Detection of Heavy Metal Ions in Water by PAA/CNTs Nanosensor

Mohamed Shaban a,*, Amin Hussein a, b

a Nanophotonics and Applications (NPA) Lab, Department of Physics, Beni-Suef University, Beni-Suef 62111, Egypt
b Department of Chemistry, Beni-Suef University, Beni-Suef 62111, Egypt

ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 26 December 2012
Accepted 27 December 2012
Available online 31 December 2012

Keywords:
Nanosensors
PAA
CNTs
SERS
Heavy metal ions

ABSTRACT

A novel technique for rapid and ultrahigh sensing of heavy metals in water based on Porous Anodic Alumina (PAA) membrane functionalized with randomly distributed Carbon Nanotubes (CNTs) of 20 nm diameters is introduced. The proposed sensor demonstrated high selectivity between three different heavy metals (Hg, Cd, and Pb) with concentrations varied from 1 to 100 ppb. The platform provides an instant and fully integrated detection method that is based on in-situ surface-enhanced Raman scattering (SERS) spectroscopy. The observed Raman enhancement is due to the excitation and interference of laser waves, which are highly dependent on the type and concentration of the heavy metal. As a result, the proposed sensor is an unprecedented fully integrated Nano platform that is easy to fabricate.

© 2012 Journal of Chemica Acta

1. Introduction

Water contamination by heavy metals is a common problem encountered in many countries due to undue deposition of metal-rich mining, agricultural, industrial and urban wastes in water resources. This problem has many health and socio-economic impacts and therefore, there is a dire need for a fast, reliable and highly sensitive sensor networks for continuous detection and monitoring of toxic heavy metal levels in soil and water resources. Nanosystems could provide unprecedented detection solution of heavy metal and toxic elements in aqueous media by combining ultrahigh sensitive nanostructures with the sample manipulation and signal detection attributes of porous membranes.

Carbon nanotubes (CNTs) are attracted much interest owing to their novel commercial nanoelectronic applications such as flat panel displays, ultra-sensitive chemical and electromechanical sensors, and hydrogen storage devices [1–4]. In addition, the applications of CNTs for the removal of hazardous pollutants from gas streams and aqueous solutions [5–8] have being studied extensively because of their highly porous and hollow structure, large specific surface area, light mass density and strong interaction between CNTs and pollutant molecules. A number of experimental studies have already been carried out on the adsorption of heavy metal ions on single wall and multiwall CNTs [7–10]. CNTs have been synthesized by numerous techniques, such as arc discharge, laser ablation, plasma-enhanced and chemical vapor deposition (CVD) of hydrocarbon gases (methane, ethane and acetylene) at rather high temperature over a catalytic material [11-14]. The deposited CNTs may be semiconductors, metals or dielectrics where the band gap of semiconducting nanotubes can be tuned by changing the tube diameter [15]. Moreover, deposition of carbon nanotubes (CNTs) inside the pores of Porous Anodic Alumina (PAA) membranes have gained much attention in recent years due to their potential use as surface enhanced Raman scattering (SERS) substrate [16]. Then the position of CNTs on the membranes will show a significant influence on the properties of the structures, especially with respect to sensor applications. For instant, the CNTs on the outer surface of the structure have more possibility to touch with the reactant than those inside. Thus, it is meaningful to load the CNTs up on the outer surface of the PAA membrane. As a result CNTs can be used to guide, enhance, emit, and modify optical fields, phenomena that can used for novel applications such as sensors based on SERS [17–19]. In this work, an efficient method is proposed to coat the walls of the PAA membrane with random array of CNTs. This is achieved using CVD method. In this paper, we propose an ultrahigh sensitive sensor for the detection of small concentrations of heavy metals ions (Hg2+, Pb2+, Cd2+) in water. The sensor is based on in situ surface-enhanced Raman scattering (SERS) spectroscopy.

2. Experimental procedure

2.1. Preparation of Catalyst

PAA membrane was prepared by combined two-step anodization and pore widening method [20]. PAA membrane

* Corresponding author. Tel.: +20-111-212-4309; +20-127-449-3440 fax: +2-082-233-4551; e-mail: mssfadel@aucegypt.edu, mssfadel@yahoo.com
was functionalized with CoFe$_2$O$_4$ nanoparticles. 0.5M Fe (NO$_3$)$_3$ and 0.5 M Co (NO$_3$)$_2$.6H$_2$O were mixed at 1:1. Then the PAA membrane was immersed in the solution and left in ultrasonic for 1h. The obtained membrane was dried in oven at 50°C for 1 h.

2.2. Preparation of CNTs

The C$_2$H$_2$ chemical vapor deposition was carried out in a ceramic tube equipped with a temperature and gas flow controller. The N$_2$ gas was passed for 10 minutes over the functionalized PAA membrane at 600°C. N$_2$/C$_2$H$_2$ (5:1 V/V) mixture was then passed to the system for 50 minutes. Passing N$_2$ gas was then continued through the reaction chamber until the temperature of the tubular furnace dropped. The prepared CNTs/PAA membrane was drying in oven at 120°C.

2.3. Sample Characterization

A scanning electron microscope (SEM) and EDX were used to characterize the morphologies and structures of the PAA membranes and CNTs. After injecting very small amounts (i.e., < 0.1 µl) of water contaminated with heavy metals, the sensing principle is based on heavy metals detection by using surface-enhanced Raman scattering (SERS) spectroscopy. The SERS spectrum was measured over the PAA and CNTs/PAA samples ($\lambda_{ex}$= 532 nm, P = 50 mW, acquisition time = 20 s).

3. Results and discussion

3.1 Nanoporous Anodic Alumina (PAA) Membrane

The surface properties of the blank PAA membrane were characterized by SEM and EDX. Figure 1(a) illustrates a typical top-view SEM image of PAA membrane anodized for 5 min and pore widened for 70 min. This figure shows hexagonally-aligned nanopores aligned vertically on Al substrate. The pore diameter is about 70 nm, the interpore distance is 100 nm, and the pore density is approximately $1.42 \times 10^{10}$ cm$^{-2}$. The EDX pattern in Fig.1 (b) shows the signals of Al and O elements. The quantitative results were 52% Al and 48% O for Al$_2$O$_3$. The remained of the Al signal comes from the Al substrate.

Figure 1: (a) Top view SEM image and (b) EDX of PAA membrane anodized for 5 min and pores widened for 60 min.

3.2 PAA-CNTs Coated Morphology

In order to functionalize PAA membrane with CNTs, PAA was coated with CNTs by CVD. Figure 2 (a and b) shows top view SEM images of CNTs/PAA membrane at different magnifications. As shown in Fig.2, the active dots on the top surface of PAA have acted as seeds for growing long CNTs of diameter ~ 20 nm. Figure 2(c) shows Raman spectrum of multiwall CNTs. This figure shows two significant bands having peaks at about 1582 cm$^{-1}$ and 1354 cm$^{-1}$. The peak at 1582 cm$^{-1}$, referred to as ‘G’ band, is a tangential vibrational mode of graphene sheet. A distinct band at 1354 cm$^{-1}$ (D band) is related to the amorphous carbon or defects in the graphene sheet.

Figure 2: (a and b)Top view SEM images of PAA membrane coated with randomly distributed CNTs of 20 nm diameter and (c) Raman Spectrum of multiwall CNTs.

Figure 3: Demonstrating sensitivity. Raman Spectra of 0.1 µL of Cd solution on CNT/ PAA membrane.
3.3 Sensor sensitivity

In order to realize SERS measurements, the Raman spectrum was measured by a Raman microscope with 514 nm excitation laser and spot size 1µm. Sensitivity of PAA/CNTs sensor is demonstrated in Fig. 3 where different concentrations of Cd ranging from 1 ppb to 100 ppb were measured. This figure shows significant increase in the detected signal with increasing the concentration. The trapping of PAA/CNT with adsorbed heavy metals provides a performance improvement because of the increase in the number of analyte molecules in SERS-active hot spots within the detection volume in addition to the excitation and interference of optical waves within this volume.

3.4 Test of Selectivity

The proposed sensor demonstrated high selectivity between three different heavy metals (Hg, Cd, and Pb) at 20 ppb concentration (see Fig. 4). In this case, the accumulation of different analyte molecules and the additional formation of hot spots are demonstrated in the response of Pb with the highest Raman intensity and guide peak at 1342 cm⁻¹, whereas Hg shows medium intensity and guide peak at 1330 cm⁻¹ and Cd shows the lowest Raman intensity and guide peak at 1334 cm⁻¹.

![Figure 4: Demonstrating selectivity. Raman Spectra of 0.1 µL of Hg, Pb and Cd 20 ppb solution on CNT/PAA membrane.](image)

4. Conclusion

For direct, simple, and cheap monitoring of heavy metals with concentrations varied from 1 to 100 ppb, CNT/PAA sensor has been developed. The metal detection involves rapid collection of dispersed metal-bound nanoparticles from a sample solution at the surface of the sensor, followed by the SERS measurements. The sensor was evaluated as a function of different concentrations and different elements.

References