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Nanocubic magnesium oxide: Towards hydrazine sensing

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ABSTRACT

The magnesium oxide (MgO), which is a thermodynamically stable material, has great property of sensing in liquid medium. To keep this point, the present work was designed to show the preparation of cubic shaped MgO nanoparticles (CNMgO) by wet chemical reaction and their sensing purposes in presence of hydrazine solution. The processed material was characterized with X-ray diffraction pattern (XRD) to evaluate their crystalline property, whereas the morphology of nanostructure was examined with transmission electron microscopy (TEM), reveals the size of obtained material is in the range of ~100 nm with cubic form. The chemical functional changes were analyzed via the FTIR spectroscopy; authenticate the conversion of hydroxide in to metal oxide. The Thermo-gravimetric analysis (TGA) was obtained the phase transition of prepared and annealed MgO was obtained at 350–400 °C temperature. The oxidation and reduction potential of CNMgO in hydrazine solution was analyzed from lower to higher (from 0.1 to 1mL/100 mL PBS, 1 mL to 5 mL/100 mL PBS, 10 µL to 100 µL/100 mL PBS) concentration via cyclic voltammetry (CV). On the basis of the results and their observations, we have also described the possible pictorial mechanism of sensing of hydrazine in presence of prepared CNMgO.

1. Introduction

The industrial compound Hydrazine (N_2H_4), which behaves like ammonia, has wide applications in various industrial arenas such as treatment for boiler water or oxygen scavenger [1], fuel cells [2], rocket propellants [3], plastic foaming, polymerization [4], crosslinking agents, dyes [5,6], blowing agent [7], photographic chemicals etc [8]. Including this, hydrazine has larger applications in pharmaceutical for instance it acts as anti-tubercular drug [9], anti-cancer [10], anti-depression [11], anti-fungal [12], antiviral, pesticides etc [13]. Although, it has various applications of hydrazine, but it can cause the irritation, corrosion and are sensitive for respiration, damage human's liver, kidney and brain [14]. As per the Environmental Protection Agency (EPA), hydrazine is neurotoxin in nature and has been classified as human carcinogen [15]. Hence it's its urgent need to develop an alternative sensitive method, which should be economical, effective and highly desirable for to trace and detect the hydrazine amount [16]. Towards this area, till to date various methods have been developed for the determination of hydrazine such as chromatography, fluorescence, spectrophotometry, chemiluminescence etc [17–19]. The recent advancement in area of nanoscience and nanotechnology, which is based on nanostructures (nanoparticle, nanotubes, nanocubes, nanorods, nanowires, tetrapods etc), facilitates to detect the hazardous compounds via electrochemical studies due to their strong, effective physico-chemical, electrical, magnetic, luminescent and catalytic properties [20–25]. These unique properties of nanomaterials provide faster, sensitive and economical detection ways for various chemical and biochemical substances. Many works has been done towards the development of amperemetric, voltammetric and electrochemical sensors. Over various types of sensors, hydrazine based electrochemical sensors, which has low cost, good accessibility, selectivity, and high sensitivity and has much attention due to their applicability in various areas [26–28].

Among various metal oxides, MgO is one of the most important functional materials due to their own merits and its diversity in terms of morphologies, properties in various applications [29–31]. These versatile properties of MgO provides an opportunity to recognize itself as one of the most multifunctional materials; therefore it can be used many ways such as in hydrogen storage [32], chemical and biological sensors [33], solar cells and diodes [34], electroluminescence devices [35], photonic crystal devices photocatalyst [36], ultraviolet lasers [37], photo-detectors, etc [38]. Over various applications, the utilization of MgO nanostructures as sensor-electrode received a considerable attention and interest recently due to its high surface area, smaller in size, high thermal stability, greater catalytic properties, and high sensitivity, better performance allows rapid analysis for device fabrication

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in the form of an electrochemical sensors/biosensors or biochips [39,40].

In the present manuscript, a facile and very rapid method has been introduced for the synthesis of cubic nanomagnesium oxide (CNMgO) via solution process. The prepared CNMgO have been characterized in detail in terms of their physicochemical parameters such as the crystalline property of the prepared CNMgO was assessed via XRD, whereas the morphological analysis of CNMgO was performed via TEM. The chemical finger print of the prepared nanomaterial was assessed via room temperature FTIR spectroscopy. In addition to theses the thermal efficiency of the prepared material was analyzed via TGA and Derivative thermo-gravimetric (DTG). The prepared nanostructures efficiently were utilized as effective electron mediators for the fabrication of highly sensitive hydrazine chemical sensor. The fabricated hydrazine sensor based on MgONPs exhibits a good electrocatalytic activity towards electrochemical oxidation of hydrazine analyzed via the cyclic voltammetry (CV) detection at low, medium and high range of hydrazine concentration. To the best of our knowledge, this is the first report which demonstrates the utilization of cubic shaped nanomagnesium oxide nanoparticles for the fabrication of efficient hydrazine chemical sensor. By this work, it could be concluded that simply synthesized MgONPs can be used as efficient electron mediators for the fabrication of effective hydrazine chemical sensors.

2. Materials and methods

2.1. Experimental

The synthesis of MgO was carried out by using soft chemical and hydrolytic process. For the formation of nanostructures, the entire chemicals were purchased from Aldrich chemical corporation, U.S.A and utilized as received. In a typical chemical reaction for the synthesis of MgO nanoparticles, 3×10^{-2} M of $Mg(NO)_3.2H_2O$ and alkali sodium hydroxide (NaOH, 0.3 M) were dissolved in a 100 mL deionized water to form white colored solution under continuous stirring (~30 min). The resultant solution was refluxed at 90 °C for 6 h in a refluxing pot. The reaction was monitored with noting changes in pH value from 9.5 till neutral pH (7.0). The white precipitate was observed in the refluxing pot, filtered with distilled water, solvent methanol (MeOH), ethanol (EtOH) and acetone to remove the byproducts and ionic impurities in the refluxing pot. After the completion of washing, the content powder was dried in an oven for overnight at 60 °C.The resultant white powder was then calcined at 250 °C in air with a heating rate of 5 °C/min in an ambient air for 1 h (h) and the white powder was used for sensor fabrication.

2.2. Characterization

2.2.1. Crystalline, morphological and compositional measurement

The crystalline property of chemically prepared as grown and annealed powder samples were analyzed via XRD (PANalytical X′ Pert X-ray diffractometer) with a scintillation detector in reflection mode ($Cu_{K\alpha}$ radiation (λ = 1.54184 Å). The analysis was performed from 10 to -85° at scan speed of 4°/min at an accelerating voltage of 40 kV and current was 40 mA. The morphological studies of the synthesized and annealed powder were carried out by using TEM (JEOL JEM, 2010; Hitachi Japan) working with an acceleration voltage of 200 kV. For the TEM measurement of grown and annealed MgO nanostructures, the powder was ultrasonically dispersed in an ethanol solvent for 10 min and placed a droplet of MgO nanostructures the suspension on a copper grid (~400 mesh) and dried at room temperature. The chemical bonding or functional behaviors of synthesized and annealed nanostructures were analyzed with the help of FTIR spectroscopy (FTIR, Perkin Elmer's GX spectrophotometer) in the range of 4000–400 cm^{-1} with using KBr pellets.

2.2.2. Electrochemical measurements

The Electrochemical measurements were carried out on Autolab Potentiostat/galvanostat, PGSTAT 204-FRA32 control with NOVA software (Metrohom Autolab B.V.Kanaalweg 29-G, 3526 KM Utrecht, The Netherlands) in three electrode system. The working electrode was MgO modified glassy carbon electrode, platinum (pt) work as a counter whereas Ag/AgCl used as a reference electrode. Prior to coat the slurry of prepared materials (70% MgO (4.9 mg), 30% (2.1 mg) ethyl cellulose in 200 µL PBS) on the surface of Glassy carbon electrode (GCE), it was polished with polishing cloth, followed by multiple washing with distilled water (DW) thoroughly. Finally, a certain amount (~25–30 µL) of viscous slurry prepared materials was casted on the electrode surface which was then dried at 60 °C for 2 h to get a homogenous and dried layer over the carbon electrode surface. Phosphate buffer solution (PBS, pH = 7.4) was used as a background media. The prepared PBS (pH 7.2) was purged with nitrogen (N_2) gas for 10 min prior to all the electrochemical experiments. PBS sensor with hydrazine was used as an electrolyte. A wide concentration range of hydrazine (concentration from 0.1, to 1 mL/100 mL PBS, 1 mL to 5 mL/100 mL PBS, 10 µL to 100µL/100 mL PBS) was used to determine the sensing characteristics. The current response was measured from −0.2 to +2.0 V. For studying the electrical response at various concentrations, run with the scan rate 100 mV/s with or without hydrazine in 10 mL PBS.

3. Results and discussion

3.1. X-ray diffraction pattern

The XRD pattern describes the crystalline properties, particle size, phases of the prepared nanostructures. Fig. 1a depicts the XRD pattern of as grown MgO nanostructures, whereas Fig. 1b shows the diffraction pattern of annealed sample at 250 °C temperature. From the obtained graph its shows that various peaks were observed in the spectrum. The peak position at (14.51°), (20.02), (24.50), (28.31), (31.23), (33.95), (35.79), (47.04), (56.15), (62.37), (66.13), (67.57), (68.82), (72.18), (76.55), and (81.03°), these peaks corresponds to Mg peak as can be seen in the JCPDS cards (01–1141). Fig. 1b shows the sample annealed at 250 °C in air for 1 h, as the temperature/annealing increases various crystalline peaks were observed in the spectrum. The intensity of MgO peaks can be seen and confirm from the JCPDS cards (04–0829, 27–0759).

3.2. Morphological characterization (TEM results)

The structural elucidation of as processed and annealed magnesium structures were observed via TEM. It can be seen clearly from Fig. 2a that the nanostructures aspects like to cubic shaped particles. From the obtained data, the average size of the as grown nanostructures is about

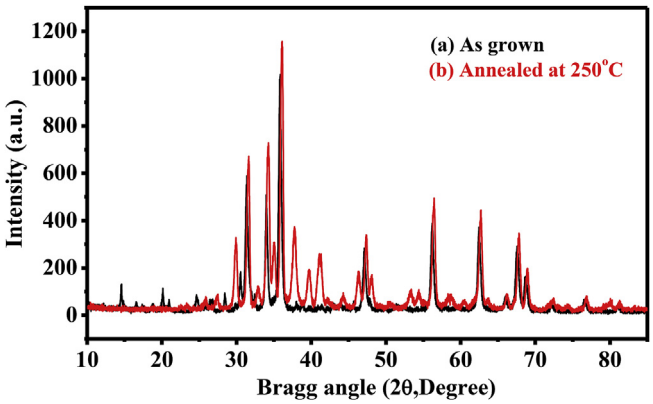

Fig. 1. The X-ray diffraction pattern of prepared powder of magnesium oxide of grown (a) and annealed at 250 °C (b) temperature for an hour.