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Co-electrodeposited rGO/MnO_2 nanohybrid for arsenite detection in water by stripping voltammetry

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ABSTRACT

Herein, we report noble metal free, cathodically co-electroreduced rGO/MnO_2 nanohybrid (NH) on glassy carbon electrodes for arsenite (As (III)) detection in water by square wave anodic stripping voltammetry (SWASV). Cyclic voltammetry, scaning electron microscopy, X-ray diffraction, trasnsmission electron microsocpy and Fourier transform infra-red (FT-IR) spectroscopy were used to probe the rGO/MnO_2/GCE surface, revealing the formation of NHs. The arsenite sensing parameters such as deposition potential and time was optimized allowing a detection range of 0.1 ppb to 50 ppb in 0.1 M acetate buffer. This *in-situ* fabricated NHs electrodes exhibit favourable sensitivity of 0.175 μA/ppb with a theoritical limit of detection of 0.05 ppb for arsenite, which is well below the levels set by World Health Organization. Moreover, the fabricated electrode exhibited good selectivity, stability and reproducibility, in near alkaline condition without using any noble metal as sensing electrode component, desirable for practical application. These findings suggest the possibility of a cost effective electrochemical sensing electrode for a portable embedded system to determine As (III) in water.

1. Introduction

Nano sized metal oxide adsorbents are considered as one of the promising contenders for removal of toxic heavy metal ions from water bodies due to their merits such as high surface area and catalytic activities by means of size quantization effect [1,2]. In this direction, a plethora of metal oxides based on manganese, iron, molybdenum, alumina, zirconium, *etc* have been reported for effective removal of prevalent groundwater inorganic arsenic in particular arsenate (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$) and arsenite (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$), which are also classified as a class I carcinogen by the International Agency of Research on Cancer (IARC) [3–9]. This ubiquitous element of ground water ranges from 0.5 to 5000 μg/L in more than seventy countries worldwide and is of geogenic origin [10]. Whereas, the World Health Organization (WHO) recommended maximum contamination level (MCL) of arsenite in drinking water as 10 μg/L, thus, it becomes extremely important to detect and monitor its concentration in aqueous systems.

Manganese oxide materials have been extensively investigated in the past and were applied in a wide range of fields, such as electrochemical super-capacitors, biosensors, lithium ion batteries, *etc* [11–14]. In recent years, it has also been reported for removal and detection of arsenic in water due to its stability and excellent adsorption capability towards arsenic [15–18]. Since the electrochemical performance of any electrode is closely associated with its adsorption capability and electrocatalytic activity, therefore, the integration of adsorbents with another material is practiced to enhance the electrochemical performance of electrode, which includes noble metals, ionic liquids, *etc* [17,19,20]. Shoguo *et. al* reported lately the sensitive and selective determination of As(III) in aqueous solution using co-electrodeposited MnOx/Au nanoparticles (NPs) composites to a level of 0.057 μg/L [17]. They proposed the effective role of catalytic and electro active Au in the composite film to achieve reported sensitivity.

Of-late, graphene (GN) and its associates are also of great attention in electrochemical chemo/biosensor as a conductive platform due to their easy fabrication, low cost, large surface-to-volume ratio, high conductivity & electron mobility at room temperature (RT) and robust mechanical properties [21]. Besides, the presence of oxygen-containing groups on its edges or surface facilitates easy discrimination of target analytes based on their respective peaks, which is commonly overlapping in case of other materials [22]. The competitive and increased number of publications in the year

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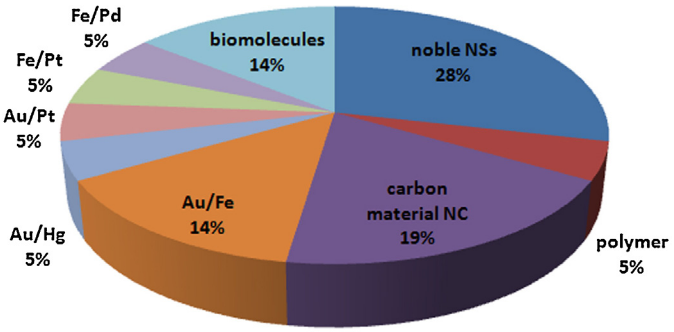

Fig. 1. Pie chart on materials reported for As (III) detection in year 2015 alone.

2015 alone (Fig. 1) on GN and its associates based electrochemical sensors for arsenic, clearly endorses about its most promising electronic properties. Owing to such exceptional properties and increasing trends towards their use in electrochemical sensor for arsenite, rGO can perhaps be an alternative component to noble metals in NCs utilizing arsenite selective adsorbents.

Motivated by this, herein we report, manganese oxide/rGO nanohybrid (NH) for arsenic detection in aqueous system, which is not investigated yet to the best of our knowledge. The proposed NH utilize the high adsorption capability and stability of manganese oxide films, in conjugation with excellent electro-catalytic properties of reduced graphene oxide (rGO) over other platforms. The proposed electrode was thoroughly examined for arsenite detection using SWASV to find limit of detection (LOD), sensitivity, interference, stability and reproducibility.

2. Material and methods

2.1. Reagents

All the chemicals used in the present study were of analytical grade and further were used as such without any purification. Graphite flakes were gifted by Asbury Graphite Mills, Inc (Asbury, NJ). Sulphuric acid (H_2SO_4, 97%, E. Merck India Ltd.), hydrogen peroxide (H_2O_2, 30%, Sigma-Aldrich chemicals Pvt. Ltd., Bangalore), hydrogen chloride (HCl, 35%), potassium permanganate ($KMnO_4$, 99.9%, Loba Chemie pvt. Ltd., Mumbai), and Ortho-phosphoric acid (H_3PO_4, 85%, Merck specialists Pvt. Ltd., Mumbai) were used for the synthesis of GO (GO). Manganese (III) acetate ($C_4H_6MnO_4\,4H_2O$), glacial acetic acid (CH_3COOH), sodium acetate, and sodium sulphate (Na_2SO_4) was procured from Sisco Research Labs Pvt. Ltd., Andheri Mumbai, India and potassium ferricyandie (K_3FeCN_6), potassium ferocynadie ($K_4FeCN_6\,3H_2O$), potassium chloride (KCl) was purchased from Loba Chemie Pvt. Ltd., Mumbai, and were used for the electrochemical synthesis and characterization of rGO, MnO_2 and rGO/MnO_2 NHs, respectively. Arsenic salt, arsenic trioxide (As_2O_3) was purchased from Loba Chemie pvt. Ltd., Mumbai and further used for all the reported sensing studies. Interference studies were done with chloride salts of lead ($PbCl_{2,}$ Molychem, Mumbai), copper ($CuCl_2\,2H_2O$), nickel ($NiCl_2\,6H_2O$, Spectrochem Pvt. Ltd. Mumbai, India), zinc ($ZnCl_2$), cadmium ($CdCl_2\,H_2O$), cobalt ($CoCl_2\,6H_2O$, and nitrate salt of lead ($Pb\,(NO_3)_{2,}$ Loba Chemie Pvt. Ltd., Mumbai). All aqueous solutions were prepared with ultrapure water (>18 MΩ) obtained from a Milli-Q Plus (Millipore) water purification system.

2.2. Instrumentation

Entire electrochemical synthesis, characterization and sensing measurements were performed with a computer controlled (CHI 140A) electrochemical workstation using conventional three electrode configuration; bare or modified Glassy Carbon (GC), platinum and Ag/AgCl as working (diameter = 3 mm), counter and reference electrode, respectively. The morphological and structural analysis of fabricated electrodes were probed by scanning electron microscope (SEM, FEI Inspect F50 Microscope) and transmission electron microscope (TEM, Hitachi H-7500), respectively. The elemental analysis was mapped with energy dispersive X-ray analyser (HITACHI SU8010). For TEM analysis, the films were sonicated for 1 h in ethanol prior to drop cast on copper grid and air dried. Optical characteristics were studied with IR-spectrophotometer (Varian 670-IR) in the 4000–400 cm^{-1} scan range. X-ray diffraction patterns were obtained by diffractometer (X'PERT-PRO, Phillips PANalytical, USA) with Cu-Kα (λ = 1.54 A°, 45 mA, 45 keV) radiation.

2.3. Fabrication of rGO/MnO_2 NHs electrodes

The Graphene oxide (GO) was synthesized from natural graphite by simplified Hummers method with little modifications [23], and the obtained suspension (1 mg/mL) was used further for characterization & electrochemical reduction. Prior to modification, GC electrode was polished in gradually decreasing order (1.0 μm, 0.3 μm and 0.05 μm) with alumina slurry, then sonicated (for 20 min) and washed in isopropanol & DI water, respectively, to remove residual alumina, and finally blow dried in N_2. Subsequently, 5 μL of GO (1 mg/mL) was drop casted onto the pre-treated GC electrode and dried in N_2 blowing to come up with final version of GO/GC electrodes.

The rGO/MnO_2 NHs electrodes were fabricated by one step electrochemical cathodic reduction method according to the earlier reported research [24]. In this process, the co-reduction was performed in aqueous (0.1 mol/L Na_2SO_4) electrolyte containing 0.05 mol/L $Mn(OAc)_2$ using cyclic voltammetry (potential range: 0 to −1.5 V (*vs.* reference) at a scan rate of 50 mVs^{-1} for 8 segments). For comparison, rGO/GC and MnO_2/GC electrodes were fabricated by CV of bare GC electrode in aqueous solutions of 0.1 mol/L Na_2SO_4 alone and 0.1 mol/L Na_2SO_4 electrolyte containing 0.05 mol/L $Mn(OAc)_2$, respectively, with the potential cycling from 0 to −1.5 V at a scan rate of 50 mVs^{-1} for 8 segments.

2.4. Electrochemical analysis

The performance measurements of the fabricated electrodes were mapped by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in 1 mol/L Na_2SO_4 aqueous electrolyte solution. On the other hand, SWASV was used for observation of arsenic sensing behaviour of modified electrodes under optimized conditions. Unless stated anywhere, 0.1 M acetate buffer (pH = 5.0) was used as a supporting electrolyte for all the sensing studies under nitrogen environment. Arsenic stock solution (1000 ppm) was prepared by dissolving arsenic in DI water containing 25% sodium hydroxide and pH was maintained (range:2–3) using hydrochloric acid.

Initially, As (0) was deposited onto modified electrode at −0.7 V accumulation potential for a certain time under stirring condition by reduction of As (III) in 0.1 M acetate buffer. The anodic stripping of electrodeposited metal was performed in the positive potential range (−0.1–−0.6 V) under following conditions: frequency = 15 Hz; amplitude = 25 mV; increment potential = 4 mV; and Ag/AgCl as reference electrode.

The electrode was renewed after each stripping experiment by applying a preconditioning potential of 0.7 V under non-stirring condition to remove the target metal. Similar experimental conditions were duplicated during stability and reproducibility study. For interference studies, 0.1 M stock solution of various cations (Cu, Cr, Pb, Ni, Hg, Cd and Zn) was added in concentration 10 folds to that