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Surface enhanced Raman scattering substrates based on titanium nitride nanorods

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ABSTRACT

TiN nanorod arrays (NRs) were prepared using a hydrothermal process followed by nitridation in ammonia atmosphere. The fabricated TiN NRs were characterized by UV–vis spectroscopy, X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The Surface-enhanced Raman scattering (SERS) activity of these substrates was evaluated by using Rhodamine (R6G) and crystal violet (CV) as the probe molecules. Results showed that TiN NRs prepared at 900 °C exhibited the strongest Raman enhancement performance. The average sizes of the TiN NRs were 57 nm. The TiN NRs had an absorption peak around 524 nm, which related to surface Plasmon resonance. Compared to the CV molecules, the R6G molecules can obtain a higher enhancement in our substrate. The enhancement factor (($8.9 \pm 0.2) \times 10^3$) and the R6G detection limit (10^{-6} M) were achieved. The results showed that the TiN NRs are a kind of promising materials as SERS sensor.

1. Introduction

Surface-enhanced Raman scattering (SERS) technology provides a powerful tool for ultrasensitive vibrational spectroscopy. Hence it has attracted much attention from analysis, chemistry, and biology fields [1–6]. Generally, materials used as SERS substrates are mainly metallic (in particular Ag, Au, Cu noble metals) nanoparticles (NPs) or some types of nanostructure (such as metal nanoshells [7], metal nanowires [8], and metal nanodots [9,10], nanoporous films [11]). These metallic nanostructures have exhibited high SERS performance due to the localized surface plasmon resonances (LSPRs) in the surface of metal plasmonic NPs, which can lead to a strong enhancement of the electromagnetic (EM) field on the interface. However, these metallic nanostructures have suffered problems such as high-cost, low stability and poor biocompatibility [12]. These problems have been partly solved by using semiconductors as SERS-active substrates, such as TiO_2 [13] and ZnO [14]. Nevertheless, the sensitivity of these semiconductors is comparatively low. Thus, development of the SERS-active substrate still remains an important aspect of the SERS study.

Recently, Titanium nitride (TiN) has drawn considerable attention due to its optical properties, which can exhibit resonant plasmon characteristics [15–18]. Some reports have found that TiN can produce electromagnetic field enhancements which similar to those of gold nanostructure [19–21]. In addition, TiN has outstanding thermal, chemical, and mechanical stability properties [22]. Thus, TiN nanostructures have attracted wide interests in developing novel SERS substrate [23]. As a novel TiN nanostructure, TiN nanorods (NRs) not only own the intrinsic properties of the TiN materials, its array configuration and the large surface area are would also make it be an appropriate candidate to develop a practical SERS sensor.

In this work, TiN NRs were first applied as SERS substrate, which shows SPR similar to that of gold. TiO_2 NRs were firstly prepared through a hydrothermal method, and then TiN NRs were obtained by the nitridation treatment of TiO_2 NRs at 800–1000 °C in ammonia atmosphere. To characterize the SERS activity, the Raman enhancement properties were measured. The results indicated that the TiN NRs prepared at 900 °C exhibited the highest SERS enhancement.

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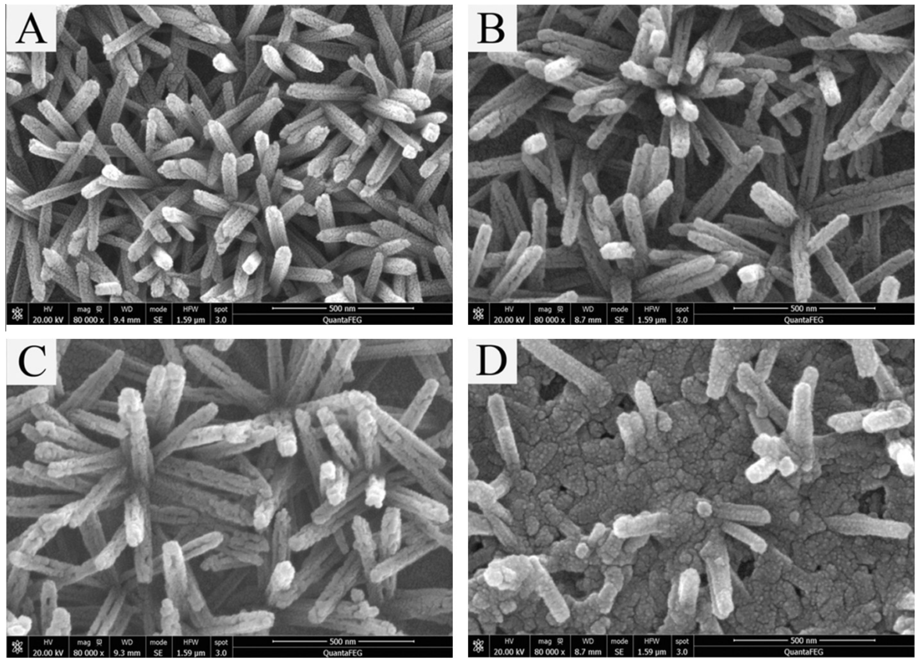

Fig. 1. SEM images of (A) TiO_2 NRs and TiN NRs prepared at different nitridation temperatures: (B) 800 °C, (C) 900 °C, and (D) 1000 °C.

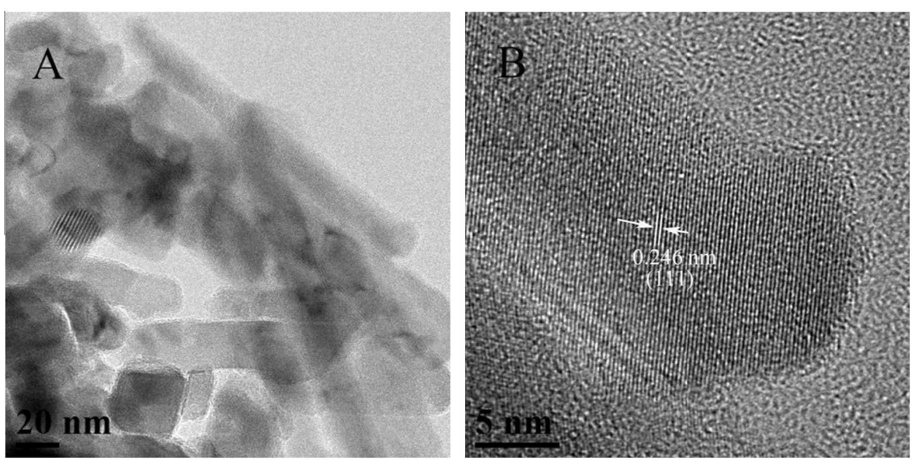

Fig. 2. (A) TEM image of TiN NRs prepared at 900 °C and (B) its high-resolution TEM image.

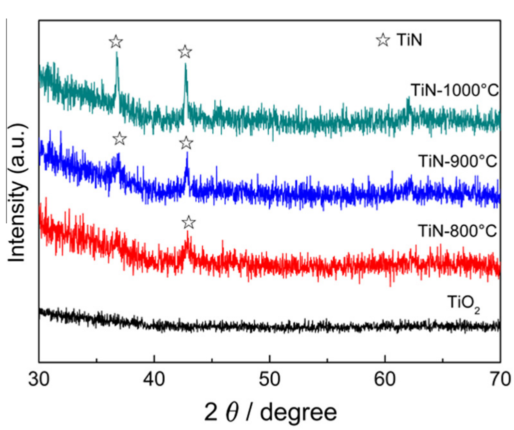

Fig. 3. XRD patterns of TiO_2 NRs and TiN NRs prepared at different nitridation temperatures.

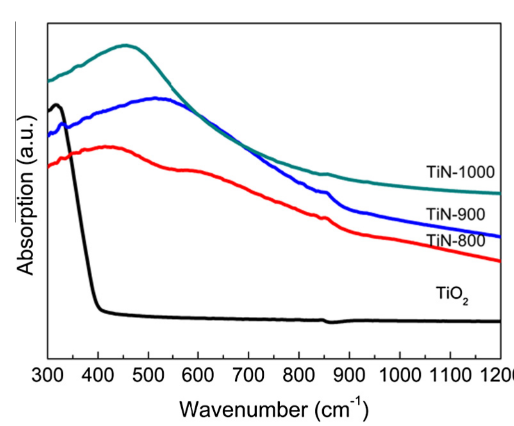

Fig. 4. UV–vis absorption spectra of TiO_2 NRs and TiN NRs prepared at different nitridation temperatures.