Journal of Colloid and Interface Science 516 (2018) 364–370

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

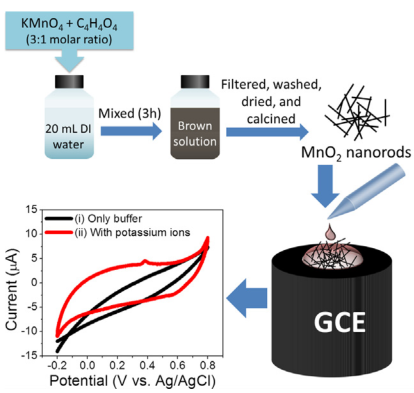
Regular Article

Synthesis of manganese oxide nanorods and its application for potassium ion sensing in water

Min-Sang Ahn [1], Rafiq Ahmad [1], Jin-Young Yoo, Yoon-Bong Hahn *

School of Semiconductor and Chemical Engineering, Nanomaterials Processing Research Center, Chonbuk National University, 567 Baekjedaero, Deokjin-gu, Jeonju-si, Jeollabuk-do 54896, Republic of Korea

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 November 2017
Revised 17 January 2018
Accepted 21 January 2018

Keywords:
Manganese oxide
Nanorods
Low-temperature
Sol-gel method
Potassium ion
Non-enzymatic sensor

ABSTRACT

Potassium is an important body mineral that control the cellular and electrical functions in the body. The potassium ion concentration change in human serum causes the risk of acute cardiac arrhythmia. Hence, it is important to monitor the potassium level in drinking water/food to control the intake and prevent its effect. This paper reports synthesis of manganese oxide (MnO_2) nanorods using low-temperature sol-gel method for the fabrication of non-enzymatic potassium ion sensor. The detailed investigation of the as-synthesized MnO_2 nanorods were carried out using field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The morphological and structural observations revealed that this method yield small nanorods with average length and diameters of about 210 ± 10 nm and 20 ± 3 nm, respectively. Further, as-synthesized α-MnO_2 nanorods were used to fabricate non-enzymatic potassium ion sensor following the deposition of α-MnO_2 nanorods on glassy carbon electrode (GCE) with the help of conductive binder. The electrochemical characterizations of fabricated non-enzymatic potassium sensor showed good sensing performance (i.e. sensitivity, selectivity, long term stability, and reproducibility). Moreover, applicability of the sensor to detect potassium ion in water samples were also demonstrated.

1. Introduction

Potassium dissolved in water with other electrolytes (i.e. sodium and chloride) is significantly important for cellular and

* Corresponding author.
E-mail address: ybhahn@chonbuk.ac.kr (Y.-B. Hahn).
[1] Authors contributed equally to this work.

https://doi.org/10.1016/j.jcis.2018.01.081

electrical functions. They are collectively called as "body minerals/electrolytes", which help to control and maintain the vital body functions. However, abnormal (excessively high or low) level of potassium ions can increase the risk of cardiovascular disease (heart arrhythmias), weakens health of bones, and hypokalemia [1,2]. As the abnormal levels of potassium ions are seriously harmful, there is need to control daily potassium intake and take an adequate amount of potassium containing foods and drinking water. It is recommended to take 2000–4000 mg of potassium in the daily diet. However, there are many processed foods that may contain high or lower levels of potassium. Also, it is important to make sure that drinking water contains normal level of potassium. Therefore, a simple and cost-effective detection technique is preferred for monitoring levels of potassium in water and food samples. Among the available methods (i.e. fluorescent sensor, chemosensors, luminescence, chromatography, and electrochemical based methods) for potassium detection, electrochemical based methods have advantages and are getting more attentions due to their small size, easy to operate, simple and low-cost fabrication process, and fast response time [3–9]. Hence, for developing suitable and high performance electrochemical based sensors, efforts are made to synthesize various nanomaterials with desired morphology and application specific properties [10–13].

Nanostructures of semiconducting metal oxides have been extensively used for various applications and it is well-known that the size, morphology, and specific surface area of synthesized structures govern their successful and potential application [14–18]. Recently, as an attractive transition metal oxide, manganese dioxide (MnO_2) offers different morphologies (i.e. nanowires, nanoneedles, nanotubes, nanofibers, nanoparticles, flower-like, and nanorods), which has been used in the field of catalysis, molecular adsorption, ion exchange, energy storage, and biosensor fabrication due to its attractive chemical, electrochemical and physical properties [19–23]. For example, Das et al. synthesized nanoscale hierarchical flower-like MnO_2 and used them to study photocatalytic activity during organic dyes degradation under natural sunlight irradiations [24]. Kim et al. utilized hierarchical nanoporous MnO_2 for adsorption of cationic dye molecules (methylene blue) with high dye removal efficiency [25]. Liu et al. synthesized hierarchical pine tree-like α-MnO_2 architectures using a facile one-step method and used for excellent catalytic performance in the catalytic combustion of dimethyl ether [26]. In another report, Cheng et al. also used α-MnO_2 nanostructures for catalytic combustion of dimethyl ether [27]. Yang et al. reported an inexpensive, facile, and scalable method to fabricate the hierarchical porous 3D structure using MnO_2 nanowires for supercapacitor applications [28]. Also, MnO_2 based hybrid materials are extensively used for different applications, i.e. Shafi et al. used α-MnO_2/h-MoO_3 hybrid metal oxide materials for potential application in electrochemical charge storage devices and as photocatalyst for dye degradation [29]. Borysiewicz et al. reported transparent supercapacitors using ZnO/MnO_2 nanostructured electrodes, where MnO_2 nanoparticles helped to get high capacitance [30].

Despite the successful use of MnO_2 nanostructures for different applications, its use for electrochemical based sensing applications has been less explored. Recently, Shu et al. fabricated electrochemical based biosensor using ultrathin MnO_2 nanosheets to detect hydrogen peroxide (H_2O_2) in living cells [31]. Hah et al. fabricated glucose sensors using MnO_2 nanowires, which showed peroxidase-like activity during non-enzymatic detection of glucose [32]. Wang et al. obtained enhanced biosensing activity for the detection of ractopamine and salbutamol using MnO_2 nanoflowers based sensing electrodes [33]. Vilian et al. used MnO_2 decorated reduced graphene oxide (rGO) sheets for the fabrication of a glucose biosensor [34]. Han et al. utilized genetically engineered phage-templated MnO_2 nanowires to fabricate electrochemical based glucose sensors and obtained excellent sensing performance [35]. However, further improvement in sensing performances, limit of detection, and response time of the MnO_2 based sensors are needed. Hence, the aim of this research work is to synthesize controlled morphology of MnO_2 for better electrocatalytic property. Additionally, the use of α-MnO_2 nanorods for non-enzymatic potassium sensors fabrication is not explored yet.

Here, we report the synthesis of α-MnO_2 nanorods in large quantity using low-temperature sol-gel solution method. The detailed morphological analysis of as-synthesized α-MnO_2 nanorods showed that the synthesized nanorods are small in size (average length = 210 ± 10 nm) and well-crystalline. In order to characterize the electrochemical properties of α-MnO_2 nanorods, non-enzymatic potassium ion sensing electrodes were fabricated using slurry of α-MnO_2 nanorods and binder. The electrochemical behavior of the as-fabricated electrodes was characterized for the non-enzymatic detection of potassium ions. The fabricated α-MnO_2 nanorods/GCE (working electrode) exhibited good sensitivity and selectivity, long term stability, reproducibility, and applicability for potassium ion detection in water samples.

2. Experimental details

2.1. Reagents

Potassium permanganate ($KMnO_4$, 97%), fumaric acid ($C_4H_4O_4$, ≥99%), potassium chloride solution, and Tris(hydroxymethyl)ami nomethane (Tris, pH 7.4) were purchased from Sigma-Aldrich. The ultra-pure deionized (DI) water obtained from μPURE HIQ (resistance = ∼18 MΩ cm) was used for all washing and solution making.

2.2. Synthesis of α-MnO₂ nanorods and preparation of sensor electrodes

α-MnO_2 nanorods were synthesized using sol-gel method (Fig. 1a). First, $KMnO_4$ and $C_4H_4O_4$ were added in 20 mL DI water in the molar ratio of 3:1, which formed a brown solution. After the exothermic reaction, solution was mixed for 3 h using magnetic bar at 800 rpm. Then, the obtained sol-gel solution was filtered under reduced pressure and obtained a black xerogel. Next, the xerogel was kept in an oven and dried overnight at 60 °C followed by calcined at 450 °C for 4 h.

Before preparation of sensor electrode, the glassy carbon electrode (GCE) having geometrical area of 0.07 cm^2 was cleaned using alumina slurries and Rayon polishing pad. Then, as-synthesized α-MnO_2 nanorods (0.05 g) and ethylene glycol (100 μL, as binder) were taken in an Eppendorf tube and sonicated for 10 min. The obtained slurry (2 μL) of α-MnO_2 nanorods were drop-casted on GCE surface and dried at 60 °C in an oven. All prepared electrodes were stored at room temperature for further study.

2.3. Characterizations

The morphology, elemental composition, and crystallinity of α-MnO_2 nanorods were analyzed using field-emission scanning electron microscopy (FESEM, SUPRA™ 40 V) with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, JEOL-JEM-2010). The crystalline phase of the α-MnO_2 nanorods was determined using X-ray diffractometer (XRD, Rigaku). To measure the electrochemical properties, an Ivium CompactStat.e from Ivium Technologies was used as electrochemical measurement station connected to computer. The conventional electrochemical cell contains three electrodes: Ag/AgCl (reference electrode), platinum (Pt, counter electrode), and prepared α-MnO_2 nanorods/GCE