Synthesis and characterisation of new types of nanoresonators for Raman analysis of surfaces

Heman Abdulrahman¹, and Andrzej Kudelski¹

¹ Faculty of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland, e-mail: hemin.80@mail.ru

Surface analysis of various materials (especially in the in situ conditions) is very important from the economic and scientific point of view. Such studies are especially difficult for so-called buried interfaces (e.g., the surface of the solid sample in the liquid or the high pressure gas), a situation which occurs in very important from the practical point of view interfaces of various biological samples in their “natural” environment. One of the tools which can be used for investigations of such interfaces is developed by Tian et al. shell-isolated nanoparticle-enhanced Raman spectroscopy – SHINERS [1]. In this approach, the analysed surface is covered with the layer of plasmonic nanoparticles (the plasmonic core is covered by the thin layer of transparent material) and then the Raman spectrum of the investigated sample is recorded. Metal cores of nanoparticles act as electromagnetic resonators, significantly enhancing the electric field of the incident electromagnetic radiation, and hence leading to very large increase of the Raman signal (the increase of the efficiency of Raman scattering is roughly proportional to the fourth power of the field enhancement). The ultrathin protecting coating does not damp surface electromagnetic enhancement, however, separates nanoparticles from direct contact with the probed material and keeps them from agglomerating [2, 3].

In this contribution we present some new types of nanoresonators for SHINERS measurements. For example, for measurements in the alkali environment we developed Ag@MnO₂ nanoresonators. Such nanostructures are significantly more efficient in the enhancing Raman signal than the previously used for SHINERS measurements in the alkali environment Au@MnO₂ nanostructures. In comparison to highly active in SHINERS spectroscopy Ag@SiO₂ nanostructures, Ag@MnO₂ nanoparticles are significantly more stable in alkaline media. We have also developed very efficient method of synthesis of highly efficient anisotropic silver nanoresonators covered by various protecting layers (e.g., SiO₂, MnO₂ or TiO₂) – for example see Fig. 1. To increase the efficiency of the synthesis of composite nanoresonators, and to decrease the unwanted agglomeration of formed nanostructures, before deposition of the oxide layer (e.g., SiO₂, MnO₂ or TiO₂) silver nanoparticles have been covered with very thin AgₓS layer.

The higher SHINERS activity of anisotropic nanoparticles is probably due to many sharp apexes and edges on their surface. Some examples of practical SHINERS measurements will be also presented.

Fig. 1. TEM images of nanoresonators for SHINERS measurements: left – Ag@AgₓS@SiO₂, right – Ag@AgₓS@MnO₂.

Keywords: surface-enhanced Raman spectroscopy; shell-isolated nanoparticle-enhanced Raman spectroscopy; SHINERS

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References