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HfO_2-wrapped slanted Ag nanorods array as a reusable and sensitive SERS substrate for trace analysis of uranyl compounds

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ABSTRACT

SERS has been used for rapid and trace analysis of uranyl compounds due to its fast response and high sensitivity. However, the difficulties in preparing stable and reusable SERS substrate as well as quantitative detection severely restrict its practical application prospects. Herein, HfO_2-wrapped slanted Ag nanorods array was used as SERS substrate for sensitive analysis of trace uranyl compounds for the first time. The proposed substrate with uniform surface roughness and well-distributed Ag nanorods showed excellent spectral reproducibility, while the ultrathin HfO_2 film fully covering Ag nanorods effectively improved the substrate stability and contributed to its cyclic utilization. Besides, quantitative detection of trace uranyl ions was achieved by using this substrate with an ultra-low detection limit of 8.33 ppb. Most importantly, SERS spectra of varied uranyl hydroxides at different pH values together with *in situ* SERS spectrum of $UO_2(CO_3)_3^{4-}$ were recorded on this substrate, building the correspondence between SERS band position of $O{=}U{=}O(\nu_1)$ and uranyl species. Thus, SERS technique based on this substrate could be a promising method for both concentration detection of uranyl ions and structure identification of some uranyl compounds in trace level, indicating high potential application prospects in the environmental monitoring.

1. Introduction

As one of the most important nuclear resources, uranium exhibits extensive and essential employments in the nuclear industry; however, considerable quantities of uranium-contained substances have been released to the environment through nuclear accidents, nuclear tests, and uranium mining. Uranyl $\left(UO_2^{2+}\right)$, the most stable chemical species of uranium in the natural water environment, is regarded as a highly toxic carcinogen, posing significant threats to public health [1,2]. Hence, rapid analysis of trace uranyl compounds has become an attractive issue in the environmental monitoring. The current analytical methods mainly divide into two categories, one is used for the concentration detection of uranyl compounds, such as UV–vis adsorption spectrometry [3,4], fluorescence spectra [5,6], electrochemical process [7,8], ICP-AES [9], ICP-MS [10,11] and etc; and the other can characterize the structure information of uranyl compounds, such as IR spectra [12,13], Raman scattering [14,15], organic mass spectra [16,17], X-ray adsorption spectra based on synchrotron radiation [18,19] and etc. Despite providing detailed and useful content or composition information of uranyl compounds, those methods lack the capability to enforce trace analysis or require expert operator, sophisticated and expensive equipment, time-consuming sample preparation as well as high cost, limiting their practical applications in environmental monitoring. Particularly, almost none of them can take account of both concentration detection and structure analysis. Hence, developing an analytic technique available for the both is urgently needed due to its high application values.

Surface enhanced Raman scattering (SERS) has been paid great attention due to its extraordinary high sensitivity, fast response, and molecular structure identification. As a surface-sensitive technique, SERS can significantly enhance Raman signals of analyte molecules adsorbed onto the rough surfaces of noble metals [20], and its extraordinary high sensitivity mainly results from electro-

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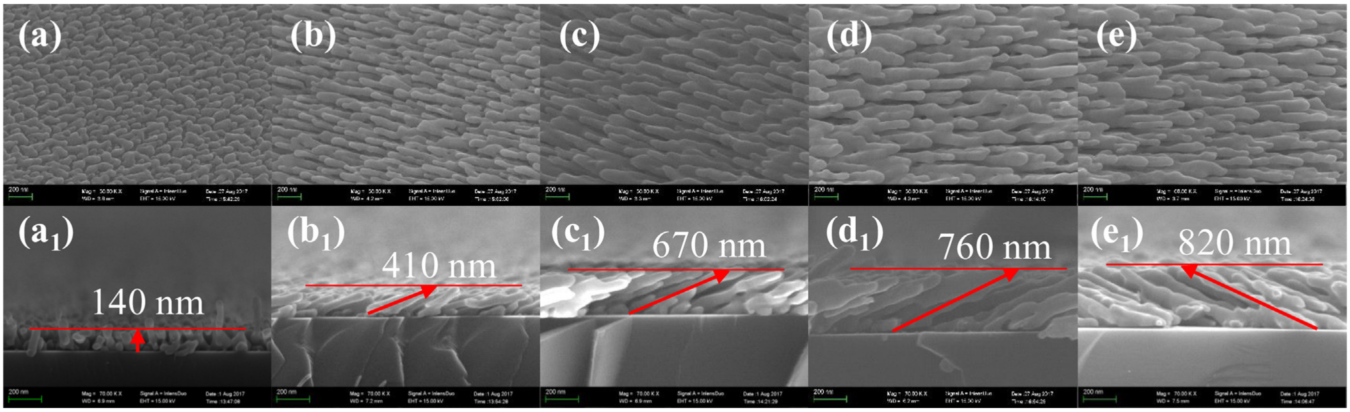

Fig. 1. The typical top-view (a–e) and side-view (a_1–e_1) SEM images of Ag@HfO_2-1 cycle substrates with different lengths of Ag nanorods.

magnetic enhancement (EM) produced by laser-induced surface plasma resonance [21]. Thus the SERS-based method is gradually developed into trace analysis for chemical species of biomolecules [22,23], organic substances [24–26], and heavy metal ions [27,28]. Due to the short-range sensitivity of SERS technique, SERS sensitivity can be effectively promoted by shortening the distance between analyte molecules and metal surface [29]. Besides, the improvement of SERS sensitivity can also be achieved by the production of Raman "hotspots" (the sites possess large electromagnetic field and usually exist between neighboring nanoparticles), which improves the Raman scattering enhancement factors as high as 10^{14} [30]. To date, there have been quite a few reports focusing on the SERS of uranyl compounds since Dai et al. first found the SERS effect of uranyl nitrate [31]. The employed SERS substrates include silver-doped sol-gel film [32], silver nanoparticles [33,34], surface-modified silver [35–37] or gold nanoparticles [38,39] and so on. Despite some achievements has been made in the SERS of uranyl compounds, there still exists some questions that need to be further solved, for instance: (1) the commonly used substrates are based on bare Ag nanostructures, which easily lose SERS activity due to the oxidation of Ag atoms in the atmosphere; (2) most substrates cannot be recycled, resulting in high analysis costs inevitably; (3) the SERS substrates lacking of homogeneity and stability leads the quantitative detection of uranyl hard to be achieved; (4) most importantly, despite some achievements have been made in the SERS detection of trace uranyl ions, the structure identification of uranyl compounds based on SERS technique is still quite deficient. Thus, developing a reusable, stable and homogeneous SERS substrate with high density of "hotspots" may be the key to solve these problems.

In this study, HfO_2-wrapped slanted Ag nanorods array as SERS substrate was used for trace analysis of uranyl compounds. As the outstanding discreteness, regularity and orientation, slanted Ag nanorods array possesses strong SERS effect [40]. Quite a few inert oxides (SiO_2, TiO_2, Al_2O_3, HfO_2 and etc.) have been commonly used as protective shells to coat the Ag nanostructures in the previous studies [41–46]. Among these oxides, HfO_2 possessed favorable advantages for SERS analysis: (1) HfO_2 owns strong chemical stability, insoluble even in some acidic solutions; (2) HfO_2 possesses high melting point and low thermal conductivity, preventing the substrate from thermal damage induced by high-power laser to guarantee its SERS activity; (3) the light can pass through HfO_2 thin film with only a few attenuations, which produces few effects on the light-induced electro-magnetic of Ag nanorods surface. Hence, with improving both the Ag nanorods stability and SERS sensitivity, HfO_2 is selected as the protective shell in this study. Herein, our proposed substrate exhibited satisfactory reusability as well as the excellent reproducibility of SERS spectra; besides, the outstanding quantitative detection of trace uranyl ions could be achieved by using this substrate; considering practical application, SERS spectra of common uranyl hydroxides and $UO_2(CO_3)_3^{4-}$ (the dominant uranyl species in the natural aqueous solution) were also discussed in this research. Noticeably, we found that SERS based on this HfO_2-wrapped slanted Ag nanorods array could realize both the trace detection of uranyl ions and structure identification of uranyl hydroxides and $UO_2(CO_3)_3^{4-}$.

2. Experimental

2.1. Reagents and instruments

2.1.1. Reagents

Uranyl acetate dihydrate and uranyl nitrate hexahydrate were purchased from Alfa Aesar company. Nitric acid, sodium hydrate, and other reagents were obtained from Kelong Chemical company of China. All the reagents were analytical pure, and directly used without any further purification process. Deionized water (resistance: 18.2 MΩ) was used for solution dilution in the whole experiment.

2.1.2. Instruments

Scanning electron microscope (SEM, JEOL-JSM-7001F, Japan), high-resolution transmission electron microscope (HRTEM, JEOL-JEM-2011, Japan), electronic beam evaporation system (Thermionics, America), atomic layer deposition system (MNT-100, China), and Raman spectroscope (Horriba700, Germany).

2.2. Preparation of HfO_2-wrapped slanted Ag nanorods array

The monocrystalline Si (001) wafer was used as the supporting base, on which slanted Ag nanorods were fabricated through glancing angle deposition process (GLAD) in an electronic beam evaporation system. Before the deposition process, the background vacuum was set at 5×10^{-6} Pa to inhibit the oxidation of Ag atoms, and the Si wafer was placed above the crucible and the incident angle of the vapor flux was 86°. The deposition rate was ~0.75 nm/s, and the process was terminated when the length of Ag nanorods increased to 260, 640, 1120, 1300, and 1500 nm measured by a quartz crystal microbalance (QCM).

Then, the Ag nanorods were wrapped with HfO_2 shell in an atomic layer deposition (ALD) system at 80 °C. As the precursors to synthesize HfO_2, tetrakis (dimethylamino) hafnium (120 °C) and water (40 °C) were pumped into the reaction chamber separately. The high purity N_2 (0.15 MPa) was employed as purge gas as well as the carrier of precursors. Typically, one complete cycle process included four steps: (1) Pumped tetrakis (dimethylamino) hafnium,