Nanoporous chromium thin film for active detection of toxic heavy metals traces using surface-enhanced Raman spectroscopy

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Abstract

In this work, nanoporous Cr thin film was designed by a novel method for the detection of toxic heavy metals based on surface-enhanced Raman spectroscopy. Nanoporous Cr thin film has been deposited on an aluminum substrate through a developed etching/DC electrodeposition technique of the hexagonal porous anodic alumina (PAA) template/Cr nanoparticles, respectively. The structures and morphologies of the fabricated samples were investigated by different characterization tools. The FE-SEM illustrates nanoporous Cr particles of rough surfaces and different sizes are formed on the Al substrate. Also, there are ultrafine Cr nanoparticles covered the surface of the Cr nanoporous film that can act as hot-spots during the detection of heavy metal ions. The proposed sensor established high selectivity at low concentrations between different heavy metal ions (Pb²⁺, Hg²⁺, Cd²⁺). Also, it showed excellent selectivity towards Pb²⁺ over the other metal ions. Hence, this category of sensors could be applied for sensitive determining of Pb²⁺, Hg²⁺, Cd²⁺ in contaminated water.

Introduction

In the whole world, drinking water contamination by toxic elements such as Pb²⁺, Hg²⁺, and Cd²⁺ is a big issue, which has many health and socio-economic impacts [1–3]. Hence, a quick and extremely sensitive device is required for identifying heavy metals traces in polluted waters. Raman scattering is a spectroscopic method for the detection of pollutants in water. Raman spectroscopy is a non-contact and non-destructive technique that analyzes only a small volume of a substance without requiring any preparation [4, 5]. Raman spectrum has a wide range of applications for both qualitative and quantitative chemical and biological analyses because of its high selectivity and low absorption of aqueous solution [6, 7]. Also, it can be used in identification the carbon nanomaterials such as graphene and carbon nanotubes [8–10]. This is due to the Raman spectrum provides information about the rotational and vibrational transitions modes of the molecule. Hence, it serves as a fingerprint for each material.

Unfortunately, the intensity of the Raman signal is relatively weak [11]. Raman signals can be enhancements by adsorbed analyte onto a rough metal surface with a nanostructure texture [12]. This method is identified as surface-enhanced Raman spectroscopy (SERS). The fabrication of the substrates for SERS with high reproducibility, good uniformity, inexpensive, and long-term stability is a very big challenging.

In recent years, the porous anodic alumina (PAA) template has great attention as a template for the fabrication of different nanostructures [13–18]. This is related to its simple technology, high-throughput, inexpensive, good stability and controllability. Porous anodic alumina (PAA) is a self-organized material with a highly ordered 2D hexagonal porous structure. PAA was fabricated by electrochemical oxidation (anodization) of high purity aluminum in acidic electrolytes. Metal nanoparticles can be deposited on the surface of PAA templates and used them as sensors based on SERS [19–22].

On the other hand, chromium (Cr) has attracted the attention in electronic and spintronic industries due to its magnetic, optical and electric properties [23]. Cr is a typical transition metal element with abundant electrons in the outer shell of its electronic configuration [24]. It has surface plasmons that improve the interactions...
between the incident electromagnetic waves and analytes. Moreover, the sizes of Cr grains are tiny with low surface mobility and high chemical stability [25]. In addition, Cr is an oxygen active material leading to very stable nucleation centers and high adhesion property which allows the deposition of the homogeneous surface with a huge surface/volume ratio. Therefore, Cr is a good material for designing nanostructured SERS substrates. In this study, an innovative etching/DC electrodeposition technique has been developed to grow Cr nanostructures on the surface of Al substrates. The fabricated Cr/Al template is used as ultra-high sensitive sensors based on SERS spectroscopy to detect small levels of Hg²⁺, Pb²⁺, and Cd²⁺ ions in aqueous media.

**Methods and experimental details**

**Fabrication of PAA template**

A uniform PAA template was fabricated by using a two-step anodization technique. The 1st and 2nd anodizations were carried out for 5 h and 8 min, respectively, in 0.3 M C₂H₂O₄ at 42 V and 9 °C. The applied voltage was decreased from 42 to 12 V with a rate of 1 v min⁻¹ and then maintained at 12 V for 12 min to thin the barrier layer of PAA. The pore widening was performed at room temperature in 6 wt% H₃PO₄ for 50 min.

**Fabrication of nanoporous Cr film**

The Cr nanoporous thin film was formed by the electrodeposition at a very high current density (J = 4000 mA cm⁻²) for 45 min@ 60 °C. The PAA substrate was used as a cathode while the Pt sheet acted as an anode. Chromic acid (25.0 g CrO₃) and sulfuric acid (0.1 ml H₂SO₄) were dissolved in 100 ml distilled water and used as an electrolytic bath.

**Characterization techniques**

Morphological studies of the PAA template and Cr nanostructures are scanned using field emission (FE)-scanning electron microscope (ZEISS Gemini SEM). Energy dispersive x-ray (EDX) spectroscopy (Oxford ISIS 300) was used to observe the chemical compositional of nanostructures. X-ray diffraction (XRD, PANalytical Philips X’Pert Pro MRD) was used to study the crystal structure of the fabricated nanostructured films.

**SERS measurements and heavy metals detection**

A small drop (0.5 μl) of ion-contaminated water (Pb²⁺, Hg²⁺, and Cd²⁺) was injected into the top surface of the nanoporous Cr substrate at the room temperature. Raman scattering spectroscopy was used to detect heavy metals ions. The SERS measurements were performed using Enwave Raman microscopy provided with a 532 nm laser of spot 1 μm. For each run, 532 nm laser beam with power P = 100 mW is incident on the ion-contaminated water positioned above the surface of the substrate and data collected for 20 s.

**Results and discussion**

**PAA template morphology**

Figure 1 shows the images of the PAA template anodized in oxalic acid for 8 min and pore widened for 0.84 h. These images display nanopores arrays with hexagonal distribution and aligned vertically on the Al substrate. The nanopores of PAA have a high uniformity in their shape, height, diameter, and density. These images display nanopores arrays with hexagonal distribution and aligned vertically on the Al substrate. The fabricated Cr/Al template is used as ultra-high sensitive sensors based on SERS spectroscopy to detect small levels of Hg²⁺, Pb²⁺, and Cd²⁺ ions in aqueous media.

The XRD and EDX techniques were used for the analysis phase structure and chemical composition of the PAA. The XRD diffraction chart in figure 2(A) shows that the crystal orientation of PAA forms an aluminum oxide with a cubic structure and a lattice constant a = b = c = 0.4 nm. The sharp peak suggests that the well crystallized PAA template can be easily produced by using two steps anodization method. The (400) plane is the preferred orientation which appeared in the chart at 2θ = 44.75° (card No. 77-0403). The diffraction peak at 2θ = 38.52° corresponds to (311) crystal plane. There are no extra traces peaks corresponding to Al or C. The EDX pattern of the PAA illustrates that signals from O and Al only observed (figure 2(B)). The quantitative analysis for the alumina is 37.84% O and 62.25% Al. No impurities of S, Cr or C are detected by the EDX pattern. This is indicating that the PAA is pure Al₂O₃.

**Cr nanopores thin film**

Cr electrodeposition on the PAA/Al template was carried out at a 4000 mA cm⁻² and 60 °C for deposition time 0.75 h. The Cr film formed on the Al substrate in two steps. Firstly, the electrochemical etching of the pore walls
of the PAA and the barrier layer at the bottom of some pores due to the presence of H$_2$SO$_4$ in the electrolyte. Secondly, the deposition of Cr nanoparticles on the Al substrate as a consequence of the full etching of the barrier layer of PAA. Figures 3(A)–(D) shows four different magnifications of the electrodeposited nanoporous Cr film on the Al after 0.75 h.

The surface of the substrate was totally covered by continuous Cr film, which indicates the homogeneous deposition of this film. The Cr film is composed of many aggregates and accumulates of Cr micro/nanoparticles randomly distributed on the Al substrate. These Cr nano/microparticles have semispherical shapes with different diameters. The diameters of Cr particles are ranged from 5.32 to 10.74 μm. The high magnification FE-SEM images show that the Cr particles have a rough surface which contains very small nanopores with irregular shapes. The larger number of Cr particles with nanopores represents highly surface area which is an advantage for sensor enhancements. Figure 3(D) shows that the surface of the Cr nanoporous film is covered with ultrafine Cr nanoparticles (average diameter 2.77 nm). These nanoparticles can act as hot-spots during the detection of heavy metal ions by Raman measurements.

The nanoporous Cr film is very thick. It has a thickness of about 30 μm as shown in the cross-sectional FE-SEM image (figure 3(E)). This is due to the electrodeposition occurs at very high current density (4000 mA cm$^{-2}$) and high temperature (60 °C) for a long time (45 min).

The Cr/Al film was analyzed by EDX as shown in figure 4 to verify the chemical composition of the fabricated nanostructure. The EDX chart indicates the signals of Cr, Al, and O elements. There are four peaks relevant to Cr. The quantitative results were 89.94% Cr, 3.01% Al, and 7.05% O. This shows the high purity of the manufactured nanostructures.
Sensing properties and SERS measurements for Cr/Al
Raman spectroscopy is an optical technique to study the vibrational, rotational, and other low-frequency modes in the adsorbed molecules yielding that give structural information on the molecules and their local interactions [26]. The SERS is a surface-sensitive method characterized by increasing the Raman intensity signal by the molecules that adsorbed on roughened nanostructured noble metallic surfaces.

To perform SERS measurements, the Raman scattering was scanned by using a Raman microscope of a green laser source (532 nm). The Cr/Al nanopores film was loaded with 0.5 μl of water contaminated with Cd2+, Hg2+, and Pb2+.

Test of selectivity
The proposed sensor established high selectivity at low concentrations between different heavy metal ions. Figure 5 displays Raman spectra of Hg, Cd, and Pb solutions on Cr/Al substrate at 4 ppm concentration. In this case, the accumulation of various analyte molecules is revealed in the response of Pb2+ with the highest Raman intensity whereas Hg2+ shows the medium intensity and Cd2+ shows the lowest Raman intensity. There are three peaks appear for each metal in the range from 700 to 1200 cm⁻¹ as seen in figure. The highest peak (peak II) is located at 1054, 1052, and 1050 cm⁻¹ for Cd2+, Hg2+, and Pb2+, respectively. This may be due to the peak position depends upon the vibrational energy states which related to the chemical structure of the molecules responsible for the scattering [27, 28]. Raman spectrum of Cr/Al uploaded with 0.5 μl after mixing the three
heavy metal ions (Hg$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ solutions) at concentration 4 ppm is shown in figure 5(B). As seen in this figure, the peak II is located at 1050 cm$^{-1}$ which matches to the same peak for Pb$^{2+}$.

Sensor sensitivity

The sensitivity of the Cr/Al sensor is illustrated in figure 6, whereas Pb$^{2+}$ ions with different concentrations from 1 to 10 ppm were applied. Figure 6(A) displays Raman spectra of Pb$^{2+}$ solution on Cr/Al substrate. A significant increase in the Raman peak with increasing concentration can be seen in this figure. The trapping of adsorbed heavy metals on the Cr/Al rough surface improves the scattering performance due to an increase in the number of analyte molecules in SERS-active hot-spots within the detection volume as well as the interference and excitation of light waves within this volume. The SERS enhancement is ascribed to two mechanisms: electromagnetic and chemical enhancement [29, 30]. The fabricated Cr nanostructures have smaller nanopores which lead to strong coupling and resonance (electromagnetic enhancement). Moreover, the attached Cr nanoparticles on the nanoporous film’s surface (figure 3(D)) were led to the creation of extra hot-spots that causes the accumulation of the analyte molecules (chemical enhancement). This reveals the dependence of the vibrational energy mode on the molecule’s structure and the high sensitivity of the manufactured Cr/Al substrate. The intensity of the detected signals is therefore increased.

Figure 6 (B) displays the variation of the logarithmic intensity of peaks I, II and III with different Pb$^{2+}$ concentrations. According to the logarithmic fitting of the experimental data, solid lines of figure 6(B), the logarithmic of peaks I, II and III intensities are given by the empirical equations:

$$\text{Log (intensity of peak I) } = 0.0416 C_{\text{Pb}^{2+}} + 2.2420, \quad (R^2 = 0.983)$$

$$\text{Log (intensity of peak II) } = 0.0380 C_{\text{Pb}^{2+}} + 2.4331, \quad (R^2 = 0.988)$$
Log (intensity of peak III) = 0.0427 C_{Pb^{2+}} + 2.3682, \quad (R^2 = 0.994)

Where $C_{Pb^{2+}}$ is the Pb$^{2+}$ ions concentration in ppm and $R^2$ is the correlation coefficient between the experimental and the fitting data.

Based on the fitting equations, the relationship between the logarithm of Raman peak strength and Pb$^{2+}$ ion concentration can be used to determine the Pb$^{2+}$ ion concentration in drinking water by using the intensity of Raman peak. The slope of the line and the value of the correlation coefficient ($R^2$) for peak III are higher than the other peaks (I and II). Therefore, this peak provided the highest sensitivity with the best fitting.

**Conclusion**

This work presents an accounting technique of heavy metal ions in aqueous solutions based on the SERS method. Sensitive SERS counting of Pb$^{2+}$, Cd$^{2+}$, Hg$^{2+}$ was performed using a Cr nanoporous thin film electrodeposited on Al. The selective heavy metals counting using the proposed Cr nanoporous structure was explored for Pb$^{2+}$, Cd$^{2+}$, Hg$^{2+}$. Significant peaks shifts were observed in the SERS data. It showed good selectivity toward Pb$^{2+}$ over other metal ions at very low concentrations (1–10 ppm). The enhancement in the Raman signal is due to electromagnetic and chemical enhancement. Then, the proposed sensor offered a simple and cheap method for selective and sensitive counting of heavy metal ions at low concentrations in water.

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