Journal of Hazardous Materials 211–212 (2012) 389–395

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Vertically aligned Ag nanoplate-assembled film as a sensitive and reproducible SERS substrate for the detection of PCB-77

Chuhong Zhu[a], Guowen Meng[a,*], Qing Huang[b,*], Zhulin Huang[a]

[a] Key Laboratory of Materials Physics, and Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China

[b] Key Laboratory of Ion Beam Bioengineering, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China

ARTICLE INFO

Article history:
Received 25 March 2011
Received in revised form 21 June 2011
Accepted 27 July 2011
Available online 10 August 2011

Keywords:
SERS
Detection
PCBs
Ag nanoplate
Sensitive
Reproducible

ABSTRACT

Vertically aligned Ag nanoplate-assembled film has been achieved by spin-coating Ag seeds on an ITO substrate and subsequent electrodeposition in a mixed aqueous solution of $AgNO_3$ and citric acid. As sufficient hot spots are located in the deep gaps between the neighboring nanoplates across the whole substrate, the Ag nanoplate-assembled film shows strong Surface enhanced Raman scattering (SERS) effect, together with good signal reproducibility. Therefore, the Ag nanoplate-assembled films were tried as robust, highly sensitive and reproducible SERS substrates for the rapid detection of 3,3′,4,4′-tetrachlorobiphenyl (PCB-77) and a detection limit of about 10^{-6} M was reached. For further reducing the detection limit, a layer of decanethiol was modified on the Ag nanoplate surface to capture the PCB-77 molecules efficiently, and a lower detection limit of 10^{-7} M was achieved. A linear dependence was found between the logarithmic concentrations of PCB-77 and the intensities of the fingerprint peaks. Furthermore, the Ag nanoplate-assembled film can also be used as a SERS substrate to distinguish characteristic peaks of different polychlorinated biphenyls (PCBs) in their mixed solutions. Therefore the vertically aligned Ag nanoplate-assembled film has potentials as effective SERS substrates in rapid and direct detection of trace PCBs.

1. Introduction

Polychlorinated biphenyls (PCBs) were heavily used from the 1930s to the 1970s in industry, mainly as insulation in electrical transformers [1]. As no effective control on waste disposal during that period, PCBs spread throughout the environment. Awareness of PCBs' presence in the environment and their toxicity to human and wildlife lead to a ban in 1979 on sale and production [2]. But PCBs can still be found today in high concentrations in snow [3], soils [4], waste disposal sites, natural waters, and in the aquatic life of these waters [5–10]. PCBs can cause harmful biological effects, such as toxicity, mutagenicity, carcinogenicity, and endocrine disrupter activity [5,11–14]. PCBs can bio-accumulate in fatty tissues through food chains [10], so even small exposures may eventually reach dangerous levels. Rapid and sensitive detection of PCBs is therefore extremely important. Traditional techniques for detecting PCBs mainly include high-resolution capillary gas chromatographic columns with an electron capture detector [15,16], immunoassays [17], ion detection technique [18], and high-resolution mass spectrometry [16]. But these methods are generally costly and time-consuming.

Surface-enhanced Raman scattering (SERS) has attracted great interest due to its high sensitivity in trace molecular detection [19]. The noble metal (especially Au and Ag) nanometer-scale gaps [20], sharp tips [21] and edges [22] are believed to have highly concentrated electromagnetic fields associated with strong localized surface plasmon resonance (LSPR) so that "hot spots" occur at these positions. For an effective SERS substrate, it is generally required to have not only enough hot spots to ensure high sensitivity, but also uniformity of the substrate to ensure good reproducibility for SERS measurements in practice. To achieve high sensitivity and reproducibility of SERS substrates, nanoparticle colloids [23,24] and periodic nanostructures [25,26] have been developed. Nanoparticle colloids can induce enormously enhanced SERS signal at some local hot spots due to the aggregation of the colloids, but it is difficult to achieve reproducibility because it is hard to ensure the hot spots to be homogenously distributed on the substrate. Nanometer-scale lithography techniques can be used to fabricate periodic nanostructures with a moderate enhancement (10^5–10^6) and high reproducibility [23], but they are usually expensive. Moreover, both theoretical and experimental studies prove that the control of gaps between nanostructures on SERS substrates in the sub-10-nm regime is very critical to

---

* Corresponding author.
E-mail addresses: gwmeng@issp.ac.cn (G. Meng), huangq@ipp.ac.cn (Q. Huang).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.07.118

attain optimum SERS effect [20,26–28]; however the fabrication of uniform and dense periodic gaps in such a small scale remains a big challenge.

Previously, we achieved arrays of Ag nanosheet-assembled micro-hemispheres that were successfully used as highly sensitive and reproducible SERS substrates for the detection of 3,3′,4,4′-tetrachlorobiphenyl (PCB-77) [29]. In that case we had to "see" one of the hemispheres first under the optical microscopy of the confocal microprobe Raman system, and then measured Raman signals from the observed micro-hemisphere. If the density of the Ag micro-hemispheres is high enough to form a compact film of Ag micro-hemispheres or vertically aligned nanoplates, the structural uniformity of the whole substrate could be much improved, and it would be much easier for SERS measurement in practical applications. Based on these ideas, here we present a low-cost and simple Ag seed-assisted electrodeposition on indium tin oxide (ITO) substrates for the fabrication of large-area compact films consisting of vertically aligned Ag nanoplates with sufficient deep sub-10-nm gaps between the neighboring nanoplates. As sufficient hot spots are located in the deep gaps between the neighboring nanoplates across the whole substrate, the Ag nanoplate-assembled film shows strong SERS effect, together with good reproducibility. Therefore, the as-prepared Ag nanoplate-assembled films can serve as cost-effective, sensitive, reproducible and robust SERS substrates for rapid trace detection of persistent organic pollutants such as PCB-77. As PCBs cannot be easily adsorbed onto the surface of Ag nanoplate-assembled film, in this work, a partition layer (decanethiol self-assembled layer) was assembled onto the SERS substrate to concentrate the target PCB molecules within the surfaces of the SERS substrate through its efficient van der Waals interactions with the hydrophobic PCBs. It is demonstrated that the detection limit of PCB-77 can be really reduced by decanethiol modification on the surface of the Ag nanoplate-assembled film.

Compared with the previously reported SERS substrate consisting of Ag nanosheet-assembled micro-hemispheres [29], now we can randomly choose a spot on the film to get SERS signals rather than have to "see" one micro-hemisphere before getting SERS signals, since this new SERS substrate is made up of a large area film consisting of uniformly and densely distributed Ag nanoplates on an ITO substrate. In addition, the lower detection limit of PCB-77 achieved by using the Ag nanoplate-assembled film modified with decanethiol as a SERS substrate (10^{-7} M) is even lower than that obtained by using Ag nanosheet-assembled micro-hemispheres (3×10^{-6} M). Although aligned Ag nanorods were also used as a SERS substrate for the detection of 2,3,3′,4,4′-pentachlorinated biphenyl, however there appeared some unexplained bands in the SERS spectra [30].

2. Experimental

2.1. Apparatus and reagents

The resultant compact Ag nanoplate-assembled film was characterized by using X-ray diffraction (XRD) (Philips X'pert-PRO), scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscope (TEM, JEOL 2010) and Ultraviolet–Visible-Near-Infrared spectrophotometer (Hitachi, U-4100). The compact Ag nanoplate-assembled films were cleaned by using a plasma cleaner (PDC-32G, high power) for 10 min, and then used as SERS substrates. SERS measurement was conducted on a confocal microprobe Raman system (Renishaw, inVia) with the excitation wavelength of 532 nm. During SERS measurement, the laser light was vertically projected onto the samples with a resultant beam diameter of ~5 μm.

The reagents, sodium citrate, citric acid, R6G, PCB-77, $NaBH_4$, and $AgNO_3$ were analytical grade.

2.2. Preparation of the Ag nanoplate-assembled film

The film comprising vertically aligned Ag nanoplates on an ITO substrate was fabricated via spin-coating Ag seeds on the ITO substrate and subsequent electrodeposition in a mixed aqueous solution of $AgNO_3$ and citric acid, as shown schematically in Fig. 1. Silver colloidal solution was first prepared. Typically, 0.5 mL of 60 mM $AgNO_3$ and 1 mL of 35 mM sodium citrate were added to 98 mL of deionized (DI) water. The mixed solution was stirred for several minutes. Then, 0.5 mL of an aqueous 20 mM $NaBH_4$ solution, which had been aged at room temperature for 2 h, was added quickly, stirred for 1 h and then aged at room temperature for 24 h before use. ITO substrates (1 cm × 2 cm) were ultrasonically cleaned in acetone and then in ethanol for 1 h, respectively. A droplet of the prepared Ag colloidal solution (0.1 mL) was spin-coated on the cleaned substrate on a custom-built spin coater. The coating area on the substrate was fixed to be about 1 cm in diameter. After that, the substrate was dried at 40 °C. For the synthesis of Ag nanoplate-assembled film, 0.1 g $AgNO_3$ and 0.9 g citric acid were added to 50 mL DI water, followed by stirring until complete dissolution of the solute. Such an aqueous solution was used as the electrolyte in the electrodeposition. A rectangular graphite sheet was used as anode and a piece of ITO glass (2 cm × 0.5 cm) spin-coated with Ag seeds was used as cathode, respectively. The electrodeposition of the Ag nanoplate-assembled film was carried out under a constant current density of 170 $\mu A\,cm^{-2}$ for 20 min at room temperature. The ITO glass with the electrodeposited products was then taken out, cleaned with DI water several times and dried with high-purity flowing nitrogen.

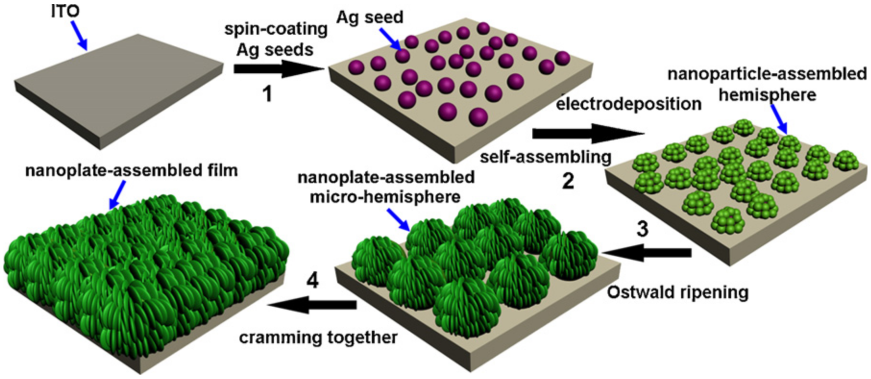

Fig. 1. Schematic for the fabrication of vertically aligned Ag nanoplate-assembled film. (1) Spin-coating Ag-seeds on an ITO substrate. (2) Ag seed-assisted electrodeposition of Ag nanoparticle-assembled hemispheres. (3) Transformation of Ag nanoparticle-assembled hemispheres into nanoplate-assembled micro-hemispheres by Ostwald ripening. (4) Ag nanoplate-assembled micro-hemispheres cramming together to form vertically aligned Ag nanoplate-assembled film.