An electrochemical sensing platform of cobalt oxide@gold nanocubes interleaved reduced graphene oxide for the selective determination of hydrazine

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Abstract
Reduced graphene oxide-cobalt oxide nanocube@gold (rGO-Co3O4@Au) nanocomposite was prepared using a one-pot hydrothermal synthesis. The nanocomposite was characterized using the UV-Vis absorption spectroscopy, field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX) mapping, X-ray diffraction (XRD) and Raman analyses. The EDX mapping analysis showed the uniform distribution of Au nanoparticles on the Co3O4 surface that made the surface more roughness. The higher degree of reduction of GO was confirmed from the increased intensity ratio of the D and G bands (ID/IG) of the Raman spectrum during the hydrothermal synthesis. The rGO-Co3O4@Au nanocomposite exhibited good electrocatalytic activity towards the oxidation of hydrazine in phosphate buffer (pH 7.2). The detection of hydrazine was carried out using amperometry technique and the current response was linear in the range of 10–620 μM. The limit of detection was found to be 0.443 μM. The selectivity of the nanocomposite for the sensing of hydrazine was studied with the interferents such as NO3⁻/Cl⁻, SO4²⁻, Ag⁺, Na⁺, K⁺, ethanol, 4-nitrophenol, ascorbic acid and glucose. The sensing of different concentration of hydrazine present in the real water samples was analysed and an appreciable recovery was found.

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1. Introduction

Hydrazine is toxic, colorless and flammable molecule [1]. It is classified as a human mutagenic and carcinogen in group B2 by the Environmental Protection Agency (EPA), United States. It could cause severe injury of lungs, liver, nervous system, spinal cord, temporary blindness and dizziness, pneumonia and kidney damaging [2,3]. In addition, acute exposure to hydrazine could result in death [4]. Hydrazine and its offshoots are well-known environmental toxic pollutant, are widely used in rocket fuel [5], fuel cell systems [6], photographic chemicals, insecticides, herbicides, emulsifiers, blowing agents, textile dyes and corrosion inhibitors in various chemical, pharmaceutical and agricultural industries [7–9]. Since hydrazine is being suspected as carcinogenic and mutagenic, the detection of hydrazine in biological systems has attracted considerable attention in recent decades [10]. There are numerous analytical techniques available for the sensitive determination of hydrazine that includes spectrophotometry [11], amperometry [12], titrimetry [13], chemiluminescence [14], fluorimetry [15], electrochemical and especially, electroanalytical methods [16–18]. The techniques other than electroanalytical methods are complicated, more laborious and also are unable to determine real time concentration of hydrazine [19].
electrochemical techniques offer the opportunity for portable, economical, sensitive and rapid methodologies to determine the amount of hydrazine molecule [20]. Electrochemical oxidation of hydrazine on carbon electrode produces nitrogen and water that do not cause environmental pollution, have already been investigated widely [10,21]. However, electrochemical oxidation of hydrazine is associated with higher oxidation overpotential due to sluggish kinetics at the bare electrode surface [22]. Therefore, several attempts have been made to circumvent this problem using chemically modified electrode’s (CME) surface with new class of materials like metals, metal oxides and their nanocomposites supported by conducting platform [7,23]. The CME have the potential to minimize the overpotential problems and helps in increasing the oxidation current based on their easy, economical, and labor-free operation along with sufficient sensitivity and selectivity [19,24].

Nanotechnology-driven materials have attracted extensive attention in the recent years because of their unique structures and catalytic properties [24,25]. The modification of an electrode by the incorporation of nanomaterials in conjunction with one another to form novel composites like Pt-Cu/silicon [26], TiO2–Pt [27], Pd-modified TiO2 [28] and Au@PtPd [29] is particularly a topic of interest because of determination sensitivity, selectivity and stability of the electrochemical sensing assay [30]. The synergistic effect of these materials plays a vital role in the determination of target analyte [31]. Therefore, considerable attention has also been paid to highly conducting materials for supporting nanosized particles such as, Co3O4/MWCNT [32], Ag/TiO2/graphene [33], Ag/PPy/GCE [34], ZnO/MWCNTs/GCE [35], AuNPs/rGO [36], ZnO–rGO [7], rGO-Co3O4 nanograin [37] and silica/graphene [38]. The conducting support materials are widely used in enhancement of catalyst dispersion, heterogeneous catalysis, electrocatalysis and the stability for sensitive determination of hydrazine [39]. Because of their extraordinary electronic conductivity and availability of accessible surface area for the nanosized catalyst, they could enhance the performance in the electrocatalytic activity [40]. Graphene has been one of the most interesting material because of its electronic and electrocatalytic properties, being investigated widely in electrochemical applications [41,42]. It has attracted much scientific and technological interest due to its physiochemical properties like high theoretical surface area (2630 m2 g−1) for a single layer graphene sheet [43,44], excellent room temperature thermal conductivity (~5000 W m−1 K−1) [45], strong mechanical strength (~40 N/m), high Young’s modulus (~1.0 TPa) [46] and excellent electrical conductivity [47,48].

Here, we undertook an approach to synthesize Au nanoparticle deposited rGO-Co3O4 nanocubes using a hydrothermal process. The Co3O4 nanocubes incorporated into rGO behaved as template for growing Au nanoparticle. The Co3O4 nanostuctures are considered as promising candidate amongst many other metal oxides, since Co3O4 has fascinating optical, magnetic and transport properties. Co3O4 has a well-defined electrocatalytic redox activity with high theoretical capacity (890 mAh g−1), low cost and chemically stable state [49,50]. The rGO-Co3O4@Au nanocomposite modified glassy carbon electrode was used as a sensing platform for the detection of hydrazine in phosphate buffer (pH 7.2). The detection limit of hydrazine was found to be 0.443 μM with the sensitivity of 0.58304 ± 0.00466 μA μM−1. A least possible concentration of Au (0.2133 mM) was used to enhance the sensitivity of rGO-Co3O4 nanocubes towards hydrazine determination. The recovery analysis was also carried out in the water collected from different sources and the good recoveries were found. The nanocomposite displayed good sensitivity even in the presence of 50-fold higher concentration of interferent species.

2. Experimental methods

2.1. Materials

All the chemicals used for this study were of analytical grade and were used as received without further purification. Graphite flakes were purchased from Asbury Inc. (USA). Potassium permanganate (KMnO4, >99%), sulphuric acid (H2SO4, 98%), Phosphoric acid (H3PO4, 98%), hydrochloric acid (HCl, 35%), and ammonia solution (NH3, 25%) were obtained from R & M Chemicals. Cobalt acetate tetrahydrate (Co(CH3COO)2.4H2O) was purchased from Sigma Aldrich. Hydrogen tetrachloroaurate (III) trihydrate (HAuCl4-3H2O) precursor was obtained from ABCR GmbH & CO. KG. Hydrogen peroxide (H2O2, 35%) was purchased from System. Hydrazine hydrate (N2H4·H2O, 50–60%) was received from Sigma Aldrich.

2.2. Synthesis of rGO-Co3O4@Au nanocomposite

GO was prepared by simplified Hummers method route [51]. Graphite flakes (3 g), H2SO4 (360 mL), H3PO4 (40 mL), and KMnO4 (18 g) were mixed under stirring at room temperature. The mixture was stirred for three days to achieve the complete oxidation of the graphite. The colour of the mixture changed from dark green to dark brown. Ice containing H2O2 solution was used to stop the oxidation process and controlling the temperature. The colour of the mixture changed to bright yellow, indicating a high oxidation level of graphite oxide. The formed graphite oxide was washed three times with 1 M of HCl aqueous solution and repeatedly several times with de-ionised water to achieve a pH of 5–6. The washing process was carried out using a simple decantation of supernatant via the centrifugation technique. During the process of washing with de-ionised water, the graphite oxide experienced exfoliation, which resulted in the thickening of the GO solution and finally the formation of the GO gel. To prepare rGO-Co3O4@Au nanocomposites, 1 mmol of Co(CH3COO)2.4H2O solution was first prepared into 10 mL of DI water. The solution of Co(CH3COO)2.4H2O was slowly added into the well-sonicated 8 wt% GO (1 mg/mL) solution under stirring. The solution was allowed to stir for 1 h, so that the cobalt ions could intercalate in between the different layers of graphene sheets. After that, 2 mL of Au (8 mM) solution was added to the reaction mixture drop-by-drop and stirred for 30 min. A 15 mL ammonia (6%) solution added into the above solution and left it for another 15 min. Finally, the mixture (75 mL) was transferred into Teflon-lined of volume capacity 100 mL and it was subjected to hydrothermal treatment for 12 h at 180 °C. The autoclave was cooled down at room temperature and the precipitation was collected and washed with DI water and ethanol several times. The washed product was dried in hot air oven at 60 °C for 24 h and the powder form of rGO-Co3O4@Au nanocomposite was collected for further studies. For the optimization of the Au content, the rGO-Co3O4@Au nanocomposites were prepared with 2, 4, 6, 8 and 10 mM of Au by following the same procedure and the nanocomposites were named as rGO-Co3O4@Au (2 mM), rGO-Co3O4@Au (4 mM), rGO-Co3O4@Au (6 mM), rGO-Co3O4@Au (8 mM) and rGO-Co3O4@Au (10 mM). The controlled materials such as rGO, Co3O4 and rGO-Co3O4 nanocomposite were prepared in the absence of other components.

2.3. Characterization techniques

The high-resolution transmission electron microscopy (HRTEM) and field emission scanning electron microscopy (FESEM) including energy dispersive X-ray (EDX) mapping spectrum of rGO-Co3O4@Au nanocomposite were analysed using JEOL JEM-2100F
and JEOL JSM-7600F fitted with EDX and elemental mapping, respectively. The crystalline nature and phase identification of rGO-Co3O4@Au nanocomposite were analysed using Philips X’pert X-ray diffractometer with copper Kα radiation (λ = 0.15418 nm) at a scan rate of 0.02 degree-sec⁻¹. Raman spectra were acquired using Renishaw inVia 2000 system green laser emitting at 514 nm.

2.4. Electrochemical measurements

A conventional three electrode electrochemical cell was used to carry out all electrochemical studies. The chemically modified electrode was prepared by drop-casting 5 μL of rGO-Co3O4@Au nanocomposite (1 mg/mL) on glassy carbon electrode (GCE) surface (d = 3 mm) and allowing it to dry at room temperature (25 °C). The rGO-Co3O4@Au coated GCE was used as working electrode. Prior to the electrochemical experiments, the GCE was cleaned electrochemically in 0.5 M H2SO4 and mechanically by rubbing on 0.05 micron alumina slurry. Nitrogen purged 0.1 M phosphate buffer (pH 7.2) was used as the electrolyte throughout the electrochemical studies. Platinum wire and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Hydrazine hydrate (N2H4·H2O) was used as the analyte for detection at the rGO-Co3O4@Au modified GCE surface. All the electrochemical studies were carried out by using PAR-VersaSTAT-3 Electrochemical Workstation.

3. Results and discussion

3.1. Formation, morphology and elemental mapping analysis of rGO-Co3O4@Au nanocomposite

In the synthesis of the rGO-Co3O4@Au nanocomposite, the Co2+ ions were strongly adsorbed on the surface of highly negatively charged GO because of the electrostatic attraction with oxygen functional groups of GO [52]. The Co2+ ions formed coordination with ammonia present in the reaction mixture and thus, made Co(NH3)62+ ions. During the hydrothermal treatment, both the oxidation of Co(NH3)62+ ions as well as the reduction of GO into rGO occurred with the aid of ammonia [50,53]. The nucleation of Co3O4 nanostucture formation was controlled in the presence of ammonia and thereby, it directed the growth of Co3O4 nanocubes under the proposed experimental conditions. In addition, these Co3O4 nanocubes acted as nanospacers in preventing the restacking of rGO sheets. The Co3O4 nanocubes could strongly attach onto the rGO sheets because of the unexposed Co3O4@Au nanocubes. The observation of the rough surface confirmed the agglomeration of Co3O4 nanocubes and a high rate of 0.02 degree-sec⁻¹. Raman spectra were acquired using Philips X’pert X-ray diffractometer with copper Kα radiation (λ = 0.15418 nm) at a scan rate of 0.02 degree-sec⁻¹. Raman spectra were acquired using Renishaw inVia 2000 system green laser emitting at 514 nm.

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The morphology of the rGO-Co3O4@Au nanocomposite was studied using the FESEM and HRTEM analyses. Fig. 1A and B displays the FESEM images of the rGO sheets and Co3O4 nanocubes. The cubical morphology of the Co3O4 nanostuctures was retained after the formation of rGO-Co3O4 nanocomposite (Fig. 1C). The rGO sheet prevented the agglomeration of Co3O4 nanocubes and a high population of Co3O4 nanocubes was deposited on the rGO sheets. The observation of the rough surface confirmed the formation of Au nanoparticles on the surface of the Co3O4 nanocubes after the formation of the rGO-Co3O4@Au nanocomposite (Fig. 1D). From the TEM analysis, a homogeneous dispersion of Co3O4@Au nanocubes on the rGO sheets was clearly observed (Fig. 2). The formation of Au nanoparticles was confirmed from the surface plasmon resonance (SPR) absorption of Au nanoparticles present in the nanocomposite. Fig. 2E shows the absorption band at 554 nm which corresponds to the SPR feature of the Au nanoparticles. The mean particle size of the Co3O4@Au nanocubes was calculated to be 35 nm from the FESEM analysis by considering 170 particles (Fig. 2F). The d-spacing values were calculated from the lattice fringes observed on the surface of the Co3O4@Au nanocubes. On the other hand, the small lattice fringes come under observation belongs to Au nanoparticles in Fig. 2D with the lattice distance of 0.25 nm corresponding to the Au (1 1 1) plane. This also confirms the formation of Au nanoparticle on the surface of Co3O4 nanocubes.

The distribution of elements present in the rGO-Co3O4@Au nanocomposite was studied using the EDX elemental mapping analysis (Fig. 3). The EDX spectrum of the rGO-Co3O4@Au nanocomposite showed the signatures of elemental O, Co, C and Au and thereby confirmed the presence of the same in the nanocomposite (Fig. S1). The elemental peaks of Au appeared with very low intensity suggesting a very low concentration of Au present in the nanocomposite. Moreover, the wt.% used in EDX table is in good agreement with the wt.% used for synthesis of rGO-Co3O4@Au. Fig. 3A shows the FESEM image of the nanocomposite and the elements O (black colour), Co (green colour), C (blue colour) and Au (red colour) were scanned as shown in the EDX mapping profile of rGO-Co3O4@Au nanocomposite (Fig. 3B). The independent elemental O, Co, C and Au distributions are shown in Fig. 3C–F and it displayed a clear distribution of Au nanoparticles on Co3O4 nanocubes. The large area coverage of black (Fig. 3C), green (Fig. 3D) and blue (Fig. 3E) colours indicated the dense package of Co3O4 nanocubes in between the rGO sheets and on the surface of the rGO sheets. Fig. 3F shows the elemental distribution of Au on the surface of Co3O4 nanocubes and some area of the image seems to be empty because of the unexposed Co3O4@Au nanocubes.

3.2. XRD and Raman analyses

The crystalline nature of the present nanocomposite was studied using XRD analysis. Fig. 4 depicts the XRD pattern of rGO, Co3O4, rGO-Co3O4 and rGO-Co3O4@Au (8 mM) nanocomposite. The XRD pattern of GO has a sharp and high intensity peak at 20 value of 10.8 corresponds to lattice plane (0 0 1) before reduction (Fig. S3) and after reduction, it disappeared and two more broad peaks appeared at the 20 values of 26.0 and 43.1 corresponding to the lattice (0 0 2) and (1 0 0) planes, respectively, showed the disorderedly stacked rGO [55]. All the other peaks observed at 31.3°, 36.9°, 44.8°, 55.7°, 59.3°, 65.2° and 77.3° correspond to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (4 4 0), (5 1 1) and (5 3 3) crystal planes of face centred cubic Co3O4, respectively (JCPDS Card No. 42-1467) [56]. There is no peak observed for rGO due to the very thin and well exfoliated sheets of rGO and, Co3O4 behaves like nanospacers between the different layers of rGO sheets as confirmed by FESEM analysis. It confirmed that Co3O4 nanocubes intercalate quiet well and prevent the rGO sheets from restacking after reduction and there is no bulk graphite present observed in XRD of rGO-Co3O4 [56]. The XRD pattern recorded for rGO-Co3O4@Au (8 mM) nanocomposite in Fig. 4d showed that out of four Au peaks observed at the 38.2°, 44.4°, 64.7° and 77.7° corresponding to the Au lattice planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) have the 20 values as similar as Co3O4. These Au peaks merged with the Co3O4 peaks and it could be seen from the XRD pattern of rGO-Co3O4@Au nanocomposites that with the increase in Au content from 2 mM to 10 mM the Au peaks became more intense in the rGO-Co3O4@Au nanocomposites (Fig. S3I) (JCPDS 04-0784) [57]. So, the existence of these peaks in XRD pattern is further evidence of Au presence/deposition on Co3O4 nanocubes in favor of FESEM and HRTEM images in Figs. 1 and 2 respectively.

Raman spectroscopy is an important conventional tool which is used to acquire an idea about the structural changes of carbonaceous materials. Fig. 5 shows the Raman spectrum of rGO-
Co$_3$O$_4$@Au (8 mM) nanocomposite. It is seen that GO exhibited D (1350 cm$^{-1}$) mode related to conversion of sp$^2$ hybridized carbon to sp$^3$-hybridized carbon and G (1599 cm$^{-1}$) mode related to vibration of sp$^2$-hybridized carbon (Fig. 5 inset) [58,59]. While the corresponding rGO graph has D and G bands in Fig. S4 have values of 1352 and 1605 cm$^{-1}$, respectively with D band to G band ratio (I_D/I_G) 1.07 for rGO which is higher the ratio obtained from GO (I_D/I_G, 0.878). These observations further confirmed the formation of new graphitic domains and successful reduction of GO into rGO after the hydrothermal process [60]. The Co$_3$O$_4$ nanocubes showed characteristic peaks at 192, 476, 518, 614 and 686 cm$^{-1}$ corresponding to F$_{2g}$, E$_g$, F$_{2g}$ and A$_{1g}$ modes of the crystalline Co$_3$O$_4$ [61] with D and G

Scheme 1. Synthesis of the rGO-Co$_3$O$_4$@Au nanocomposite.

Fig. 1. FESEM images of rGO sheet (A), Co$_3$O$_4$ nanocubes (B), rGO-Co$_3$O$_4$ nanocomposite (C) and rGO-Co$_3$O$_4$@Au (8 mM) (D).
bands of rGO confirming the effective formation of nanocomposite (Fig. 5). The intensity of D band was higher than that of G band present in the nanocomposite which confirmed the reduction of GO during the synthesis of the rGO-Co3O4@Au nanocomposite.

3.3. Electrocatalytic oxidation of hydrazine

The applicability of the rGO-Co3O4@Au nanocomposite was investigated towards the electrocatalytic oxidation of hydrazine using cyclic voltammetry in 0.1 M phosphate buffer (pH 7.2). Fig. 6 depicts the cyclic voltammograms corresponding to the oxidation of 0.5 mM of hydrazine at different modified electrodes. The rGO-Co3O4@Au (8 mM) nanocomposite showed the oxidation of hydrazine at +0.079 V with a catalytic current of 29.6 μA (Fig. 6e). No enhanced current response was observed with the rGO-Co3O4@Au nanocomposite in the absence of hydrazine (Fig. 6f). The bare GCE and rGO did not produce faradaic current response due to the oxidation of hydrazine (Fig. 6a & c). However, the cyclic voltammogram of Co3O4 nanocubes seems to exhibit the anodic peak of hydrazine oxidation at higher positive potential (Fig. 6b). The hydrazine oxidation was highly facilitated at the rGO-Co3O4 nanocubes modified electrode surface and the electrode showed well resolved voltammetric behavior with enormous negative shift in potential. It showed the catalytic current of 21.57 μA at the peak potential of +0.089 V (Fig. 6d). Graphene is highly conducting platform with higher electron transfer kinetics and also it prevents the Co3O4 nanocubes from agglomeration (Fig. 1c), so higher electrocatalytic activity came under observation because of synergistic effect of rGO-Co3O4 nanocomposite [62]. Furthermore, the deposition of very low concentration of Au nanoparticles on the surface of the Co3O4 nanocubes improved the electrocatalytic activity of the rGO-Co3O4 nanocomposite towards the oxidation of hydrazine. The increase of catalytic current and the decrease of overpotential were attributed to the synergistic effect of the rGO-Co3O4 nanocomposite and the highly conductive Au nanoparticles. The roughness followed by the increase of surface area of the rGO-Co3O4@Au nanocomposite also played a crucial role for the enhanced electron transfer process towards the catalytic performance. The cyclic voltammograms were recorded with rGO-Co3O4@Au nanocomposite consisting of different concentration of Au (2, 4, 6, 8 and 10 mM) for the electrocatalytic oxidation of hydrazine shown in Fig. S5. It was found that the rGO-Co3O4@Au (8 mM) nanocomposite showed the best catalytic response towards the oxidation of hydrazine.

The influence of concentration was studied at rGO-Co3O4@Au (8 mM) modified GCE surface by varying the hydrazine concentration with a scan rate of 50 mV s\(^{-1}\) (Fig. 7A). The increase in concentration ranges from 0.5 mM to 5 mM of hydrazine increased the anodic peak current for the oxidation of hydrazine due to the direct electro-oxidation of hydrazine at the rGO-Co3O4@Au (8 mM)
nanocomposite surface. The plot of peak current versus concentration of hydrazine showed a linear response (Fig. 7B). There was a shift noticed in the peak current toward more positive potential values for hydrazine concentration. The plot showed a linear range with a slope value equal to 1, the plot of log (Ipa) versus log [hydrazine] indicated that electrooxidation of hydrazine followed the first order kinetics with respect to hydrazine concentration at the rGO-Co3O4@Au (8 mM) nanocomposite modified GC electrode (Fig. 7B inset). Cyclic voltammograms were recorded for rGO-Co3O4@Au (8 mM) nanocomposite modified GCE for 0.5 mM hydrazine at different scan rates ranges from 10 to 200 mV s⁻¹ (Fig. S6A). The increase in current was observed with increasing scan rate and the calibration plot of peak current versus square root of scan rate showed a linear relation in Fig. S6B. This result indicated that the oxidation of hydrazine was a diffusion controlled process at the rGO-Co3O4@Au (8 mM) nanocomposite modified GCE [63]. Additionally, the CV curves of rGO-Co 3O4@Au (8 mM) modified GCE showed the peak potential shift towards positive potential with increasing the scan rate. A linear relation between the peak potential (Epa) and log (ν) indicated the irreversible oxidation of hydrazine at the nanocomposite modified electrode.

The diffusion coefficient (D) of hydrazine during the electrocatalysis was calculated using the Cottrell equation (eqn. (1)).

\[ I = \frac{nFD}{A} \pi^{-1/2} t^{-1/2} \]

Where \( n \) is the number of electron involved per hydrazine molecule.
during oxidation, $F$ is the Faraday constant, $A$ is the geometric area of the electrode, $C_0$ is the concentration of hydrazine, and $t$ is time. The amperometric $i$-$t$ curves were collected at the nanocomposite modified electrode for the different concentrations of hydrazine (Fig. 8A) and the plot of peak current versus $t^{-1/2}$ showed a linear relation (Fig. 8B). The slopes of the obtained linear lines were plotted against the hydrazine concentrations (Fig. 8B inset) and from this plot $D$ was determined to be $0.782 \times 10^{-6}$ cm$^2$ s$^{-1}$.

3.4. Amperometric detection of hydrazine

Amperometry is a convenient technique for the detection of low concentration of analytes and to perform the interference study. Since the rGO-Co$_3$O$_4$@Au (8 mM) nanocomposite modified electrode showed higher current response in the cyclic voltammetry, it was used as the amperometric sensor for the detection of hydrazine at low concentration levels. Fig. 9A depicted the amperometric response of the rGO-Co$_3$O$_4$@Au (8 mM) nanocomposite for the successive additions of hydrazine at an applied potential of $+0.079$ V. The current response was measured from the successive injection of 10 $\mu$M and 20 $\mu$M concentration of hydrazine at the time interval of 60 s in a continuously stirred 0.1 M phosphate buffer (pH 7.2). The rGO-Co$_3$O$_4$@Au (8 mM) modified GCE exhibited a significant and quick amperometric response towards each addition of hydrazine. The current reached its steady-state within 3 s indicating the fast electrooxidation of hydrazine at the rGO-Co$_3$O$_4$@Au (8 mM) modified GCE surface. The response current increased linearly for each addition of hydrazine over the range between 10 and 620 $\mu$M. The corresponding regression plot of current response versus concentration of hydrazine with a linear relation is shown in Fig. 9B. The oxidation current response deviates from linearity above 620 $\mu$M. This may be due to the saturation or near saturation of electroactive sites present on the nanocomposite modified electrode. The limit of detection was calculated to be 0.443 $\mu$M using the expression $\text{LoD} = 3s/slope$, where, $s$ is the standard deviation [64]. The sensitivity of the sensor was found to be 0.58304 ± 0.00466 $\mu$A $\mu$M$^{-1}$ from the slope of the linear regression. Repeated measurements were carried out to check the stability of the sensor and the current responses with
negligible decrement were observed at different days. The electrocatalytic activity of the rGO-Co3O4 nanocomposite towards the detection of hydrazine was improved by the deposition of minimum amount of Au on the Co3O4 nanocubes. The LoD can further be improved by optimizing rGO content in the nanocomposite because it mainly alters the diffusion layer thickness of the nanocomposite modified electrode.

The selectivity of the rGO-Co3O4@Au (8 mM) nanocomposite as an important aspect of sensor performance was assessed by studying the sensor response in the presence of interferents in the same phosphate buffer and the change in current response was monitored. Fig. 10 shows the amperometric current responses of hydrazine (a) and various interferents such as NO3 (b), SO42- (c), Cl- (d), Ag+ (e), Na+ (f), K+ (g), ethanol (h), 4-nitrophenol (i), ascorbic acid (j) and glucose for studying selectivity of rGO-Co3O4@Au (8 mM) nanocomposite. For the first two injections of hydrazine the nanocomposite behaved efficiently and showed a current response for the hydrazine oxidation. There was no response shown by rGO-Co3O4@Au (8 mM) for the rest of interferers even at their 50-fold higher concentration. Again, for the reconfirmation of selective behavior of rGO-Co3O4@Au (8 mM) nanocomposite, hydrazine was injected into homogeneously stirred 0.1 M phosphate buffer and it showed a rapid current response suggesting that the present rGO-Co3O4@Au (8 mM) nanocomposite was more selective towards the detection of hydrazine.
hydrazine oxidation. Moreover, the same magnitude of the current response for the addition of hydrazine was observed and it sustained the steady state current after the 3 s of response time. Two more interferent molecules such as ascorbic acid and glucose were injected after the injection of hydrazine and there was no current observed for these molecules. This study revealed good selectivity of the rGO-Co3O4@Au nanocomposite towards hydrazine sensing. Table 1 shows the comparison of analytical performance of the present nanocomposite with other reported nanomaterials. The present work stands for the novel synthesis of the rGO-Co3O4@Au nanocomposite using one-pot hydrothermal synthesis and its fast response towards the detection of hydrazine. The proposed modified electrode displayed a satisfactory performance in terms of detection limit and good selectivity.

3.5. Application to real sample analysis

To demonstrate the applicability of the present sensor in real sample analysis, the water samples were collected from different places and filtered. The hydrazine stock solution was prepared using real water samples and different concentrations of the sample were spiked into the phosphate buffer. The current response was monitored for the different amounts of hydrazine using amperometry. The measurement results showed the good recovery of hydrazine for three successive experiments and the experimental results are summarized in Table 2.

4. Conclusions

The rGO-Co3O4@Au nanocomposite was successfully...
synthesised and characterized using various techniques such as TEM, EDX mapping, XRD and Raman analyses. The temperature and the concentration of ammonia were the crucial factors in controlling the morphology of the Co3O4 nanocubes. The cubical morphology of Co3O4 was confirmed using FESEM and TEM analyses and the uniform distribution of Au nanoparticles on the Co3O4 surface was demonstrated using EDX elemental mapping analysis. The rGO-Co3O4@Au nanocomposite modified glassy carbon electrode was demonstrated as excellent electrochemical sensor for hydrazine using amperometry. It showed the linear range of 10–620 μM and the detection limit of 0.443 μM towards hydrazine detection. The nanocomposite showed the selectivity in the detection of hydrazine in the presence of interferents such as NO3-, SO4²-, Cl-, Ag⁺, Na⁺, K⁺, ethanol, 4-nitrophenol, ascorbic acid and glucose. The practical use of the sensor was also explored by spiking known concentrations of hydrazine in different water samples and good recoveries were found.

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**Appendix A. Supplementary data**

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2017.10.157.

**References**


