Synthesis of SiO$_2$@Ag core-shell photonic crystals for SERS application

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Abstract. Core-shell SiO$_2$@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).

1. Introduction
In recent years, three-dimensional (3D) metallic photonic crystals (PhCs) have received extensive attention due to the special features of PhCs (large surface area and ability to modulate light) and the plasmonic enhancement effect of noble metals. They have promising potential applications in many fields, such as plasmonic enhanced emission and surface-enhanced Raman scattering (SERS). 3D dielectric-metal core-shell PhC structures have many advantages [1]. In this paper we synthesized a new type PhC based on SiO$_2$@Ag core-shell microspheres. The obtained PhCs composites can be used for SERS application.

2. Experimental
SiO$_2$ colloidal microspheres of 230-300 nm in diameter were synthesized by the method presented in [2]. Then, 20 ml of a 0.001 M solution of ammoniacal silver nitrate and 30 ml of a 7 μM solution of polyvinylpyrrolidone (PVP-can prevent the aggregation of the Ag nanoparticles) were added to the colloidal suspension with 0,1 g of SiO$_2$ microspheres. [Ag(NH$_3$)$_2$]$^+$ ions were adsorbed on the surface of the silica microspheres. At last, the SiO$_2$@Ag composite particles were formed by a simple

Fig. 1. Illustration of the synthesis route for SiO$_2$@Ag PhCs nanocomposites.
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. The procedure for preparing SiO$_2$@Ag PhC composites is illustrated in Fig. 1.

3. Results
Basic results are presented in Fig. 2. SEM image of the synthesized SiO$_2$@Ag core-shell microspheres and EDX analysis data for an arbitrary point are shown in Fig. 2a. The wide-angle XRD patterns of the obtained SiO$_2$ and SiO$_2$@Ag microspheres are presented in Fig. 2b, the absorption spectra of the prepared bare silica and core-shell structure - in Fig. 2c and the reflection spectrum of the photonic crystal film formed by the SiO$_2$@Ag core-shell microspheres is shown in Fig. 2d. The peak in the reflection spectrum related with the photonic band gap is clearly seen near 680 nm, which should give additional gain to the Raman spectrum.

![Figure 2(a-d).](image)

- **Figure 2(a-d).** (a) SEM image of SiO$_2$@Ag nanocomposites (EDX spectrum is shown in the inset); (b) X-ray diffraction patterns of SiO$_2$ and SiO$_2$@Ag composite microspheres; (c) UV-Vis absorption spectra of SiO$_2$ and SiO$_2$@Ag microspheres; (d) specular reflection spectrum of SiO$_2$@Ag core-shell PhC film at 8° incidence angle.

5. References