



# Palladium nanoparticles decorated gaur gum based hybrid material for electrocatalytic hydrazine determination



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## ABSTRACT

A new palladium nanoparticles immobilized organic-inorganic hybrid nanocomposite material is prepared to combine the mechanical strength offered by the inorganic matrix with flexible binding sites provided by the organic polymer. The organic polymer is based on a natural polysaccharide, guar gum grafted with poly(acrylamide) and the inorganic matrix is based on silica. The nanocomposite is characterized by physico-chemical methods, surface characterization techniques and electrochemical methods. This material is coated on a glassy carbon electrode and utilized for electrocatalytic oxidation of hydrazine (HZ). Electrocatalytically HZ is oxidized at lowest overpotential ( $-0.15$  V vs. SCE) than ever reported. Based on the linear increase in catalytic current, a sensitive HZ amperometric sensor is constructed. The sensor displays two linear calibration ranges from  $50.0 \mu\text{M}$  to  $0.6$  mM and from  $0.6$  mM to  $180$  mM for HZ with high stability and reproducibility. Limit of detection is found to be  $4.1 \mu\text{M}$  with high sensitivity and selectivity. These properties make the nanocomposite film a promising electrochemical sensing platform for the determination of HZ. Chronoamperometry and cyclic voltammetry studies are used to evaluate kinetic parameters.

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## 1. Introduction

Designing electrocatalytic materials of optimum efficiency tuned for fabricating an electrochemical sensor has attracted great interest in recent years. For the last two decades, the field of polymer-based and inorganic oxides-based nanocomposites has expanded greatly and led to the development of many chemical and electrochemical sensors [1–4]. Based on electrocatalytic properties of nanoparticles (NPs) of metals like Au, Ag, Pt and Pd their incorporation in a number of organic and inorganic matrices have been used for constructing several electrochemical sensors [5–7]. A good number of techniques are introduced to prepare Pd NPs involving chemical [8] and electrochemical [9] reduction where the NPs are formed by reduction of  $\text{Pd}^{2+}$  ions in the presence of some stabilizers. Very recently, biopolymers as stabilizers of metal NPs are gaining interest because of their several attractive features such as renewability, adjustable hydrophobic/hydrophilic characters, and metal ion chelating ability [10]. Graft copolymerization of natural guar gum (GG), a natural polysaccharide composed galactose and mannose units [11] is gaining importance for developing advanced materials owing to its potentiality to improve the above desirable properties and biodegradability [12]. Despite the

advantageous properties of metal chelating groups ( $-\text{CONH}_2/\text{OH}$ ) in GG grafted with poly(acrylamide) (GG-g-PAM), being soluble in aqueous solutions cannot be used as an electrode modifier or electrochemical sensing platform. Thus to develop an efficient electrochemical sensing platform with good response to analytes in aqueous solutions, we synthesized an organic-inorganic composite from GG-g-PAM and silica precursors, where both the advantages of functionality (in GG-g-PAM) and high surface area and insoluble nature of silica can be exploited [13]. Incorporation of silica network into GG-g-PAM resulted in a new composite (GG-g-PAM-silica) with improved thermal and porosity properties. It is expected that incorporation of Pd NPs into GG-g-PAM-silica (Pd-GG-g-PAM-silica) would show extra advantageous properties like catalysis which can be explored in electrocatalytic applications and in subsequent construction of an amperometric sensor for hydrazine (HZ).

HZ and its derivatives have been recognized as potential carcinogens [14]. When absorbed through skin they produce caustic-like burn, affect blood production and also cause damages to liver and kidney [14]. Therefore development of a simple and sensitive analytical method for the determination of HZ is necessary for human health inspections and safety assessments. Electrochemical techniques offer rapid, sensitive and economical methods for the determination of HZ [14,15]. However, electrochemical oxidation of HZ at a bare electrode is kinetically slow and associated with high overpotential. Therefore, searching for new approaches as well as new materials to modify the electrode surface towards enhancing the rate of electron transfer and reducing the overpotential of the

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HZ oxidation is necessary [9,15–24]. Several redox mediators such as metal nanoparticles [9,14,16,20–24], metal oxides [17], metal complexes [15], hexacyanoferrate salts [18] and organic mediators [19] have been used to fabricate modified electrodes for electrochemical oxidation of HZ.

Pd NPs wrapped with GG-g-PAM-silica material is environment friendly and expected to have enhanced electrocatalytic properties and often improved analytical applications because of favorable interactions between the amide functional groups of GG-g-PAM-silica and Pd NPs. Similar GG-g-PAM-silica nanocomposite materials [13,25] have been tested for their use in the removal of heavy metal ions, however, so far no efforts have been made to develop this polysaccharide copolymer to incorporate metal NPs. It may also be emphasized that it is the first time, to the best of our knowledge, electrocatalytic applications of Pd NPs loaded GG-g-PAM-silica composite is explored.

## 2. Experimental

### 2.1. Chemicals and reagents

Tetraethoxyorthosilicate (TEOS, 98%) and palladium(II) chloride (>99.9%) were obtained from Sigma-Aldrich (India). Acrylamide (Merck) was recrystallized twice from methanol and dried in vacuum.  $\text{NH}_4\text{OH}$  (30%  $\text{NH}_3$ ; Merck) and commercial sample of guar gum HICHEM (Haryana, India) were used as such. Ceric ammonium nitrate (CAN) was obtained from Loba Chemie, Mumbai, India. Acetone and hydrazine hydrate (99%) was supplied by S.D Fine Chemicals, Mumbai, India. Sodium borohydride (SRL, Mumbai, India) and other chemicals were used as received. Triple distilled water was used throughout all the experiments. Phosphate buffer solution (PBS) of pH 7.0 (0.1 M) was prepared by mixing aqueous  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  solutions.

### 2.2. Apparatus and procedures

FT-IR spectra were recorded on Varian 3100 FTIR (Excalibur series) spectrophotometer using KBr disks. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were performed using SUPRA-40 Zeiss, operating at 5 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were obtained from TECNAI 20G<sup>2</sup> FEI microscope, operating at 200 kV. For TEM analysis, the powder sample was dispersed in distilled water by ultrasonication, and a drop of the suspension was placed onto a carbon-coated copper grid. X-ray diffraction (XRD) patterns of the samples were obtained on a Philips PW-1710 equipped with a graphite monochromator, employing  $\text{Cu-K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) and scanned over a range from  $2\theta = 10^\circ$  to  $80^\circ$ . UV-vis spectra were recorded with a 2802 PC UV-vis absorption spectrophotometer (Unico, USA). Thermogravimetric analysis (TGA) was done on a Mettler Toledo TGA/DSC 1 at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Nitrogen adsorption-desorption isotherm was obtained using an ASAP 2020 surface area and porosity analyzer (Micromeritics). All electrochemical experiments were performed with CHI-660 C (CH instruments) using three electrode system. Glassy carbon electrode (GC) as working electrode (area =  $0.07 \text{ cm}^2$ ), potassium chloride saturated calomel electrode (SCE) as reference electrode and Pt wire as counter electrode were employed. To remove dissolved  $\text{O}_2$ , solutions were purged with  $\text{N}_2$  for 20–30 min prior to electrochemical studies.

Well-dispersed GG-g-PAM-silica and Pd-GG-g-PAM-silica colloid (0.5 wt%) were prepared by ultra-sonication of the respective material for 30 min. Then,  $10 \mu\text{L}$  of this aqueous colloidal solution was coated on GC electrode and air dried (represented as GC/GG-g-PAM-silica and GC/Pd-GG-g-PAM-silica, respectively) to obtain a

thin film of the electrochemical sensing platform. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range 100 KHz to 0.1 Hz (for  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  redox probe) and in 100 KHz to 1 Hz (for HZ oxidation) using 5 mV amplitude.

### 2.3. Synthesis of GG-g-PAM

The graft copolymer GG-g-PAM was synthesized by  $\text{Ce}^{4+}$  ion induced solution polymerization method. The detailed synthetic procedure was given elsewhere [26]. Briefly, 1.0 wt% of GG and 20.0 wt% of acrylamide was dissolved in distilled water with constant stirring. Then  $\text{N}_2$  was passed through the solution for 30 min. The required quantity of CAN (1.0 wt% dissolved in water) was injected into the solution and then  $\text{N}_2$  flushing was continued for further 30 min at room temperature. The reaction was allowed to continue for 3 h after which it was terminated by addition of hydroquinone. Afterwards, the reaction mixture was treated with an excess of acetone to form precipitate and the precipitate was dried in vacuum oven and pulverized. The percentage conversion of synthesized GG-g-PAM was found to be 74%. Percentage conversion was calculated as Eq. (1)

$$\left[ \frac{\text{weight of pure graft copolymer} - \text{weight of polysaccharides}}{\text{weight of acrylamide monomer}} \right] \times 100. \quad (1)$$

### 2.4. Synthesis of the Pd-GG-g-PAM-silica nanocomposite

GG-g-PAM (1.25 wt%), TEOS (5 mL of TEOS in 2.5 mL ethanol) and ammonia (1.7 mL of 12 N) were prepared separately. The above three solutions were mixed in a reaction vessel and kept under mild stirring for 12 h at  $40^\circ\text{C}$ . Then the mixture was slowly evaporated at  $60^\circ\text{C}$  for about 3 h and then  $80^\circ\text{C}$  for about 1 h until a dry material was obtained (GG-g-PAM-silica) [25]. Thus obtained GG-g-PAM-silica material is further dried at  $100^\circ\text{C}$  for 4 h and pulverized. For the preparation of Pd-GG-g-PAM-silica nanocomposite, in a typical experiment 3 wt% colloidal solution of GG-g-PAM-silica in water was equilibrated with 1 wt%  $\text{PdCl}_2$  (8 mL) for 12 h followed by addition of an excess of  $\text{NaBH}_4$  with vigorous stirring at  $0^\circ\text{C}$ . The stirring was continued for further 2 h then filtered, washed with water and dried in an oven at  $80^\circ\text{C}$  for 4 h. Schematic representation of Pd-GG-g-PAM-silica is shown in supplementary information Scheme S1.

## 3. Results and discussions

### 3.1. Characterization of the composite materials

FT-IR spectrum of GG-g-PAM (Fig. 1a) shows a broad band at  $1660 \text{ cm}^{-1}$  for combined amide I ( $>\text{C}=\text{O}$  stretching) and amide II (NH bending) bands, a strong broad band at  $3426 \text{ cm}^{-1}$  for -OH stretching, a band at  $2930 \text{ cm}^{-1}$  for C-H stretching and at  $1460 \text{ cm}^{-1}$  for C-N stretching [26]. In the IR spectrum of GG-g-PAM-silica (Fig. 1b) a broad peak at  $1112 \text{ cm}^{-1}$  is assigned to the combination of LO (longitudinal-optic) and TO (transverse-optic) components of Si-O-Si asymmetric stretching modes [25], while the band at  $795 \text{ cm}^{-1}$  is associated to symmetric Si-O-Si stretching vibrations [13,25]. The band at  $470 \text{ cm}^{-1}$  is attributed to oxygen ring breathing mode of four membered rings of cyclic tetra siloxanes [25,27],  $970 \text{ cm}^{-1}$  peak is assigned to Si-O stretching and the broad band at  $3447 \text{ cm}^{-1}$  can be assigned for -OH stretching [13]. A significant change in the spectrum of Pd-GG-g-PAM-silica is observed in the region of  $1200 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  (Fig. 1c). Intensities of symmetric Si-O-Si stretching frequency at  $795 \text{ cm}^{-1}$  and Si-O stretching

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