Silver nanoparticles formed on the photo-thermo-refractive glass as a new platform for SERS applications

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Metal nanoparticles have attracted considerable interest in a variety of fields due to their unique optical properties attributed to surface plasmon resonance (SPR). Surface-enhanced Raman scattering (SERS) is one of the most important application utilizing noble metal nanoparticles. During the past several years, SERS effect has attracted considerable attention for its potential applications in chemical detection and biological labeling. One of the versatile method to grow SERS-active silver nanoparticles on a glass substrate is ion exchange (IE) combined with subsequent heat treatment (HT) at applied electric field (thermal poling) or HT in a reducing atmosphere [1].

At present, photo-thermo-refractive (PTR) glasses that are already used widely in photonics can be classified as polyfunctional materials combining, in themselves, the properties of several monofunctional materials such as the photorefractive, holographic, laser, luminescent, and plasmonic ones. PTR glass was shown to possess excelent IE properties that can be used for formation of optical waveguides, luminescent silver clusters or plasmonic nanoparticles [2]. Out diffusion of silver ions and formation of thin silver films on the surface was observed after heat treatment of the ion-exchanged PTR glasses. This paper is devoted to study effect of heat treatment parameters on optical and SERS-active properties of silver nanopaticles formed on the surface of ion-exchanged PTR glasses.

Glass blocks of samples based on the $14Na_2O$–$3Al_2O_3$–$5ZnO$–$71.5SiO_2$–$6.5F$ (mol. %) matrix of typical PTR glasses were synthesized. Planar polished samples 1 mm thick were prepared for further investigation. Silver ions were incorporated into the PTR matrix-based glasses by ion exchange diffusion. The PTR glass samples were immersed in a bath with a melt of nitrate mixture $5AgNO_3/95NaNO_3$ (mol %) at temperature 320 °C for 15 minutes. The ion-exchanged samples were then heat-treated in air at various temperatures in the 350ºC−500ºC range for 1-7 h. A drop of 8×10^{-7} mol/l R6G aqueous solution with ~ 5 mm diameter was deposited on the samples to investigate SERS-active properties of silver films on the surface of the PTR glasses. The Raman spectra were measured after drying the R6G drop with Confocal Raman microscop (Renishaw), the laser beam (633 nm) was focused at the sample surface with a 50x/0.55 objective lens.

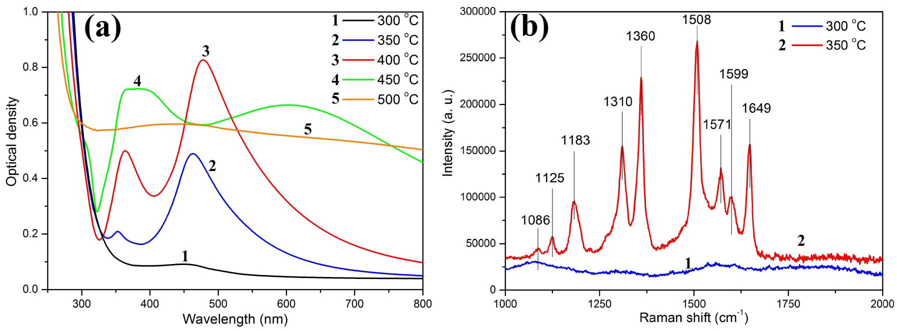

Fig. 1 Absorption spectra of the PTR glass samples after the IE and HT at different temperatures for 3h (a), and Raman spectra of R6G deposited on the PTR glass samples after the IE and HT at 300 and 350 °C for 7h (b).

One or two absorption bands related to the SPR of silver nanoparticles were observed in the spectra of the ion-exchanged and heat-treated PTR glasses (Fig. 1a). Spherical silver nanoparticles formed in the PTR glasses with ion exchange method are characterized the SPR absorption band centered at 410-420 nm. Splitting in the SPR absorption can be caused by the interaction between nanoparticles or deviation of nanoparticles shape from spherical.The amplitude of the SPR absorption increses with rising HT temperature up to 400 °C. Absorption spectrum of the sample heat-treated at 500 °C shows no absorption peaks that can be axplained formation of a continuous silver film. Our experiments reveal SERS-active properties of silver nanoparticles formed on the surface of the PTR glasses (Fig 1b). The registered R6G spectrum is in a good agreement with literature data [3], except a line at 1086 cm^{-1} assigned to the PTR glass.

The results show that ion-exchanged PTR glasses can be used for SERS applications. The SERS-active silver films were formed with ion exchange and heat treatment in air that allows for simplifying the technology of producing SERS substrates.

1) V. V. Zhurikhina et al., *Nanoscale Res. Lett.*, **2012**, *7*, 676.
2) Y. M. Sgibnev *et al.*, *J. Lumin*., **2016**, *176*, 292.
3) E. C. Le Ru *et al*., *J. Phys. Chem. C*, **2007**, *111*, 13794.