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The Identification of the Inorganic Pigments in the Cultural Heritage Objects Using Surface-Enhanced Raman Scattering

E. Shabunya-Klyachkovskaya, S. Vaschenko, V. Stankevich, and S. Gaponenko

Abstract The Ge/Si nanostructures with Au coating were used for surface enhanced Raman scattering by inorganic α-HgS microcrystals. The enhancement factor in the case of using these nanostructures like SERS-active substrates was higher than in the case of using Ag gel-film. We also compared Raman scattering efficiency in dependence on the laser excitation wavelength.

To date, surface enhanced Raman scattering (SERS) is known as one of the most sensitive technique for the identification of small quantities of analytes. Since organic molecules are much smaller than the nanoobjects used like SERS-active substrates, SERS is often used for the identification of the organic art pigments. To identify inorganic art pigments, micro-Raman spectroscopy is usually applied.

In our recent work (Klyachkovskaya et al., Plasmonics 6:413–418, 2011) we were able to get 100-fold enhancement of the Raman spectra of ultramarine microcrystals. In addition, it was shown that self-assembled Ge/Si nanostructures coated with a noble metal can be used like very perspective SERS-active substrates. In this paper, we use these substrates for surface enhanced Raman scattering by inorganic α-HgS microcrystals (vermilion). In addition we compare Raman scattering efficiency in dependence on the type of SERS-active substrate and the laser excitation wavelength.

So, two types of SERS-active substrate were used for the experiments. The first of them were the self-assembled Ge/Si nanostructures and the second one were the gel-films of the silver nanoparticles (10–25 nm in size). The Ge/Si nanostructures were grown by chemical vapor deposition (Stoica et al., Nanotechnology 18:455307, 2007). Silver sol has been prepared via Ag ions reduction with dextroglucose under heating (Fang et al., Chem. Phys. Lett. 401:271–275, 2005). The Raman measurements were performed in the backscattering configuration at room temperature.

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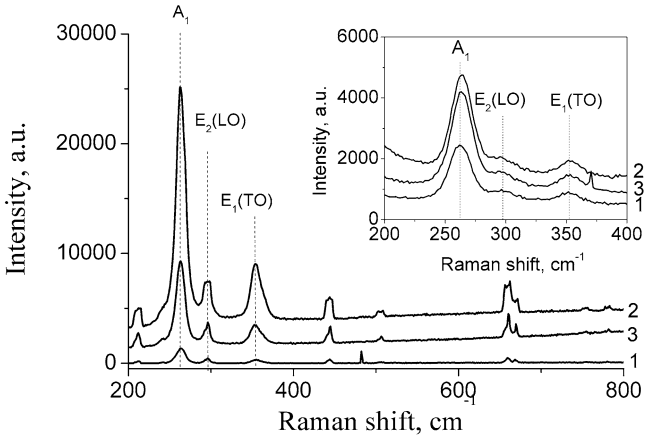

Fig. 32.1 Raman (1) and SERS spectra of vermilion, obtained using the Si/Ge – nanostrucres (2) and Ag gel film (3). The wavelength of excitation is 632.8 nm. In the inset: Raman and SERS spectra of vermilion excited with the Nd:LSB laser (531 nm)

The Nd:LSB laser (531 nm) as well as the He-Ne laser (632.8 nm) were used for Raman spectra excitation. The registration system consists of a spectrograph with a diffraction grating 1,200 grooves per mm (Solar TII S3901) and a CCD matrix, which is cooled with liquid nitrogen (Princeton instruments).

The bands at 262 cm^{-1} (secondary vibration of A_1), 296 cm^{-1} ($E_2(LO)$ optical phonon transverse vibrations) and 351 cm^{-1} ($E_1(TO)$ secondary longitudinal oscillations) occur in the Raman spectra. When Raman spectra are excited with the He-Ne laser (632.8 nm), the intensity increases in 15 fold in the case of using the Si/Ge nanostructures like the SERS-active substrate and in five fold in the case of using the silver gel-film as the substrate (see Fig. 32.1). In the case of using the Nd:LSB laser (531 nm) for Raman spectra excitation, the intensity increases only 1.9 and 1.7 fold, respectively (see the inset in the Fig. 32.1).

The dependence of the enhancement on the type of the SERS-active substrate may be related to their topography. The Ge islands on the Si substrate have a quadrangular pyramid shape, which leads to resonance with dipole plasma oscillations (Sajanlal et al., Nano Rev 2(0), 2011). In result, the local electric field at the top of the "pyramids" is essentially magnified. Additionally, the gold is the inert metal unlike the silver which is easily oxidized. As for the dependence of the Raman intensity on the excitation source, it's probably due to the fact that the He-Ne laser has a narrow contour of the excitation line and works in single mode unlike the Nd:LSB one, that has quite wide contour of the excitation line and excite Raman scattering over a wide range.

So, obtained results can be applied for the optimization SERS technique for the identification of the inorganic pigments in the Cultural heritage objects. The authors are grateful to Prof. D. Grutzmacher for providing the Ge/Si nanostructures for the experiments.

Keywords SERS • Vermilion • Inorganic pigments • Si-Ge nanostructures