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Synthesis of SiO₂@Ag core-shell photonic crystals for SERS application

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Abstract. Core-shell SiO₂@Ag composite spheres with dense, complete and nanoscaled silver shell were prepared by using facile chemical reduction method. Self-assembly of the composite microspheres into 3D photonic crystals (PhCs) was carried out using the vertical deposition method. The core-shell PhCs composites were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectroscopy and energy dispersive X-ray spectroscopy (EDX). The results of amplification of Raman scattering by these composite substrates are presented.

1. Introduction

In recent years, three-dimensional (3D) metall-dielectric photonic crystals (PhCs) have attracted much attention due to the special features of PhCs (large surface area and ability to modulate light) and the plasmonic enhancement effect of noble metals [1]. They have promising potential applications in many fields, such as plasmonic enhanced emission [2] and surface-enhanced Raman scattering (SERS) [3]. 3D PhCs are periodic structures which can be generated by a controllable self-assembly method of the spherical colloidal particles [4, 5]. They have photonic band gaps (PBG) which forbid propagation of light in certain frequency ranges [6]. This work is aimed to provide a simple and effective way to significantly enhance Raman signals by the synergetic interaction of the surface plasmon resonance of metallic nanostructures and the photonic band gap (PBG) effect of the photonic crystal. For this purpose, we synthesized a new type PhC based on close-packed SiO₂@Ag core-shell microspheres. The obtained PhCs composites can be promising for SERS application.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) for synthesis of SiO₂ microspheres, AgNO₃ for the synthesis of Ag nanoparticles and polyvinylpyrrolidone (PVP-can prevent the aggregation of the Ag nanoparticles) were acquired from Sigma-Aldrich enterprise. Methylene blue (MB) and glucose were obtained from Reachim. Menzel-Gläser glass coverslips of 24×24×0.4 mm, thoroughly washed in ethanol and acetone, were used as substrates for the deposition of SiO₂@Ag core-shell microspheres.

2.2. Preparation SiO₂@Ag core-shell microspheres and photonic crystals based on them

SiO₂ colloidal microspheres of 230-300 nm in diameter were synthesized by the method presented in [7]. Then, 20 ml of a 0.001 M solution of ammoniacal silver nitrate and 30 ml of a 7 μM solution of



PVP (can prevent the aggregation of the Ag nanoparticles) were added to the colloidal suspension with 0,1 g of SiO₂ microspheres. [Ag(NH₃)₂]⁺ ions were adsorbed on the surface of the silica microspheres. At last, the SiO₂@Ag composite particles were formed by a simple reduction process in the presence of 10 ml 2 mM glucose at 50 °C for 3h. The obtained composite was collected by centrifugation and washed three times with deionized water. Self-assembly of core-shell nanocomposites into 3D PhC was implemented by the vertical deposition method [8]. The procedure for preparing SiO₂@Ag PhC composites is illustrated in Fig. 1.

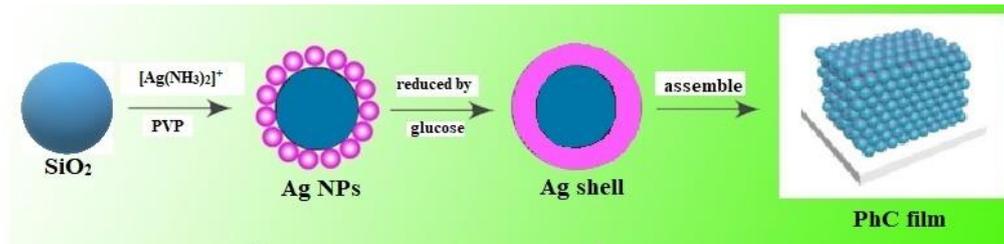


Figure 1. Illustration of the synthesis route for SiO₂@Ag PhC nanocomposites.

2.3. Characterization

The absorption spectrum of solutions and the reflection spectrum of photonic crystal films were recorded with a Lambda 950 spectrophotometer (Perkin Elmer). Images of the surface microstructure and EDX analysis of composite films were obtained using a scanning electron microscope (SUPRA 50 VP, Carl Zeiss, Germany) with the accelerating voltage of 7–21 kV (SE2 and VPSE detectors). Synthesized samples were characterized by X-ray diffraction (XRD) on a Rigaku D/MAX 2500 diffractometer (rotating anode, Cu K α radiation, step scan mode with a step of 0.02° over 2 θ = 10 – 70°, Rietveld refinement). Raman spectra were collected with DXRxi Raman Imaging Microscope (Thermo Fisher Scientific) equipped with a $\times 50$ magnifying lens and a green solid-state laser (λ = 532 nm). Hundred accumulations were made for each spectrum at 2 mW laser power and 60 Hz operating frequency. For the study SERS of MB, PhC films were vertically immersed in a 50 μ M ethanol-based MB solution and kept there for 1 minute, followed by air drying.

3. Results

The X-ray diffraction patterns of the obtained SiO₂ microspheres and SiO₂@Ag core-shell nanocomposites are shown in Fig. 2a. For pure silica particles, there is only a broad scattering maximum centered at 22.5°, corresponding to amorphous silica [9]. Yet, for core-shell composites, except amorphous silica characteristic diffraction peak, it also exhibits three well-resolved diffraction peaks at 2 θ angles of 37.9°, 44.1° and 64.3° in the range of approximately 10° to 70°, which can be indexed to the (111), (200) and (220) reflections of face-centered cubic silver (JCPDS Card No. 87-0720), indicating that the Ag nanoparticles with high crystallinity could be obtained on the surface of SiO₂. In addition, we also can find that the peaks are a little broader than that of bulk silver because the silver grain size is relatively small. The UV-Vis spectroscopy is one of the most widely used techniques for structural characterization of silver nanostructures [10]. The absorption spectra of the prepared bare silica and core-shell structure are shown in Fig. 2b. The bare silica colloids do not show any UV-Vis absorption in the range of 300 nm to 800 nm, but the core-shell composites show an obvious absorption peak at around 438 nm due to the excitation of the Mie plasmon resonance associated with the silver nanoparticles (NPs) on the surface of SiO₂. Compared to pure Ag NPs, the absorption peak shifts from \sim 400 nm to 438 nm [11, 12]. The possible reason for the red shift can be attributed to much larger size of silver nanoparticles and higher coverage on the silica surface as indicated in Fig. 3 (SEM). The results are consistent with the previous reports [10, 13]. The strong dipole-dipole interactions between neighboring nanoparticles and Mie scattering of silver shell would promote red shift and broadening of the plasmon bands for silver clusters attached on silica spheres.

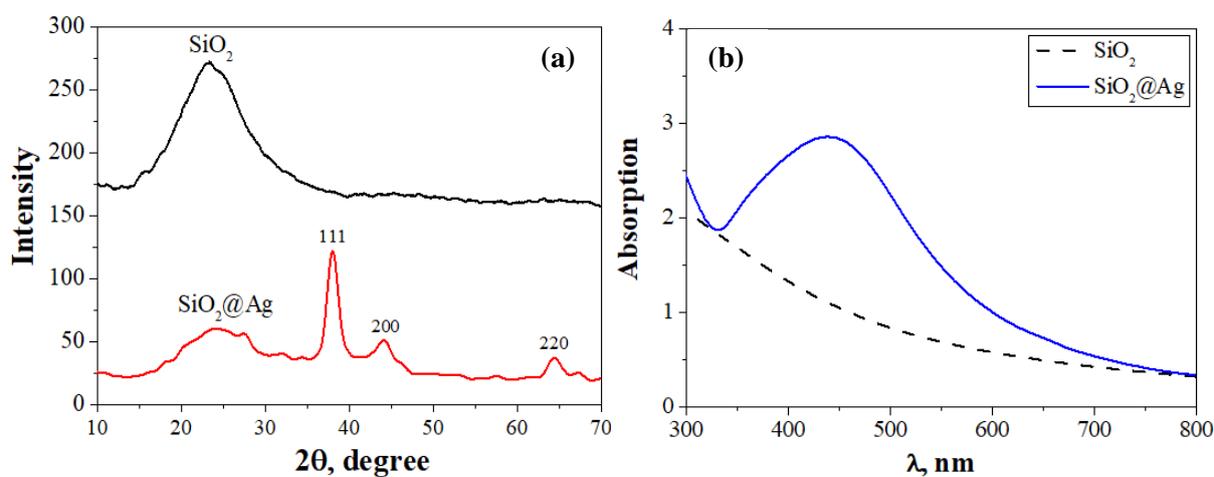


Figure 2(a, b). (a) X-ray diffraction patterns of SiO_2 and $\text{SiO}_2@Ag$ composite microspheres; (b) UV-Vis absorption spectra of SiO_2 and $\text{SiO}_2@Ag$ microspheres.

SEM image of synthesized nanocomposites $\text{SiO}_2@Ag$ core-shell microspheres are shown in Fig. 3a. All of the particles are spherical in shape and the average diameter is about 235 nm. The chemical composition of resulting $\text{SiO}_2@Ag$ composite has been analyzed by EDX elemental analysis as shown in Fig. 3a (inset). In this pattern, only Si, O, and Ag peaks are clearly shown and no other peaks are detected. The atomic ratio of Si and O is about 1:2, and the total content of Ag element is about 15 wt. %. This means that such a concentration of silver shell is enough for a successful coating of silica microspheres in the present study.

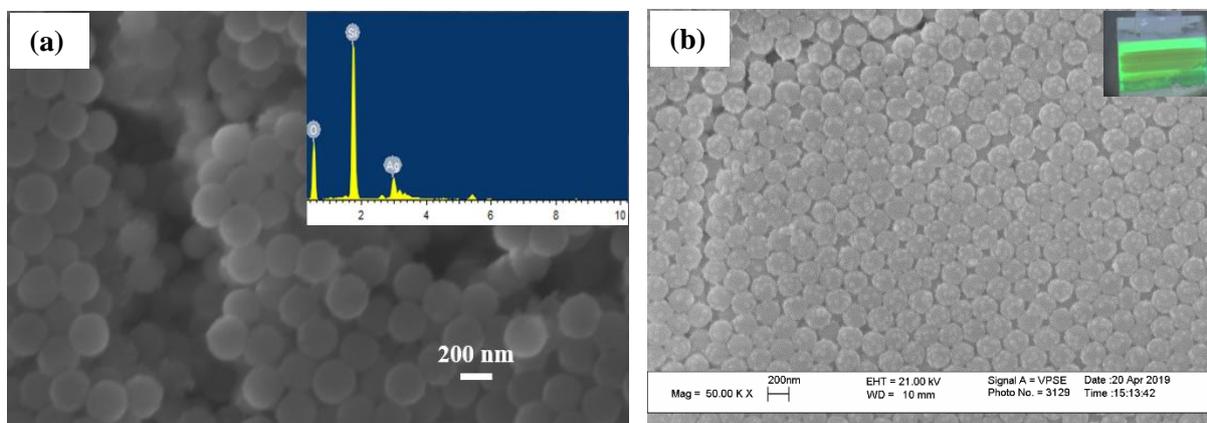


Figure 3(a, b). (a) SEM image of $\text{SiO}_2@Ag$ nanocomposites (EDX spectrum is shown in the inset); (b) SEM image of self-assembled $\text{SiO}_2@Ag$ into 3D PhC (photograph of PhC film shown at inset).

The SEM images of the surface of the PhC films (Figure 3b) confirmed that the $\text{SiO}_2@Ag$ microspheres can self-assemble into an ordered PhC structure with the help of vertical deposition method [8].

Next, the optical properties of the obtained PhC films were investigated. The reflectance spectra (Figure 4) of PhC films fabricated from $\text{SiO}_2@Ag$ microspheres with different average diameters were measured closer to normal incidence to detect the PBG arising from the periodicity of the $\text{SiO}_2@Ag$ PhC films.

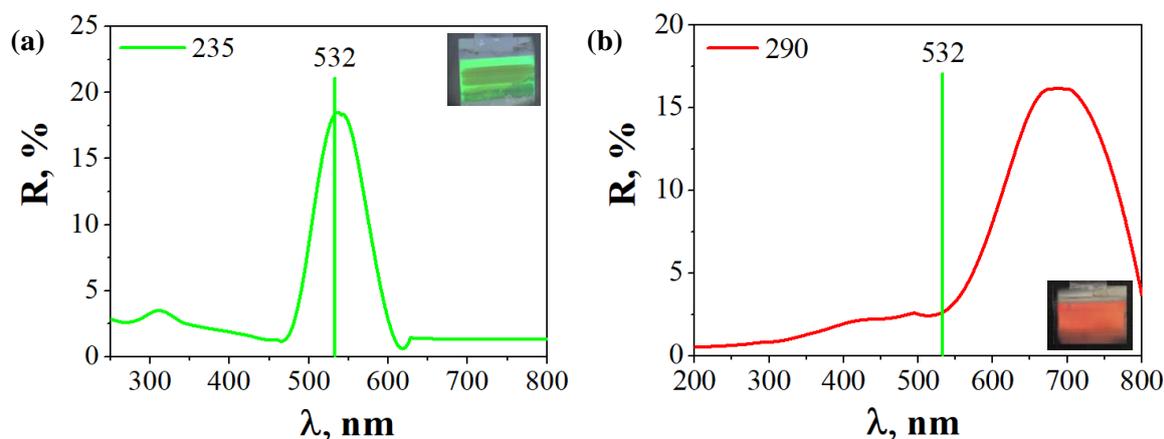


Figure 4(a, b). (a) Reflection spectra of the $\text{SiO}_2@Ag$ PhCs films prepared from self-assembled microspheres with 235 nm average diameters; (b) With 290 nm average diameters (Insets: Digital photographs of the films).

The peak positions of $\text{SiO}_2@Ag$ PhC films with different diameters of $\text{SiO}_2@Ag$ microspheres (235 and 290 nm) were $\lambda = 536$ and 688 nm, respectively, and these films displayed the corresponding structure colors, as shown in the insets of Figure 4a-b. The vertical line in the reflection spectra indicates the position of the Raman laser wavelength ($\lambda = 532$ nm). Owing to the existence of a PBG, the PhCs can be used to modulate localized electric fields effectively, and it is expected that through a combination of the effects of plasmonic resonance and PBG, the Raman scattering signals can be enhanced more significantly. The Raman spectra of the two prepared PhC films (PBGs at $\lambda = 536$ and 688 nm) after absorption of MB ($C = 50 \mu\text{M}$) are illustrated by Figure 5.

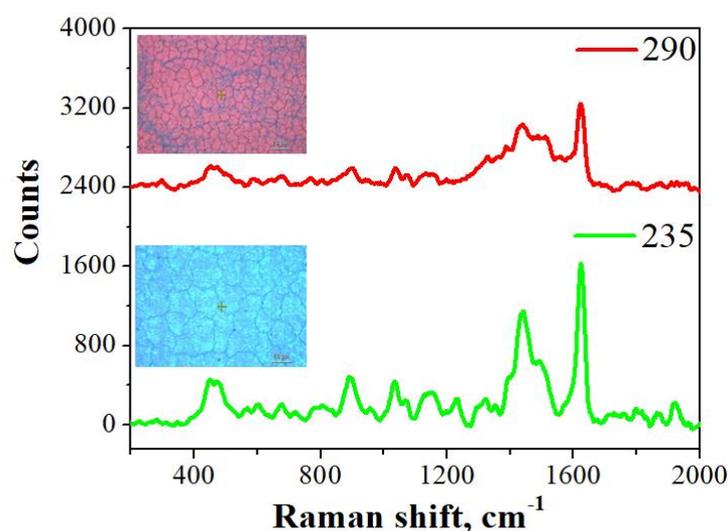


Figure 5. SERS spectra of MB adsorbed in porous PhC substrates with different PBGs. Numbers in the figure correspond to the diameters of the microspheres in nm. Insets: Optical microphotographs of surface areas where the Raman spectra were measured.

It is obvious that the $\text{SiO}_2@Ag$ PC films with a PBG at $\lambda = 536$ nm showed the highest sensitivity, compared to the sample where PBG is located at $\lambda = 688$ nm. In the SERS measurement, the wavelength of laser is $\lambda = 532$ nm, which is located close to the center of the PBG at $\lambda = 536$ nm. This means that the higher density of electromagnetic modes at the PBG band center leads to a larger light-matter interaction and results in greater enhancement of Raman scattering.

4. Conclusions

In summary, monodisperse SiO₂@Ag core-shell microspheres, consisting of Ag nanoparticles coated by SiO₂, were obtained. The SiO₂@Ag PhC films were prepared by self-assembly of the SiO₂@Ag core-shell microspheres with the help of vertical-deposition method. The strong SERS effect was established for the SiO₂@Ag PhC films used as SERS substrates. The position of the PBG is one of the main factors determining the enhancement of Raman scattering.

Acknowledgments

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References

- [1] Jiajie B, Genrui F, Suli W, Xin S, Hongbo X, Shu-Fen Zh 2017 *ChemistryOpen* **6** 637
- [2] Niu W, Su L T, Chen R, Chen H, Wang Y, Palaniappan A, Sun H, Tok A I 2014 *Nanoscale* **6** 817
- [3] Wu C Y, Huang C C, Jhang J S, Liu A C et al. 2009 *Opt. Express* **17** 21522
- [4] Yablonovitch E 1987 *Phys. Rev. Lett.* **58** 2059
- [5] Galisteo-Lopez J F, Ibisate M, Sapienza R et al. 2011 *Adv. Mater.* **23** 30
- [6] Ge J, Yin Y 2011 *Angew. Chem. Int. Ed.* **50** 1492
- [7] Klimonsky S O, Bakhia T, Knotko A V, Lukashin A V 2014 *Dokl. Chem.* **457** 115
- [8] Jiang P, Bertone J F, Hwang K S and Colvin V 1999 *Chem. Mater.* **11** 2132
- [9] Zhang Q S, Ye J W, Tian P, Lu X Y, Lin Y, Zhao Q, Ning Q L 2013 *RSC Adv.* **3** 9739
- [10] Tang S C, Tang Y F, Zhu S P, Lu H M, Meng X K 2007 *J. Solid State Chem.* **180** 2871
- [11] Khan Z, Al-Thabaiti S A, Obaid A Y, Alyoubi A O 2011 *Colloid. Surface. B* **82** 513
- [12] Steinigeweg D, Schlucker S 2012 *Chem. Commun.* **48** 8682
- [13] Xu C, Li W J, Wei Y M, Cui X Y 2015 *Mater. Design* **83** 745