**Fig. 7** (A) Chronoamperometric response at GCE/RGO/ZnO–Au for successive additions of 0.05  $\mu$ M hydrazine into a continuously stirred N<sub>2</sub> saturated 0.1 M PBS (pH 7.4). E<sub>app</sub>: + 0.1 V. The inset graph is the expanded view of the initial additions. (B) Calibration plot for the hydrazine sensor.

where  $S_b$  is the standard deviation obtained from five measurements of the blank signal i.e. 0.008 µA and m is slope of the calibration plot (1.344 µA/µM). The LOD is found to be 18 nM. The sensitivity of the sensor is determined to be 5.54 µA µM<sup>-1</sup> cm<sup>-2</sup>.

Table 1 shows a comparison of the sensitivity and LOD for the hydrazine sensors based on graphene nanocomposites<sup>31-38</sup> with the values obtained in the present work for RGO/ZnO-Au

nanocomposite modified GCE. From the compiled data, it can be inferred that the GCE/RGO/ZnO-Au shows a better sensor performance with a relatively lower LOD and higher current sensitivity compared to several graphene-based nanocomposite modified electrodes.

#### 3.7 Reproducibility and stability

The reproducibility and stability of the GCE/RGO/ZnO-Au nanocomposite electrode were investigated. A set of 10 replicate

measurements for 40  $\mu$ M of hydrazine yielded a relative standard deviation of 1.5%. The stability of the GCE/RGO/ZnO-Au was examined by monitoring the decrease in the current response after successive cycling of the modified electrode in the potential range of -0.2 to 0.6 V in 0.1 M PBS containing 40  $\mu$ M hydrazine for 100 cycles. At the 100<sup>th</sup> cycle, the peak heights of the cyclic voltammograms retained 93 % of the initial value and no obvious potential shift was observed. These results demonstrate that the proposed sensor has excellent reproducibility and stability.

Table 1 Comparison of analytical parameters for detection of hydrazine over various modified electrodes

Electrode material	Detection limit (µM)	Sensitivity (µA µM <sup>-1</sup> cm <sup>-2</sup> )	Over potential (V)	Ref
Graphene	1.000	-	0.31	31
<sup>a</sup> PB-graphene	7.000	-	0.35	32
Co–Graphene	0.100	0.562	0.3	33
<sup>b</sup> PANI-Graphene	150.4	0.330	0.1	34
Au/graphene	0.100	1.786	0.2	35
CuS/RGO	0.300	0.008	0.3	37
AuPd/Graphene	0.200	-	0.1	38
RGO/ZnO-Au	0.018	5.540	0.1	Present work

<sup>a</sup>PB -Prussian blue, <sup>b</sup>PANI-Polyaniline,

#### 3.8 Interference studies and real sample analysis



The selectivity is an important aspect of sensor performance and can be assessed by studying the sensor response in the presence of likely interferences. **Fig. 8** Chronoamperometric response at GCE/RGO/ZnO–Au at 1  $\mu$ M of (a) hydrazine and each 100  $\mu$ M of (b) Na<sup>+</sup>, (c) K<sup>+</sup>, (d) BrO<sub>3</sub><sup>-</sup>, (e) NO<sub>2</sub><sup>-</sup> and (f) Pb<sup>2+</sup> ions in 0.1 M PBS (pH 7.4) E<sub>app</sub>: + 0.1 V.

In this study, interferences including sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), bromate (BrO<sub>3</sub><sup>-</sup>) and lead ions (Pb<sup>2+</sup>) ions were investigated. Fig. 8 shows the chronoamperometric response obtained for 1  $\mu$ M hydrazine along with successive additions each of 100  $\mu$ M of the interfering species. The experimental conditions are the same as used in sensor calibration. At first the RGO/ZnO-Au modified GCE exhibits well defined response towards the addition of 1  $\mu$ M hydrazine. It is found from the results that Na<sup>+</sup>, K<sup>+</sup>, NO<sub>2</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup> and Pb<sup>2+</sup> have very low interference (< 3%) on hydrazine determination. Hence the GCE/RGO/ZnO-Au nanocomposite has good selectivity towards the oxidation of hydrazine.

In order to evaluate the practical use of the developed sensor for the determination of hydrazine, ground water sample was spiked with different concentrations of hydrazine and analyzed under

optimized conditions using chronoamperometry and the results are shown in Table 2. The average recovery is about 114.7%.

**Table 2** Determination of hydrazine in ground water sample usingGCE/RGO/ZnO-Au.

Added (µM)	Found (µM)	Recovery (%)	Average	
			Recovery (%)	
0.20	0.22	110.0		
0.40	0.47	117.5	114.7	
1.00	1.21	120.0		
1.20	1.34	111.6		

#### 4. Conclusions

In summary, a novel nanocomposite film GCE/RGO/ZnO-Au has been synthesized by a simple electrochemical procedure. The presence of ZnO and Au in the graphene nanocomposite has been confirmed by SEM and EDX techniques. Cyclic voltammetry studies reveal that the GCE/RGO/ZnO-Au electrode shows excellent electrocatalytic effect for the oxidation of hydrazine with a decrease of 0.27 V overpotential and 2.4 fold increase in peak current in comparison to GCE/ZnO-Au. The GCE/RGO/ZnO-Au modified electrode has been demonstrated for the selective and sensitive determination of hydrazine. The developed chronoamperometric sensor exhibits a low detection limit of 18 nM and a high sensitivity of 5.54  $\mu$ A  $\mu$ M<sup>-1</sup> cm<sup>-2</sup>. The fast amperometric response offers good scope for its use in practical applications. The results of interference studies reveal that the fabricated sensor exhibits high selectivity towards the electrocatalysis of hydrazine.

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# An electrochemical synthesis strategy of ZnO microspheres-Au nanocomposite on reduced graphene oxide for the sensitive detection of hydrazine in water samples

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RGO/ZnO-Au nanocomposite towards the toxic hydrazine sensor.