

ABSTRACT

Surface-Enhanced Raman Spectroscopy (SERS) is a powerful spectroscopic technique for molecular identification at low detection limits. The enhancement of the usually weak Raman scattering occurs on or near nanoparticles (usually noble metals-based) with the appropriate morphological and surface properties, as the electromagnetic field generated by the localised surface plasmon resonances is amplified. Owing to its high sensitivity, SERS is frequently used in heritage science to analyse samples of cultural heritage and detect organic colourants. In this work, preparation, characterisation and optimisation of novel UV-photoreduced SERS substrates and their application for the detection of the traditional organic colourants on objects of cultural heritage, such as madder lake (alizarin, purpurin), carmine lake (carminic acid), or lac dye (laccaic acid), are presented.

Silver nanoparticles were prepared *in-situ* in the hydroxypropyl cellulose (HPC) matrix by irradiation at different wavelengths (365 and 254 nm) following the principles of green chemistry. HPC plays a role in the reduction of silver and in the stabilisation of nanoparticles. Characteristics of the dispersions were evaluated with different methods (*e.g.* UV-Vis spectroscopy, infrared spectroscopy, SERS, electron microscopy) and found to depend on the weight ratio between the silver ions and HPC, time of irradiation, and energy of the incident irradiation. Interaction at higher energies led to a higher degradation rate of the HPC matrix, also causing lower pH values of the dispersion. The latter effect was more pronounced when a lower initial concentration of silver nitrate was used. Different formulations were tested as SERS substrates with alizarin solutions and several other probes. Different spectral responses were found to be related to different surface availability and/or to differences in the micro- or macro-environment of the nanoparticles. The substrates irradiated at lower energies showed superior stability, while the substrates with a lower concentration of silver ions and irradiated with higher energies were more suitable for the detection of compounds with acidic properties (such as carminic and laccaic acid). This is due to weaker electrostatic repulsion between the compounds and nanoparticles.

The UV-photoreduced SERS substrate of higher viscosity also showed the potential for the detection of the organic colourants in colour (paint) layers without the need for prior extraction. The colourants constituting the egg tempera colour layers were detectable immediately after the application of the substrate on the surface of the paint layer, while for the detection of colourants in linseed oil colour layers a pretreatment step was required (soaking/incubating the samples in the substrate for a longer period of time or hydrolysing with vapours of hydrofluoric acid). Furthermore, by detecting the cochineal lake pigment in a layer of the cross-section of a sample taken from a polychrome work of art, we also proved that such SERS substrates allow for a highly specific detection of the spatial distribution of colourants in real samples of cultural heritage.

Keywords: Surface-enhanced Raman spectroscopy, silver nanoparticles, photoreduction, organic colourants, heritage science.