



# Palladium nanoparticles incorporated polymer-silica nanocomposite based electrochemical sensing platform for nitrobenzene detection



Pankaj Kumar Rastogi, Vellaichamy Ganesan\*, S. Krishnamoorthi

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221 005, UP, India

## ARTICLE INFO

### Article history:

Received 2 June 2014

Received in revised form 15 September 2014

Accepted 25 September 2014

Available online 28 September 2014

### Keywords:

Palladium nanoparticles

Organic-inorganic hybrids

Nitrobenzene reduction

Electrocatalysis

Guar gum

## ABSTRACT

A novel electrochemical sensing platform (ESP) for nitrobenzene (NB) has been developed using palladium nanoparticles decorated polymer-silica nanocomposite (represented as Pd-GG-g-PAM-silica). The polymeric part of the nanocomposite is based on a biodegradable copolymer, guar gum grafted polyacrylamide (GG-g-PAM). The nanocomposite is characterized by spectroscopic, microscopic and electrochemical methods. Pd-GG-g-PAM-silica efficiently catalyzes the electro-reduction of NB. The mechanism and kinetic parameters of the electrocatalytic reduction of NB at Pd-GG-g-PAM-silica modified glassy carbon electrodes (GCE) are evaluated in 0.1 M phosphate buffer solution (pH 7.0) using linear sweep voltammetry, differential pulse voltammetry and chronoamperometry. The observed electrochemical responses at Pd-GG-g-PAM-silica modified GCE exhibit excellent analytical performance for NB detection with high stability, reproducibility, and acceptable selectivity. This novel ESP exhibit a detection limit of 0.06  $\mu\text{M}$  with two linear calibration ranges from 1.0 to 1900  $\mu\text{M}$  and from 1900 to 3900  $\mu\text{M}$  for NB. The diffusion coefficient and catalytic rate constant for NB reduction at the Pd-GG-g-PAM-silica modified GCE is calculated to be  $3.88 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $1.82 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  respectively. In addition, the material is successfully used for the determination of NB in real water samples and the recoveries of the spiked NB are quite satisfactory.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Organic-inorganic composites (OICs) are constantly gaining significant attention in various fields [1–4]. These OICs combine both the properties of each of their components in a synergic way and frequently offer an outstanding prospect to prepare tailor-made new materials with desirable properties [1–4]. Among the different OICs reported in literatures, OICs made from organic polymers with inorganic silica precursors are escalating and may open new routes to incorporate enzymes [5,6], metal nanoparticles (NPs) [7,8] and electrochemical redox mediators [9,10]. Subsequently, they can be utilized in sensible applications in the respective fields. For example, Kale's group has used glucose oxidase incorporated polyvinyl alcohol-silica hybrid film as an electrochemical sensing platform (ESP) for glucose determination [5] and Ag NPs incorporated polyvinyl alcohol-silica hybrid film for antibacterial activity [7]. Palladium nanoparticles stabilized polyethylene glycol-silica composite has been used as catalyst for the aerobic alcohol oxidation in supercritical carbon dioxide

[8]. Therefore, OICs containing noble metal NPs remain to be explored for their utilities in the field of electrochemical sensors.

Nitrobenzene (NB) is a synthetic aromatic compound and generally does not occur naturally. NB is widely used in organic industries, petroleum refineries, insecticides, herbicides, soaps and shoe polishes. It is released into the environment mostly from industrial effluents and mainly exists in water and sediments. It is declared as a priority pollutant [11] and vastly analyzed because of its toxicity, carcinogenicity and many other adverse effects on human beings and animals. According to clean water act of USA, the maximum permissible limit of NB in drinking water is 17  $\mu\text{g/L}$  [12]. Therefore development of effective analytical method for trace level NB detection is very important. So far several analytical techniques are reported for the determination of NB using UV-vis spectrophotometry [13,14], chromatography [15], fluorescence quenching methods [16] and electrochemical methods [17–27]. However, careful comparison of the reported techniques reveals that all the methods except electrochemical methods require sophisticated instrumentation and/or time-consuming complicated sample pretreatments. Electrochemical methods exhibit advantageous properties such as superior sensitivity, fast analysis, easy to handle, cost effective, high selectivity and exceptional long term calibration stability [28]. Various types of electrode modifiers

\* Corresponding author. Tel.: + 91-542-6701609; Fax: + 91-542-2368127.  
E-mail addresses: [velganes@yaho.com](mailto:velganes@yaho.com), [velgan@bhu.ac.in](mailto:velgan@bhu.ac.in) (V. Ganesan).

like Pt NPs/macroporous carbon hybrid nanocomposites [26], bismuth-film modified carbon paste [18], mesoporous silica [19], carboxylated multi-walled carbon nanotubes [20], cyclodextrin-silicate sol-gel composite embedded gold NPs [21] have been used for NB detection. However, every approach has its own limitations such as high negative reduction overpotential, working medium (acidic or basic), no selectivity, low sensitivity, narrow linear calibration range and high detection limit. Therefore, to realize the NB reduction and its determination at low reduction overpotential in neutral pH with good selectivity, high sensitivity, wide linear calibration range and low detection limit, it is essential to explore new electrode modifiers and new electrochemical methods. To achieve this, in this study for the first time we combined the advantageous properties of naturally occurring polymer, guar gum (GG) with silica and Pd NPs and studied the electrocatalytic reduction and subsequent detection of NB at neutral pH.

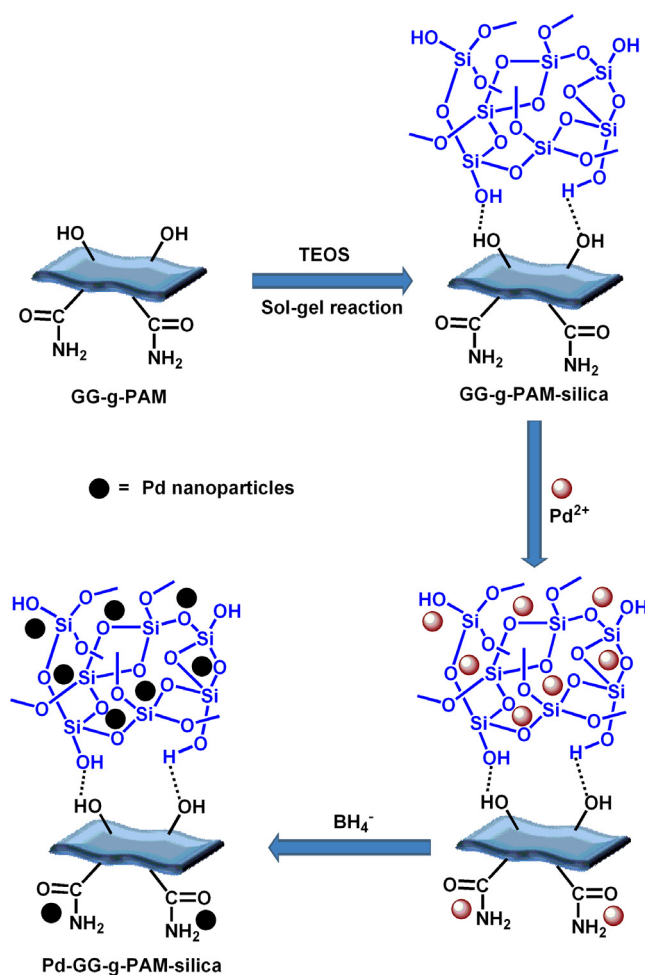
## 2. Experimental

### 2.1. Reagents and chemicals

Analytical reagent grade nitrobenzene (NB) was purchased from S.D. Fine Chemicals, India. Unless otherwise stated, all other chemicals were of analytical grade and used directly as received. Triple distilled water was used throughout all the experiments. A 0.05 M stock solution of NB was prepared by dissolving it in ethanol-water (2:3) mixture and stored in a volumetric flask at laboratory temperature. Phosphate buffer solution (PBS) of pH 7.0 (0.1 M) was prepared from aqueous  $K_2HPO_4$  and  $KH_2PO_4$  solutions and used as the supporting electrolyte solution. The OIC of GG grafted with poly(acrylamide) with silica network (represented as GG-g-PAM-silica) and Pd NPs incorporated GG-g-PAM-silica (represented as Pd-GG-g-PAM-silica) nanocomposites were prepared according to our previous report [29]. A schematic synthetic route of Pd-GG-g-PAM-silica nanocomposite is shown in [scheme 1](#).

### 2.2. Instrumentation

Ultraviolet and visible (UV-vis) spectra were recorded with a 2802 PC UV-vis absorption spectrophotometer (Unico, USA). X-ray diffraction (XRD) patterns were performed with a Philips PW-1710 X-ray diffractometer employing  $Cu K\alpha$  radiation ( $\lambda = 0.15406$  nm) and X-ray photoelectron spectroscopy (XPS) measurements were performed on an AMICUS spectrometer (UK) with  $Mg K\alpha$  radiation as the X-ray source for excitation. Scanning electron microscopy (SEM) images were collected from a FE-SEM QUANTA 200 (FEI, Netherlands), operating at 20 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were obtained using a TECNAI 20G<sup>2</sup> FEI microscope (Netherlands), operating at an accelerating voltage of 200 kV. AFM images were recorded from a NT-MDT microscope (Russia) operated by semi contact mode. Mettler Toledo TGA/DSC 1 was used for the thermogravimetric analysis with a heating rate of  $10^\circ C/min$  under nitrogen atmosphere. All the electrochemical experiments were performed with CHI-660C (CH instruments, USA) using conventional three electrodes cell at laboratory temperature. Glassy carbon (GC) electrode was used as working electrode (area =  $0.07$  cm<sup>2</sup>), a Pt wire was employed as counter electrode and potassium chloride saturated calomel electrode (SCE) served as reference electrode. Therefore, all potentials measured and reported in this work are against SCE. The supporting electrolyte solutions were thoroughly deoxygenated by bubbling high-purity nitrogen gas for 20–30 min prior to each electrochemical experiment. Electrochemical impedance spectroscopy was recorded between the frequency range 0.1 Hz to 10 KHz using 5 mV amplitude and at an applied potential of 0.2 V.



**Scheme 1.** An overview for the synthesis of Pd-GG-g-PAM-silica nanocomposite.

### 2.3. Construction of ESP

Colloidal solution (0.5 wt%) of the respective materials (GG-g-PAM-silica or Pd-GG-g-PAM-silica) were dispersed in triple distilled water by ultra-sonication for 30 min. GC electrodes were cleaned/polished using 0.05 micron alumina slurry, washed with water and sonicated for 5 min in water and dried in air. Surface of the polished GC electrodes were drop coated (typically  $10.0 \mu L$ ) and left without disruption. After the evaporation of water at laboratory temperature, a thin film of ESP was formed at the GC surface (symbolized as GC/GG-g-PAM-silica and GC/Pd-GG-g-PAM-silica, respectively). The GC/GG-g-PAM-silica and GC/Pd-GG-g-PAM-silica electrodes were subjected to five continuous potential sweeps from  $-0.8$  to  $1.0$  V at a scan rate of  $20$  mVs<sup>-1</sup> in 0.1 M PBS (pH 7.0) to get a stable current-voltage curve. Such pretreated ESPs are used in further electrochemical studies.

## 3. Results and discussion

### 3.1. Physicochemical characterization of Pd-GG-g-PAM-silica

GG-g-PAM-silica and Pd-GG-g-PAM-silica materials were characterized by UV-vis absorption, powder XRD, TGA and XPS ([Fig. 1](#)). [Fig. 1A](#) shows the UV-vis spectra of aqueous palladium(II) chloride solution (spectrum a) along with 0.5 wt% aqueous colloidal solution of Pd-GG-g-PAM-silica (spectrum b). The aqueous

Download English Version:

<https://daneshyari.com/en/article/185084>

Download Persian Version:

<https://daneshyari.com/article/185084>

[Daneshyari.com](https://daneshyari.com)