Preparation of SERS substrates by gel encapsulation of Ag nanoparticles prepared by laser ablation

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SERS effectiveness, nanoparticle stability and the overlapping from interference species eventually existing in the medium are the parameters to be considered in the application of metal nanoparticles for surface-enhanced spectroscopic techniques [1]. Silver nanoparticles (Ag NPs) are usually prepared by chemical reduction, using sodium citrate and hydroxylamine hydrochloride as reducing agents. In both cases, by-products of the reduction process can negatively affect the adsorption of the molecule of interest [2]. Ag NPs prepared by laser ablation are free from interferences, although their time stability is quite poor. For this reason, the encapsulation of Ag NPs in an agar gel can help to overcome this drawback with the addition of an increase of the SERS effectiveness [3] in the analysis of organic dyes used in artworks.

In this work Ag NPs were fabricated by pulsed laser ablation of a Ag target in milli-Q water. Laser irradiation was carried out with nanosecond laser pulses using the fundamental (1064 nm), 2nd (532 nm) and 4th harmonic (266 nm) output of a Q-switched Nd:YAG laser (pulse duration 15 ns, repetition rate 10 Hz). Two irradiation times (25 and 50 minutes) and two laser fluences (3 and 6 times the Ag ablation threshold fluence, F_{th}) were considered. Thus, 12 different Ag NPs preparations were tested to study their SERS effectiveness using Diamond Green as probe molecule. Characterization of Ag NPs was carried out by UV-Vis spectroscopy and transmission electron microscopy (TEM). Then, encapsulation of the SERS substrates on agar gels was carried out by two methods: (a) preparation of pieces of agar gel and their immersion in the Ag NPs solution for 24 hours, and (b) preparation of pieces of agar gel dissolved in the Ag NPs solution. In both cases the agar-Ag NPs were put in contact with a Diamond Green solution for 24 hours before the measurement of SERS spectra. The enhancement factor obtained by each of the Ag NPs preparations, both in solution and encapsulated, were calculated in order to study their effectiveness as SERS substrates. Best results were obtained by Ag NPs prepared by irradiation at 1046 nm and at 6xF_{th} for 50 min.

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