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Europium doped magnetic graphene oxide-MWCNT nanohybrid for estimation and removal of arsenate and arsenite from real water samples

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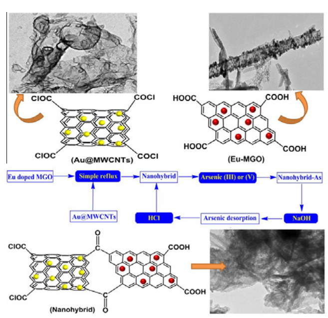
HIGHLIGHTS

- Herein, a nanohybrid of Eu doped MGO and gold nanoparticle@MWCNTs was synthesized.
- The multi-functional behavior of synthesized nanohybrid was studied.
- It used as adsorbent for effective and rapid removal of As from real water sample.
- It also shows photocatalytic behavior for oxidation of As(III) to As(V).
- The nanohybrid modified PGE was applied to detect As by electrochemical technique.

GRAPHICAL ABSTRACT

Synthesis, characterization, application and recycling procedure of Eu-MGO/Au@MWCNT nanohybrid.



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ABSTRACT

Herein, we have reported a graphene and multiwalled carbon nanotubes based nanohybrid as an adsorbent for effective and rapid removal of arsenite and arsenate from real water samples. The nanohybrid was prepared by a combination of Eu-doped magnetic graphene oxide and gold nanoparticle functionalized multiwalled carbon nanotube (Eu-MGO/Au@MWCNT). Herein, the dual behavior (i.e. as adsorbent materials and as electro-active sensing materials) of nanohybrid was explored. The resulting nanohybrid shows desirable magnetic property (15000.0 emu g^{-1}) with excellent adsorption capacity for As (III) and As (V) i.e. 320.0 mg g^{-1} and 298.0 mg g^{-1}, respectively. The proposed nanohybrid also shows very good photocatalytic behavior for oxidation of As (III) to As (V), which can be used as an effective tool for conversion of highly toxic for of arsenic to less toxic one. Additionally, the nanohybrid-modified electrode was applied to detect arsenate and arsenite by cyclic voltammetry and square wave voltammetry technique. The linear concentration range for determination of As (III) and As (V) was found from 0.99 to 100.0 μg L^{-1} and 2.0 to 85.0 μg L^{-1} with LOD 0.27 and 0.99 μg L^{-1}, respectively. The proposed nanohybrid modified electrode was also applied for the determination of arsenic in various water samples collected from differentially populated/industrial areas.

1. Introduction

Arsenic is a natural component of the earth's crust and is widely distributed throughout the environment in the air, water and land. Initially, it was used as a therapeutic agent in the treatment of

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various diseases such as leukaemia, psoriasis and chronic bronchial asthma [1]. Afterward, it was found that the acute (short-term) high-level inhalation, oral exposure or chronic (long-term) inhalation has resulted in various disorders, skin cancer etc. [2,3]. However, the greatest threat to public health from arsenic originates from contaminated groundwater. Inorganic arsenic is naturally present at high levels in the groundwater of a number of countries, including Argentina, Bangladesh, Chile, China, India, Mexico, and the United States of America. Drinking water, crops irrigated with contaminated water and food prepared with contaminated water are the sources of exposure. According to the World Health Organization (WHO), arsenic is among one of ten (10) chemicals of major public health concern. Environmental protection agency (EPA) and International Agency for Research on Cancer (IARC) has declared inorganic arsenic as a human carcinogen. Commonly, arsenic exists in both organic and inorganic forms, in which the inorganic compounds are more toxic, which exist in water either as arsenite (+3) or arsenate state (+5). Among them, the arsenite (As^{+3}) is several times more toxic than arsenate (As^{+5}) [4]. The EPA and WHO limit the concentrations of arsenic (in both forms) in drinking water to 10 ppb (parts per billion). The government and private agencies in all over the world are working in the area to reduce the contamination caused by arsenic and the major emphasis is given for fabrication of new technologies for their detection and removal.

There is variety of instrumental techniques available for the determination of arsenic including, atomic absorption spectrometry (AAS) [5], atomic fluorescence spectrometry (AFS) [6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7], inductively coupled plasma mass spectrometry (ICP-MS) [8] and voltammetry [9–12]. Some of these (e.g. ICP-MS) can serve as element-specific detectors when coupled to chromatographic separation techniques (e.g. HPLC and GC) [13]. A test kit based on the color reaction of arsine with mercuric bromide is currently used for groundwater testing in Bangladesh and has a detection limit of 50–100 $\mu g\ L^{-1}$ under field conditions [14]. Sometimes, oxidation of As (III) to As (V) is also used to decrease the content of more toxic As (III) from the water using chemical oxidants like permanganate, ozone, and chlorine were used. But these chemicals itself are very toxic and difficult to handle and need an extra step for their removal and disinfection [15]. Up to now, several research groups are working to develop new economic, rapid, technologies and/or techniques for detection and removal of arsenic, which should not depend on these above mentioned sophisticated, costly, slow and in-house laboratory techniques viz., membrane technology [16], ion-exchange methods [17], coagulation/precipitation [18] and adsorption [19]. Recently, the adsorption technique using carbon-based nanomaterials (basically carbon nanotube and graphene) become very popular for arsenic removal owing to their high efficiency, easy and simple process, less cost, good speed, regeneration ability and possibility to be applied in individual household systems [20]. Chandra et al. have synthesized water-dispersible magnetite reduced graphene oxide composites (M-RGO), which could be removed after the treatment of water with a hand-held magnet [21]. When graphene sheets are conjugated with magnetic nanoparticles, it not only enhances the adsorbing ability of graphene, but also improves their electrochemical properties [22]. Similarly, Ding et al. have also reported a Fe_3O_4@reduced graphene oxide (RGO) composite for removal of organic (dye i.e. rhodamine B) and inorganic contaminant [As(V)] from water [23]. Now days, the combination of graphene with carbon nanotubes (e.g. multi-walled) are gaining the interest of researchers owing to their enhanced electrochemical and adsorption capability, in comparison to the only MWCNT and graphene [20]. In short, both nanomaterials are complimentary to each other, for example, it is very difficult to disperse MWCNT in aqueous solution; however, MWCNT/GO hybrid aqueous suspension is highly stable. In the literature, various hybrids/composites of MWCNT and GO or RGO are reported and shows enhanced sensing [24,25], photocatalytic [26,27], electrocatalytic performances [28,29], water purification [30] and biomedical applications [31,32]. In this regard, Mani et al. reported a highly enhanced electrocatalytic performance of RGO–CNT hybrid [33]. Similarly, Palanisamy et al. have reported an MWCNT/graphene oxide (GO) hybrid biocomposite used for glucose estimation [34]. Previously, Vadahanambi et al. have reported a three-dimensional graphene-carbon nanotube-iron oxide nanostructure for the efficient removal of arsenic from contaminated water [20]. However, the role of these hybrid nanomaterials in the field of water purification is still under development stage. Recently, Sharma et al. have reported a historical perspective for magnetic graphene–carbon nanotube iron nanocomposites as adsorbents and antibacterial agents for water purification [35]. Therefore, in this work, we have tried to synthesize a new graphene-MWCNT hybrid as an adsorbent material for arsenic removal from water samples. It is a hybrid of two nanocomposites i.e. europium doped magnetic graphene oxide (Eu-MGO) and gold nanoparticle modified MWCNT (Au@MWCNT). In the first nanocomposite i.e. Eu-MGO, the magnetic nanoparticle was used for easy separation of arsenic using a simple, laboratory-used external magnet. In addition to this, it is already reported in several literatures that MNPs modified GO i.e. MGO possess higher surface area relative to the only GO, which may provide more conduction path and access for the electron-transfer of target analyte, resulting in enhanced electrochemical property of hybrid material [36]. Herein, the europium is used as a dopant to improve the electrochemical and magnetic properties of MGO. Rare-earth elements are an attractive class of dopant elements, as they give easily trivalent cations with peculiar magnetic and optical properties related to their f-electronic configuration [37]. Therefore, doping of hematite with rare-earth elements (basically Eu^{3+}) is very popular among the MGO-based nanomaterials [37]. Similarly, the incorporation of AuNPs in the nanohybrid provides two advantages: (1) the strong and specific bonding of AuNPs and any form of arsenic (III or V) via intermetallic compounds (Au–As) [38], which leads toward selective analysis of arsenic and (2) enhancement in electrochemical performance of nanohybrid. Therefore, it is assumed that the combination of these nanomaterials could able to provide a new nanohybrid material, which possesses the enhanced adsorption capability, electrochemical property and easy separation ability by the simple, hand-held magnet. The nanohybrid shows an excellent adsorption property for the both forms of i.e. As (III) and As (V), with significantly enhanced adsorption capacities of 320.0 $mg\ g^{-1}$ and 298.0 $mg\ g^{-1}$, respectively. These values are comparatively much higher than other MWCNT and/or GO-based previously reported composite. After modification onto the pencil graphite electrode, the proposed nanohybrid exhibit a very high sensitivity for As (III) and As (V) with a limit of detection 0.27 and 0.99 $\mu g\ L^{-1}$, respectively, using the square wave stripping voltammetric (SWSV) technique. Furthermore, removal of arsenic from real underground water by the adsorbent and their detection were also evaluated. Along with these, the nanohybrid is easy to recycle and reuse, make them a good candidate for water purification from arsenic contaminations. In this work, for the first time, we have proposed an adsorbent, which could be used for adsorption, removal, degradation and detection of arsenate as well as arsenite in the real samples.

2. Experimental section

The details of chemicals and instruments used in this work have been given in supporting information. The schematic representation showing the synthesis process of nanohybrid is shown in the Fig. 1.