Fabrication of silver nanoparticles decorated anodic aluminum oxide as the SERS substrate for the detection of pesticide thiram*

TAN En-zhong (谭恩忠)**

Department of Mathematics and Physics, Beijing Institute of Petrochemical Technology, Beijing 102617, China

An efficient surface-enhanced Raman scattering (SERS) substrate is developed based on silver nanoparticles decorated anodic aluminum oxide (Ag/AAO). The AAO templates were fabricated using a two-step anodization approach, and silver nanoparticles (AgNPs) were obtained by thermal decomposition of Ag nitrate in AAO. The structure of Ag/AAO hybrid substrate is characterized by scanning electron microscopy (SEM). The results show that the as-prepared SERS substrates consist of high-density AgNPs with sizes of tens of nanometers. The AgNPs are adsorbed on the surface of AAO template in the form of network structure which is called "hot spot". The SERS enhancement ability of the nanostructure is verified using thiram as probing molecules. The limit of detection is as low as 1×10^{-9} mol/L. The results indicate that the as-prepared substrate possesses excellent SERS sensitivity, high stability and uniformity enhancement.

Surface-enhanced Raman scattering (SERS) has attracted more and more attention due to its high sensitivity and the ability to provide fingerprint information of the target molecules. Particularly, it has shown outstanding sensitivity in detecting trace of analytes, sometimes even up to single molecule detection level[1-7]. However, this technique has not been widely used in practical applications. One major problem is lack of SERS substrates with high stability and sensitivity which can generate reproducible SERS spectra. Therefore, for obtaining an ideal SERS enhancement as well as high sensitivity, high stability and uniformity should be both taken into account. The template synthesis method has been shown to be a selectable approach for fabricating SERS substrates. The anodic aluminum oxide (AAO) membrane with satisfactory physical stability and chemical inertia has attracted a great deal of interest as templates in the preparation of various nanostructures, such as nanotubes, nanowires, nanorods and nanoparticles[8,9]. In this paper, we develop an easy and inexpensive method to fabricate high-density silver nanoparticles (AgNPs) decorated AAO (Ag/AAO). A lot of "hot spot" structures are obtained with uniform distribution due to AgNPs loaded on AAO in the form of network structure.

High purity aluminum was obtained from Beijing Iron and Steel Institute. Silver nitrate and thiram were purchased from J&K, Co., Ltd. Oxalic acid, phosphoric acid, chromium trioxide and sulfuric acid were purchased from Beijing Chemical Reagent Company. All the reagents except aluminum were used as received without further purification. All aqueous solutions were prepared using deionized water.

Porous AAO template was prepared by a two-step anodization method. Briefly, the aluminum foil was first rinsed with acetone in an ultrasonic bath for 10 min. In electropolishing, the aluminum was immersed in a mixed solution of sulfuric acid (mass percent of 20%), phosphoric acid (mass percent of 80%) and chromium trioxide (mass percent of 2%), and used as the anode at 9 V and 90 °C for 10 min. Then the foil was anodized first in 0.3 mol/L oxalic acid at 40 V and 4 °C for 8 h, and then was immersed in a mixture of phosphoric acid (mass percent of 6%) and chromic acid (mass percent of 1.5%) at 60 °C for 1 h. The second anodization was carried out for 1 h under the same condition.

To synthetize AgNPs, an AAO membrane was first immersed into a 1 mol/L 3-aminopropyltrimethoxysilane (APTMS) aqueous solution for 1 h, and then dried in the air. Next, the AAO was put into a 1 mol/L $AgNO_3$ aqueous solution for 30 min and then dried at 45 °C,

and one repetition was done next. Then the AAO with $AgNO_3$ was heated to 500 °C and kept in an ambient pressure furnace for 30 min.

The size and morphology of the AgNPs were characterized by Hitachi S-4800 scanning electron microscope (SEM) with accelerating voltage of 5.0 kV. For SERS detection, about 20 μL thiram solutions with different concentrations were dropped on the as-prepared substrate, respectively. After the droplet was air-dried, the Raman spectra were collected on a Jobin Yvon HR 800 micro-Raman spectrometer with 633 nm excitation from a He-Ne laser. The data acquisition time and the number of accumulations were 10 s and 2, respectively.

Fig.1 shows the typical top-view SEM images of the as-prepared Ag/AAO hybrid nanostructure. As shown in Fig.1, the diameters of AAO pores range from 50 nm to 70 nm, and AgNPs are adsorbed on the wall of the AAO with sizes of tens of nanometers. AgNPs can be observed distributing on the surface of AAO with high density in the form of network structure, which is better to achieve high SERS enhancement due to small gaps among AgNPs. The conjunctions among AgNPs can maximize the localized electric field to greatly amplify the Raman signals of target molecules.


(a)

(b)
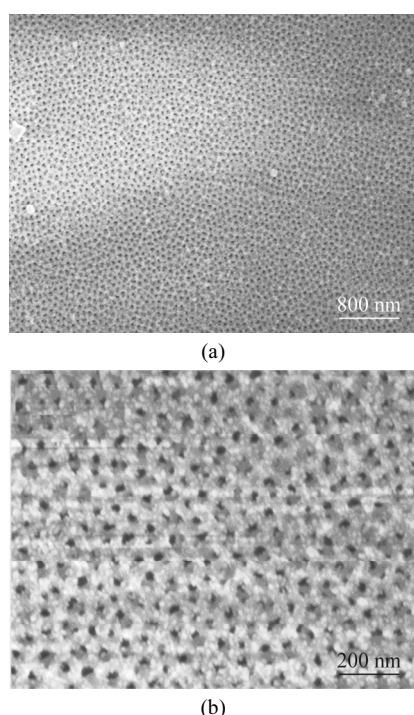
Fig.1 (a) Top-view SEM image of the typical AAO substrate and (b) the enlarged image

Thiram is one of commonly used agricultural fungicides, and it can be used to deal with weeds, apple anthrax, polymerization initiators, vulcanization accelerators and verticillium of alfalfa. However, there has been mounting concern about the residues in foods and water due to its negative effects on human health. So it is necessary to be able to detect the residues at ultra-low levels. In Fig.2, typical peaks of the SERS spectrum of thiram at 556 cm^{-1}, 755 cm^{-1}, 928 cm^{-1}, 1 139 cm^{-1}, 1 379 cm^{-1}, 1 444 cm^{-1} and 1 508 cm^{-1} are observed. The most intense peak at 1 379 cm^{-1} is assigned to the CN stretching mode and the symmetric CH_3 deformation mode. The peak at 1 444 cm^{-1} is from the symmetric CH_3 deformation mode. The peaks at 1 508 cm^{-1} and 1 139 cm^{-1} are both due to the CN stretching mode as well as the rocking CH_3 mode. The peak at 928 cm^{-1} is associated with the stretching CH_3N and C=S modes. The peak at 556 cm^{-1} arises from the SS stretching mode[10,11].

To verify the detection limit of thiram, it was dissolved in methanol with concentrations of $1×10^{-6}$ mol/L, $1×10^{-7}$ mol/L, $1×10^{-8}$ mol/L and $1×10^{-9}$ mol/L, and then the experiments were carried out using the procedure mentioned above. Using the as-prepared Ag/AAO nanostructures as SERS substrates, SERS spectra are obtained from thiram with different concentrations. As shown in Fig.2, the signal intensity of SERS spectra increases with the increase of concentration. The detection limit is as low as 10^{-9} mol/L, indicating the high sensitivity of the SERS sensor for thiram. The strong SERS effect for the nanostructures can be attributed to the fact that the Ag/AAO substrate has very high densities of both AgNPs and "hot-spot", which exist in the gaps between neighboring AgNPs.
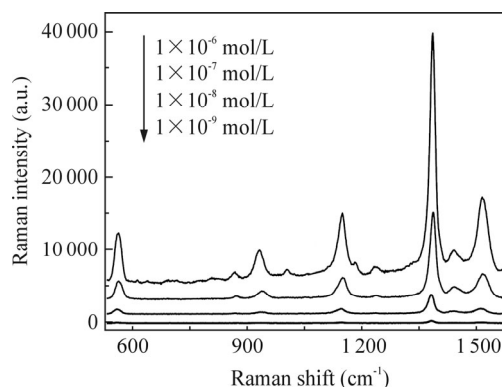
Fig.2 SERS spectra of thiram with different concentrations using Ag/AAO as SERS substrate

To study the uniformity of the Ag/AAO, SERS signals of $1×10^{-7}$ mol/L thiram on it are collected at 20 spots randomly. The SERS spectra are shown in Fig.3, and no significant change exists among 20 different locations. To verify the stability of the as-prepared substrates, they were immersed in a 1 mol/L sodium citrate aqueous solution and kept at 4 °C. About one year later, the stored Ag/AAO is used as substrate to obtain SERS signals of thiram, and the intensity drops by no more than 20% (date not shown). The results demonstrate that the Ag/AAO is a stable and uniform SERS substrate.
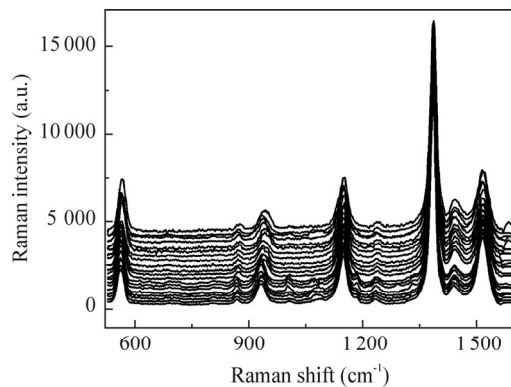
Fig.3 A series of SERS spectra of 1×10^{-7} mol/L thiram molecules collected on 20 randomly selected spots on Ag/AAO

In summary, Ag/AAO as an active SERS substrate was successfully fabricated by a simple procedure. The AAO templates were fabricated using a two-step anodization approach which was followed by decoration of AAO with AgNPs by thermal decomposition of AgNO$_3$. Using the obtained Ag/AAO nanostructures as SERS substrates, a sensitive and simple method to detect thiram is demonstrated. The hybrids exhibit a great enhancement effect on thiram due to greatly amplified localized electric field in the gaps between neighboring AgNPs. The simple preparation, high sensitivity, uniformity and stability of Ag/AAO make this hybrid nanostructure an ideal SERS substrate for the detection of harmful molecules.

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