



# Electrochemical investigation of gold nanoparticles incorporated zinc based metal-organic framework for selective recognition of nitrite and nitrobenzene



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## ABSTRACT

An electrochemical sensing platform which comprises gold nanoparticles (Au NPs) incorporated zinc based metal-organic framework (MOF-5) is developed for the sensitive determination of nitrite and nitrobenzene. MOF-5 and Au NPs incorporated MOF-5 (Au-MOF-5) are synthesized and characterized by UV-vis absorption, powder X-ray diffraction, FT-IR, scanning electron microscopy with energy dispersive X-ray analysis and elemental mapping, transmission electron microscopy and atomic force microscopy. Oxidation of nitrite is effectively electrocatalyzed at Au-MOF-5 with significant increase in oxidation current (41 and 38% in comparison with bare glassy carbon (GC) and MOF-5 coated GC (GC/MOF-5) electrodes, respectively) and with considerable decrease in the oxidation potential (0.17 and 0.25 V in comparison with bare GC and GC/MOF-5 electrodes, respectively). The electrocatalytic reduction of nitrobenzene at GC/Au-MOF-5 is confirmed by an appreciable increase in the reduction current (79 and 36% in comparison with bare GC and GC/MOF-5 electrodes, respectively) and a small shift in the reduction potential (20 mV in comparison with GC/MOF-5). The detection limit is calculated as 1.0  $\mu\text{M}$  with a sensitivity of 0.23  $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$  for nitrite and 15.3  $\mu\text{M}$  with a sensitivity of 0.43  $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$  for nitrobenzene determinations. The Au-MOF-5 based electrochemical sensing platform shows high stability and selectivity even in the presence of several interferences (including phenols, inorganic ions and biologically important molecules) with a broad calibration range. Certain kinetic parameters of nitrite oxidation and nitrobenzene reduction have also been studied by hydrodynamic voltammetry.

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## 1. Introduction

Widespread usage of nitrites and nitrates in fertilizers, rodenticides, food preservatives and corrosion prevention [1,2] exposes them into the environment. When the level of nitrite increases to a certain limit, it becomes fatal to the environment and affects human health by producing carcinogenic nitrosamines [1]. Consequently, quantitative determination of nitrites becomes necessary to address the issues related environmental, biological and clinical aspects. Similarly nitroaromatic compounds are also environmental pollutants and declared as carcinogenic. Still, they are widely used in pharmaceuticals, pesticides and in the fabrication of dyes and explosives [4]. Nitrobenzene (NB) has been categorized as one of the toxic pollutants because of its sedition, mutagenicity and tendency to accumulate in the

environment [5]. Therefore, various methods [6–10] have been explored for NB determination, including some electrochemical methods [9]. Among the several methods, electrochemical methods are cost effective and have several advantages like fast response, short analysis time, high selectivity, high sensitivity and wide range determination. To develop a cheap, sensitive and selective electrochemical route for the determination of a target analyte, suitable catalyst and catalyst support is very much preferred over the bare electrodes [1–4,11–13]. Catalytic materials which possess uniformly dispersed catalyst on them [1–4,11–13] are highly valuable for this purpose. Metal-organic frameworks (MOFs) [14,15] are suitable for the uniform dispersion of catalyst within them and can be used as efficient catalytic supports. MOFs are ordered porous materials and are gaining significant interest in the areas of catalysis [16], drug storage and delivery [17], gas separation [18], sensing and imaging [19], optoelectronics [20] and energy storage [21]. Most of the MOFs have large internal surface area with well-defined pores [22] which can be synthesized by

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simple and high-yield routes. High surface area, porosity and chemical stability of MOFs enable to load them with catalytically active metal NPs [23] which can facilitate and increase catalytic efficiency. MOFs can also be used to control shape and size of metal NPs and to grow highly active electrocatalysts to be used in electrochemical applications. The exploration of MOFs in the area of electrochemical applications is fairly recent [24]. MOFs can be effectively exploited in corrosion inhibition, energy storage and conversion (fuel cells, batteries, supercapacitors) and electrocatalytic removal of toxic compounds [24]. On the other hand, gold nanoparticles (Au NPs) catalyze several reactions including electrochemical reactions [12]. The stability and activity of Au NPs is greatly improved and can be tuned when they are immobilized on a suitable matrix [13]. In recent years, incorporation of Au NPs on variety of matrixes like polymers [25], silica materials [11,26], etc. [13,14] is explored and some of the materials are successfully applied in electrocatalytic reactions [1–4,11]. However, incorporation of Au NPs [27], on the recently known MOFs [14,15] is a new approach and recently attempted. Combining the Au NPs which have efficient catalytic properties with the MOFs which possess large internal surface area and their extraordinary structural features could be advantageous for enhancing the electrocatalytic properties. Bagheri and co-workers anchored Au NPs on copper MOF through  $-\text{SH}-\text{SiO}_2$  groups and used the resulting material to develop electrochemical sensor for L-cysteine and hydrazine [27,28]. Yuan and co-workers reported an electrochemical aptasensor for thrombin determination using Au NPs incorporated through hemin into Fe-MIL-88 MOF [29]. Thus it is noteworthy to mention that the successful utilization of Au NPs incorporated MOFs in electrocatalysis and subsequent determination of target analytes is reported rarely. The combined use of Au NPs and MOF-5 is expected to increase the efficiency of electrocatalysis process. Therefore in this work, to the best of the authors knowledge, Au NPs incorporated MOF-5 (Au-MOF-5) is reported for the first time to construct an electrochemical sensor for nitrite and NB.

## 2. Experimental

### 2.1. Reagent and chemicals

Analytical reagent grade nitrobenzene (NB), poly(vinyl alcohol) (PVA), N,N-dimethylformamide (DMF) and terephthalic acid were purchased from S.D. Fine Chemicals, India.  $\text{K}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_4$  and sodium nitrite were purchased from Qualigens Mumbai, India. Zinc nitrate was purchased from Merck, India. Tetrachloroauric acid ( $\text{HAuCl}_4$ , 99.99%) was purchased from Sigma-Aldrich and cetyltrimethylammonium bromide (CTAB, >96%) from SRL Mumbai, India. Ethanol was used after distillation and all the other chemicals were used as received. Solutions were prepared using triply distilled water.

### 2.2. Instruments

The UV-vis absorption spectra of metal-organic framework (MOF-5) and gold nanoparticles incorporated metal-organic framework (Au-MOF-5) were recorded using a 2802 PC scanning spectrophotometer (Unico, USA). PerkinElmer spectrometer (Spectrum two, UK) was used for FT-IR spectroscopic studies. Atomic force microscopy (AFM) (P 47AFM, NT-MDT company, Russia) images were recorded at room temperature in semi contact mode. X-ray powder diffraction (XRD) of the samples were examined using Philips PW-1710 X-ray diffractometer by Cu-K $\alpha$  radiation ( $\lambda=0.15406\text{ nm}$ ) from 20 to 80° (2 $\theta$ ). X-ray photoelectron spectroscopy (XPS) analysis was performed on Kratos Analytical Instrument (AMICUS spectrometer, UK)

equipped with Mg K $\alpha$  X-ray radiation. Scanning electron microscopy (SEM) images were collected from FE-SEM QUANTA 200 (FEI Netherlands) operating at 20kV. Transmission electron microscopy (TEM) images and selected area diffraction (SAED) were obtained from TECNAI 20 G<sup>2</sup> FEI microscope (at 120kV). High-resolution TEM (HRTEM) images were acquired using JEOL field emission transmission electron microscope at 200kV. Energy dispersive X-ray analysis (EDAX) was recorded from SEM VEGA 3 TESCAN at 30kV. Electrochemical studies were carried out at room temperature by three electrode system employing CHI-660C electrochemical work station (CH Instruments, USA). Saturated calomel electrode as reference electrode, platinum wire as counter electrode and glassy carbon electrode (GC) or modified GC as working electrode was used. Before the electrochemical experiments, the electrochemical cell solution was purged with  $\text{N}_2$  for 15–20 min to remove dissolved oxygen.

### 2.3. Synthesis of metal-organic framework

The zinc based metal-organic framework (MOF-5) was prepared according to the procedure reported in the literature [30] with slight modifications.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.74% w/v) and terephthalic acid (0.36% w/v) were dissolved in 250 mL DMF-ethanol (5:3) mixture in a round bottom flask. An aqueous solution of CTAB (0.68% w/v) was added into the above mixture and refluxed at 140 °C for 3 h. The formed solid product was collected by centrifugation and washed with triple distilled water and DMF. The washed product was dispersed in  $\text{CHCl}_3$  and kept for 12 h to remove DMF. This process was repeated two times for complete exclusion of DMF [27,31]. Then the product was dried in an oven at 120 °C for 6 h.

### 2.4. Incorporation of Au NPs into metal-organic framework

For the incorporation of Au NPs into the MOF-5, the precursor,  $\text{HAuCl}_4$  is introduced into a similar aliquot used for the preparation of MOF-5. That is, 1.0 mL of  $\text{HAuCl}_4$  solution was added to a mixture of CTAB-terephthalic acid- $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in water-DMF-ethanol. After thorough mixing, the mixture was refluxed at 140 °C for 3 h. During the course of reflux, color of the solution changes from pale yellow to pink due to the reduction of  $\text{Au}^{3+}$  ions to metallic Au by DMF. The product (Au-MOF-5) was centrifuged and washed with triple distilled water and DMF. Further, it was dispersed in  $\text{CHCl}_3$  and kept for 12 h to remove DMF and this process was repeated two times for complete exclusion of DMF [27,31]. The final product was dried in oven at 120 °C for 6 h.

### 2.5. Preparation of the samples

Colloidal suspensions of Au-MOF-5 (0.05%) and MOF-5 (0.05%) were prepared with 0.01% PVA solution. Then 20.0  $\mu\text{L}$  of respective samples (Au-MOF-5 (0.05%) and MOF-5 (0.05%)) was coated on a GC electrode and allowed to dry over night at room temperature. After the solvent was evaporated, these electrodes were used for further studies and denoted as GC/Au-MOF-5 and GC/MOF-5, respectively. For SEM measurements the powder samples (Au-MOF-5 and MOF-5) were carefully dispersed on a colloidal silver paste coated on an aluminum stub. For AFM, thin films of MOF-5 and Au-MOF-5 were prepared on glass plate similar to the coating on the GC electrode. For UV-vis spectra, pastes of Nujol and the respective material (Au-MOF-5 or MOF-5) were dispersed as thin film on Whatmann filter paper strips and measured. For IR spectra, pellets of MOF-5 and Au-MOF-5 were prepared with spectroscopic grade KBr.

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