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Abstract

Surface-Enhanced Raman Spectroscopy on Ag−WO_3/TiO_2 Inverse Opal Film Substrates †

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Abstract: The synergetic effects of electromagnetic and chemical enhancements via the combination of semiconductor nanomaterials with noble metal nanoparticles is crucial to the performance of surface-enhanced Raman scattering (SERS). Here, WO_3/TiO_2 photonic crystal films in the form of three-dimensional inverse opals were fabricated via the co-assembly of polymer colloidal templates with water-soluble precursors in order to simultaneously grow both constituent metal oxides with tailored electronic properties and photonic band gaps. The surface modification of compositionally tuned WO_3/TiO_2 inverse opals by Ag nanoparticles is demonstrated to be an efficient method to boost SERS efficiency in the detection of 4−mercaptobenzoic acid via the synergy of plasmonic effects with charge transfer and slow-light trapping.

Keywords: tungsten trioxide; titanium dioxide; silver nanoparticles; SERS; slow photons

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1. Introduction

Heterostructured metal oxide photonic crystals (PCs) have been attracting particular interest as an advanced approach for the fabrication of efficient dielectric SERS substrates that combine slow-photon effects with chemical enhancement [1,2]. In this work, composite WO_3/TiO_2 photonic crystal films in the form of three-dimensional (3D) macroporous inverse opals are surface modified by Ag nanoparticles in order to exploit the synergy of light trapping by 3D periodic structures and chemical enhancement with plasmonic amplification on the overall SERS effect.

2. Materials and Methods

WO_3/TiO_2 photonic crystal films were deposited via the co-assembly of monodisperse 287 nm polymer spheres with Ti(IV) bis(ammonium lactato) dihydroxide [2] and ammonium metatungstate [3] aqueous precursors on glass substrates at nominal W/Ti molar ratios of 1:0.25 and 1:2. After self-assembly, the films were calcined at 430 °C to remove the polymer matrix and crystallize the metal oxides (MOs) in the inverse opal structure. Silver nanoparticles of 10 nm diameter were deposited on the PC films, which were labelled as Ag−PC287 Y:Y, with Y:Y being the W/Ti ratio.

3. Discussion

3.1. Structural and Compositional Characterization

SEM and TEM images of the PC films display a 3D network of uniform interconnected void macropores consisting of both metal oxides according to Ti and W EDX elemental maps (Figure 1a). The photonic band gap position of the WO_3/TiO_2 PC films shifted to higher wavelengths as the WO_3 content increased, as shown by the specular reflectance (R%)

spectra for the PC287 films in Figure 1b, allowing fine tuning of the photonic properties by altering the films' composition.

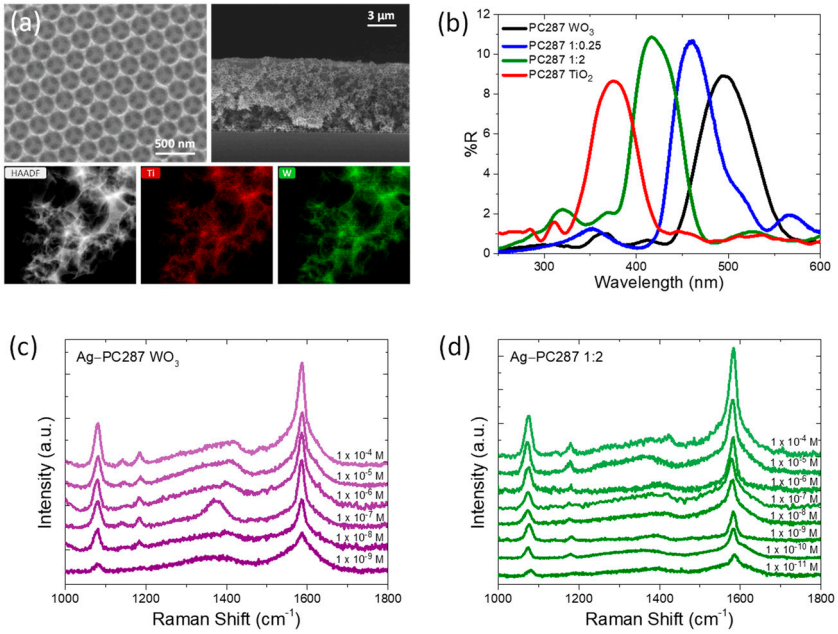

Figure 1. (**a**) (Upper) Top view and cross-section SEM images and (Lower) TEM image and elemental EDX maps of Ti and W for PC287 1:0.25; (**b**) specular reflectance (R%) spectra for PC287 films; (**c**,**d**) SERS spectra of 4−MBA on Ag−PC287 WO_3 and 1:2 substrates.

3.2. Ag−WO_3/TiO_2 SERS Substrates

The SERS activity of inverse opal films was examined using 4−MBA (4−mercaptobenzoic acid) as the probe molecule. The characteristic peaks of 4−MBA were detected on the Ag−WO_3/TiO_2 substrates (Figure 1c,d), where the dominant peaks at 1078 cm^{-1} and 1585 cm^{-1} can be assigned to the in-plane ring breathing (C−S) and the aromatic ring (C−C) vibration modes. The amplification of SERS intensity can be attributed to the enhanced electromagnetic field at the interface of the Ag and WO_3/TiO_2 inverse opal skeleton, as well as the interfacial charge transfer from MOs' conduction band to the lowest unoccupied molecular orbital (LUMO) of 4−MBA molecules. In Ag−WO_3/TiO_2 films, electron transfer between TiO_2 and WO_3 can improve charge separation and moderate recombination enabling the detection of smaller 4−MBA concentrations. The minimum analyte detection can reach very low values down to 10^{-11} mol/L for the Ag−PC287 1:2 substrate, which can also be related to the overlap of blue-edge slow photons with the Ag nanoparticles' localized surface plasmon resonance. Ag−WO_3/TiO_2 nanocomposites are proposed as highly efficient SERS substrates for the sensitive detection of biological analytes.

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Conflicts of Interest: The authors declare no conflicts of interest.

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