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Polymeric iron oxide-graphene nanocomposite as a trace level sensor of vitamin C

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ABSTRACT

The nanocomposite of graphene-iron oxide-polyvinyl alcohol (PIG) was synthesized via simple one-pot hydrothermal method and was used in the modification of pencil graphite electrode for developing an electrochemical sensor. Graphene (G) and iron oxide-graphene (IG) composites were synthesized for providing a comparative study. The structural properties of the prepared PIG were studied through X-Ray diffraction (XRD) technique, whereas the morphological analysis was conducted through field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) study. The chemical states of elements present in the prepared composite were confirmed using X-ray photoelectron spectroscopy (XPS) and the functional groups present in the composite were investigated through Fourier transform infrared (FTIR) spectroscopy. The existence of iron oxide nanoparticles along with PVA polymer in PIG composite enhances the electroactive area (0.073 cm^2) and roughness factor (0.186) along with the sensitivity of the material. The square wave voltammetry technique was used for detecting the bio-molecule i.e. vitamin C. At optimized condition, the PIG modified electrode shows a high linear range (40 μM–4100 μM), low limit of detection (0.234 μM) and higher sensitivity (1597.03 $\mu A\,cm^{-2}\,mM^{-1}$). The PIG material also provides a good stability towards detection of vitamin C.

1. Introduction

Ascorbic acid (AA) i.e. Vitamin C is a hydrosoluble six carbon lactone and it has great influence in biological activity. This biomolecule acts as an enzyme factor, reducing agent and involves in neurotransmitter enzymes [1,2]. Vitamin C has a direct impact on various biological processes like amino acid metabolism, ion adsorption and collagen carnitine. Besides these, vitamin C is also used as an antioxidants in food, pharmaceutical formulations, chemical indusrties and for cosmatic applications [2–4]. It can be used to cure disease like Alcaptonuria, Hawkinsinuria, Tyrosinemia type III, temporary Tyrosinemia of the new born. Vitamin C also cures inherited disease marked by the excretion of sulfur in urine. Human beings are not able to synthesize vitamin C from glucose. Hence it is necessary to take vitamin C from food sources [5]. On the other hand, the excess level of vitamin C in the body is also equally dangerous or harmful to health which leads to gastric irradiation and renal disorder. This causes diarrhea, hyperacidity and kidney calculi [2,3]. The level of vitamin C directly related to several diseases like cardiovascular disease, viral infection and alzheimer disease [6]. The trace level of vitamin C present in the body causes a severe disease called scurvy. Muscle weakness, rash, tiredness, joint pain and tooth loss are some typical symptoms of scurvy. For this purpose, a rapid, sensitive and accurate detection and quantification of vitamin C or AA is necessary [3].

Several techniques have been introduced in past for determining the vitamin C bio-molecule. Such techniques include spectroscopic, chromatographic, enzymatic and electro analytical methods [7]. AA donates two electrons and acts as a reducing agent during the process of electrochemical detection. The loss of the first electron leads to an intermediate state called semi-dehydro ascorbate. Following the loss of the second electron, ascorbic acid is oxidized to dehydroascorbic acid as shown in Eq. (1) [1,2].

$$\mathbf{C_6H_8O_6 \rightarrow C_6H_8O_6 + 2e^- + 2H^+} \quad (1)$$

Among various detection techniques, electrochemical analysis of AA through various chemically modified electrodes is a promising one. The simplicity, low cost and high sensitivity of this technique

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has influenced the researcher for its wide implementation. Sensor materials, based on the polymer, carbonaceous material and metal oxides have been reported several times [8,9]. Graphene is a two-dimensional (2D) sp^2 bonded honeycomb lattice. Its tremendous properties, like high specific surface area (2630 $m^2 g^{-1}$), outstanding thermal conductivity, tremendous electrocatalytic activity and high charge mobility have influenced the researcher to use it as a sensor material [10]. On the other hand, the biocompatibility and low toxicity of Iron oxide (IO) nanoparticles, have achieved a special attention in biomedical, biotechnological and biosensing field [8]. Incorporation of nanoparticle in graphene surface enhances the electroctalytic activity, electron transfer abilities and prevents their aggregation.

Various researchers have tried their best to design very high sensitive sensors by using graphene and graphene based composite. L. Liu et al. have used reduced graphene oxide and co-polymerizing neutral red (NR) composite for detecting ascorbic acid [11]. X. Zhang et al. have studied vitamin C or ascorbic acid detection by using graphene-ZnO nanocomposite [12]. A. Ejaj et al. have focused on a composite of GO-XDA-Mn_2O_3 for detecting vitamin C [13]. T. Peik-See et al. have developed Fe_3O_4- graphene composite and employed this material in sensing of vitamin C [14]. S.A Kumar et al. have developed a polymeric hybrid film of ZnO/poly (luminol) for detecting vitamin C [5,15]. The material Fe_3O_4-graphene exhibit a limit of detection of 0.42 μM towards vitamin C detection. Researchers have developed various graphene-iron oxide composite [16–22], graphene-polymer composite [23–26] and graphene-iron oxide-polymer composite [26–31] but sensing of vitamin C with a nanocomposite of polyvinyl alcohol (PVA) and iron oxide nanoparticle decorated graphene is missing.

In the same pursuit, here, we have developed polyvinyl alcohol (PVA) and iron oxide graphene (PIG) nanocomposite via one-pot hydrothermal method. The addition of PVA polymer increases the electrocatalytic activity of the sensor and provides a large surface area [32]. The excess presence of hydroxyl group provides a large number of electrons during the process. PVA also supports the composite for uniform coating on the electrode surface and also acts as a mediator for facilitating electron transfer. For comparative study graphene (G) and iron oxide (Fe_2O_3) decorated graphene (IG) were synthesized chemically. The structural confirmation regarding the material was studied through XRD technique. The chemical state of elements present in the prepared PIG composite was studied through XPS technique. The morphological and elemental analysis performed through FESEM and TEM techniques, explains the decoration or presence of iron oxide nanoparticle on the PVA-graphene complex. From the FESEM/TEM study a clear granular iron oxide nanoparticles with a particle size of 5 nm were found on the graphene sheets. Oxygen containing functional groups like hydroxyl group in the composite was analyzed through FTIR technique. Electrochemical analysis of the material was performed by cyclic Voltammetry (CV) and square wave voltammetry (SWV) technique by using pencil graphite electrode modified by the synthesized nanocomposite. PIG possesses a higher electroactive area (0.073 cm^2) and roughness factor (0.186) in comparison to G and IG nanocomposite. Finally, at all optimized conditions, SWV analysis was performed for detecting the biomolecule vitamin C or ascorbic acid. A comparative study among all three modified electrodes has explained the better response of the PIG electrode towards the detection of vitamin C. The analysis results in a linear high range of 40 μM–4100 μM along with a lower limit of detection of 0.234 μM. The sensitivity was found to be very high i.e. 1597.03 μA cm^{-2} mM^{-1}. The PIG electrode exhibits good stability up to 30 days. Then the electrode shows only 3%, 4% and 6% decrease of current response after 40, 45 and 50 days respectively.

2. Experimental section

2.1. Reagents

All the chemicals were of analytical grade and used as received. Graphite fine powder, sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), Hydrazene Hydrate and ferric chloride were purchased from Sigma-Aldrich, Germany. Hydrochloric acid (HCl), Sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), potassium ferrocyanide ($K_4[Fe(CN)_6]\cdot 3H_2O$) and Dimethylformamide (DMF) were purchased from Merck, India and Spectrochem Pvt. Ltd., India. Pencil leads were purchased from A.W. Faber-Castell (I) Pvt.Ltd.

2.2. Instrumentation

X-ray diffraction study was performed by using Bruker D8 Focus X-Ray Diffractometer. X-Ray Photoelectron spectroscopy (XPS) was performed by using ESCA+ (Omicron Nanotechnology, Oxford Instrument Germany) equipped with Aluminum Source (Alkα radiation hv = 1486.7ev). The instrument was operated at 15 kV and 20 mA. The obtained detailed XPS spectra were fitted and deconvoluted using XPS Peakfit software. Morphological analysis was studied through field emission scanning electron microscope (FESEM) of Zeiss model supra 55. High-resolution transmission electron microscopy (HR-TEM) analysis was conducted by Tecnai T-30 (300 kV FEG TEM). Fourier transform Infrared (FTIR) spectroscopy was performed through Perkin-Elmer 580B, spectrometer and finally, electrochemical measurements were performed in a three electrode cell assambly using Palm sense (Model No.PS314E171) potentionstat/galvanostat.

2.3. Synthesis of graphene (G)

First graphene oxide (GO) was produced by the well know modified Hummers method. A solution of GO and DMF (1:1) was prepared and the complete solution was kept under sonication for 3 h. Then 2.0 ml of hydrazine hydrate was added to the solution. The complete solution was refluxed. After 24 h, a black colored precipitate was collected and centrifuged thrice with water. The prepared G was dried in a vacuum oven at a temperature of 60 °C.

2.4. Synthesis of iron oxide Nanoparticles decorated graphene (IG)

A solution of GO and distilled water (1:1) was subjected for 5 h sonication in an ultrasonic bath for getting a brown color dispersion. After then 60.0 mg of anhydrous ferric chloride ($FeCl_3$) was dissolved in that solution. The pH of the solution was maintained in between 10 and 11, by adding 30% ammonia solution dropwise. The solution was stirred for 15 min and poured into an autoclave. Then the autoclave was kept inside a hot air oven at a temperature of 180 °C. After 12 h, a black colored precipitate of iron oxide nanoparticles decorated on graphene (IG) was found which was washed thrice with ethanol and distilled water. The prepared IG was dried in a vacuum oven at a temperature of 60 °C for 12 h.

2.5. Synthesis of polyvinyl alcohol based iron oxide graphene (PIG) nanocomposites

A solution of GO and distilled water (1:1) was sonicated in an ultrasonic bath for 5 h. Then 60.0 mg of anhydrous ferric chloride ($FeCl_3$) and 30.0 mg of PVA were added to the solution. The resulting solution was stirred for 1 h at 80 °C. Later the solution was placed in a stainless steel autoclave for 12 h at 180 °C. At the end of the

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