Sensors and Actuators B 237 (2016) 81–89

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

An improved non-enzymatic hydrogen peroxide sensor based on europium functionalized inorganic hybrid material—Evaluation of optical and electrochemical properties

Dongri Jin [a], Kavitha Sakthivel [b,*], Sakthivel Gandhi [c], Bui The Huy [b], Yong-Ill Lee [a,b,*]

[a] Key Laboratory for Nature Resource of Changbai Mountain and Functional Molecules (Yanbian University), Ministry of Education, Yanji 133002, China
[b] Department of Chemistry, Changwon National University, Changwon 641-773, Republic of Korea
[c] Department of Physics, Changwon National University, Changwon 641-773, Republic of Korea

ARTICLE INFO

Article history:
Received 15 March 2016
Received in revised form 2 June 2016
Accepted 14 June 2016
Available online 15 June 2016

Keywords:
Mesoporous
Europium
Optical
Electrochemical
Hydrogen peroxide

ABSTRACT

We have studied the electrochemical and optical properties of europium; a rare-earth ion functionalized ordered hybrid mesoporous silica material and evaluated its potential application for a non-enzymatic hydrogen peroxide sensor. Europium ion was introduced into the organic-inorganic hybrid mesoporous channels through complexation method. The modifications were confirmed by FT-IR whereas; the structural and textural properties of mesoporous silica are evaluated using FE-SEM, FE-TEM, and nitrogen physisorption isothermal analysis. The optical properties such as the excitation and emission behavior of rare-earth ion introduced ordered mesoporous silica was investigated using photoluminescence spectroscopy. The material is also evaluated for its electrochemical properties by the way of sensing H_2O_2 in aqueous samples by using cyclic voltammetry and chronoamperometry. It showed a linear range between 1.0 and 1400 μM. The response time of 4 s is also observed with a detection limit of 0.5 μM. It showed a good reproducibility, high stability and anti-interference ability which are considered vital for any electrochemical applications. The results obtained were quite challenging and thus, it has been applied for the detection of hydrogen peroxide in the presence of commercial disinfectant sample with satisfying results.

1. Introduction

Hydrogen peroxide is involved in various industrial processes namely bleaching, disinfection etc., due to its strong reducing and broad spectrum activity against pathogens and thus, it offers considerable safety with its adequate neutralization. Detection and quantification of a wide variety of compounds such as hydrogen peroxide, by the way of suitable molecular probes using suitable techniques, is an area where immense interests have been put in [1,2].

In the similar lines lanthanide ions have drawn a considerable attention owing to their potential for the detection of a number of cations, anions and the neutral species [3–5]. Increasing interests in the chemistry of lanthanides have been observed in the recent years and europium is one among the rare reactive earth elements. It plays a vital role in industry, materials science and life sciences and this can be ascribed to its unique electrical and optical properties [6–10]. The architecture of the lanthanide ion becomes highly important, where the versatility of the mesoporous silica has been utilized. Mesoporous silica plays a vital role in various fields *viz.*, catalysis, adsorption, phosphors for LED, sensors, biological tracers, MRI, theranostics etc. [11–20]. Its divergent application may be attributed to its various intrinsic features namely high surface area, tunable pore size, high pore volumes, hydrothermal stability and along with its biocompatibility [12]. The mesoporous materials with the help of its excellent properties can contribute to the facile transport of electrons and thus promote the electrochemical response [16].

Several strategies are generally adopted such as optical, chemiluminescence, electrochemical etc., for the detection of a wide variety of compounds including hydrogen peroxide, superoxide, xanthine etc. [21–23]. Among all these techniques, electrochemical methods have attained more interest due to its high sensitivity, simple handling, low operating expense, rapid output and its eco-friendliness when compared with the other strategies [24–29].

* Corresponding authors at: Department of Chemistry, Changwon National University, Changwon 641-773, Republic of Korea.
E-mail addresses: Kavithandavan@gmail.com (K. Sakthivel), yilee@changwon.ac.kr (Y.-I. Lee).

http://dx.doi.org/10.1016/j.snb.2016.06.078
0925-4005/

To date, there are some reports employing electrochemical technique based on $FeMoO_4$, copper, iron-silver core-shell structure, or graphene-silver hybrid as sensing materials for detecting hydrogen peroxide. Although, those methods exhibit good sensitive and selectivity there exists some deficits in those techniques, such as low reproducibility and the loss of materials from electrodes. In order to overcome these lacunas remarkable challenges has to be attempted.

Here, we have developed rare-earth especially europium introduced ordered mesoporous silica. The spherically distributed mesoporous MCM-48 (MPS) was synthesized and modified with amine terminal group where 2,6-pyridine dicarboxylic acid chloride (PDC) was linked into it. The europium ion was introduced due to the deprotonation of PDC and chelation between Eu^{3+} ions and carbonyl group of PDC. The optical and electrochemical properties of europium ion functionalized ordered mesoporous silica were analyzed. Only a few works were reported on Eu^{3+} loaded mesoporous silica. For example, Meng's group [30] used a wet impregnation method to prepare a Eu^{3+}-loaded MCM-48. Owning to doping of Eu^{3+} to mesophase silica thin film, the rare earth complex exhibited high luminescent intensity [31]. But their study focused only on the investigation on the luminescence properties of the material. Zou's group used $Eu(DPIQ)(TTA)_3$ complex into MCM-41 for oxygen sensing based on fluorescent quenching effect [32].

In this work, we have made use of Eu^{3+} loaded SBA-15 type mesoporous silica (MPS-A-PDC-Eu^{3+}) specifically for sensing applications. Initially, the —OH functionalities of MPS had been modified with amine using APTES and PDC was linked with it. The rare earth ions were coordinated with MPS using PDC. This hybrid material was synthesized using a simple complexation method where, PDC aids for the increased loading of Eu^{3+}. So that the large number of Eu^{3+} in the sample can efficiently aid to sense the hydrogen peroxide. As an efficient hydrogen peroxide sensor it showed a wide linear range, rapid response time, good anti-interference ability, high stability and reproducibility. Therefore, all these characteristic properties substantiate the efficacy of the modified electrode. Typically, it has been applied for the determination of hydrogen peroxide in the presence of commercial disinfectant sample with satisfying results. To the best of our knowledge the optical properties and electrochemical sensing studies of Eu^{3+} ions on a mesoporous silica modified electrode has not been reported so far.

2. Materials and methods

2.1. Reagents and materials

Analytical grade cetyltrimethyl ammonium bromide (CTAB) and tetraethoxysilane (TEOS), Europium nitrate, PDC, Nafion solution (5 wt%) were purchased from M/s Sigma Aldrich Co, Ltd. Glacial acetic acid was purchased from Duksan pure chemical, Kyungki and sodium acetate (anhydrous) was purchased from Samchun pure chemical Co., Ltd., Korea and used for the preparation of acetate buffer. Hydrochloric acid was purchased from Daejung Chemicals, Korea. All solutions were prepared using deionized water. All the chemicals are used as such without further purification.

2.2. Characterization techniques

The morphology and porous structure of the MPS and its derivatives were characterized by using field emission scanning electron microscopy (FE-SEM) (Tescan, MIRA IILMH, Brno, Czech Republic) and field emission transmission electron microscopy (FE-TEM) (JSM 2100F JEOL, Japan), respectively. The surface area and porosity of the hybrid materials were derived from Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) isotherms which are calculated using nitrogen physisorption analysis (Autosorb-1, Quantachrome, USA). Cyclic voltammetry experiments were performed using a galvanostat (VSP Instruments, EC lab Version 9.41, Bio-logic science instruments). Cyclic voltammograms (CV) were recorded at a scan rate of 5 mV/s in 10 mL of acetate buffer solution (pH 4.5). All measurements were recorded using a three electrode system comprising of various modified electrodes as working electrode, Ag/AgCl (Sat. NaCl) as reference electrode and platinum wire as the counter electrode. Sonication was carried out using bath sonicator (Bransonic, USA) of 100 W, 42 kHz.

2.3. Synthesis of ordered mesoporous silica

Mesoporous MCM-48 (MPS) was synthesized based on our previous reports [33] in which 2.5 g of CTAB was dispersed in 100 g of deionized water and 50 mL of ethanol. The solution was kept under stirring for about 30 min to make it homogeneous and the 10 mL of $NH_{3(aq)}$ (32 wt%) was added to it. The silica source (TEOS) was introduced into it after 10 min of stirring at room temperature. The as-prepared solution was then maintained under the same condition for 24 h and the precipitate was filtered off and washed twice with ethanol and water. Finally, the precipitate was dried under vacuum at 60 °C followed by calcination (at 550 °C for 6 h) for the removal of organic moieties.

2.4. Modification of MPS

The calcined MPS was dispersed in toluene by a simple sonication process. Later, (3-aminopropyl)triethoxysilane (APTES) was introduced for replacing hydroxyl terminal groups of MPS to amine terminals. It was then kept under reflux condition for overnight and filtered. The amine terminated product was washed thoroughly with toluene, ethanol, and water, sequentially and kept under vacuum at 60 °C for 12 h for it to be dried. The dried sample containing the amine terminated MPS-A was then taken in a round bottomed flask and dispersed in 10 mL of pyridine to which PDC-ether solution was added slowly and stirred under inert atmosphere for 4 h at room temperature. The PDC loaded material was separated through centrifugation after subsequent washing with pyridine and water. The modified material MPS-A-PDC was dried under vacuum for 12 h.

Europium was introduced to the MPS-A-PDC sample using a simple complexation of Eu^{3+} with PDC [1,34]. The MPS-A-PDC sample was dispersed in ethanol and stirred at room temperature in which the ethanolic solution of $Eu(NO_3)_3{\cdot}H_2O$ was added slowly. This was maintained under the same condition for another 4 h and finally centrifuged to separate the MPS-A-PDC-Eu^{3+} hybrid material.

2.5. Preparation of the electrode

The sample for the modification of electrode is prepared as follows. Briefly, the appropriate amounts of sample, namely MPS and MPS-A-PDC-Eu^{3+} samples, were added the 100 μL nafionic solution. The mixture was ultrasonicated for three minutes using a bath sonicator (Bransonic, USA) of 100 W, 42 kHz. Thus, the above prepared nafionic solution forms the coating for working electrode.

2.6. Fabrication of the GCE electrode surface for electrochemical studies

To obtain a clean and reproducible surface, the gold electrode was polished with drops of 1 μM polishing diamond using diamond polishing pads and with 0.05 μM alumina using alumina polishing pad. It was then ultrasonically cleaned with 1 mL acetone and then