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### ACCEPTED MANUSCRIPT

# Colloidal Lithography with Electrochemical Nickel Deposition as a Unique Method for Improved Silver Decorated Nanocavities in SERS Applications

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- \*E-mail: andrej.orinak@upjs.sk, Phone: +421-55-2342321, Fax: +421-55-6222124 Highlights
- Colloidal litography
- Electrochemicaly deposition of Nickel supporting layer
- Effect of depposition time of Ni supporting layer and Ag nanoparticles to SERS enhancement
- FDTD simulation confirmatory the experiments results
- Concentration dependece, time stability and good reproducibility of Ni/Ag SERS active substrates

#### **Abstract**

Two types of metallised nanocavities (single and hybrid) were fabricated by colloid lithography followed by electrochemical deposition of Ni and subsequently Ag layers. Introductory Ni deposition step iniciates more homogenous decoration of nanocavities with Ag nanoparticles. Silver nanocavity decoration has been so performed with lower nucleation rate and with Ag nanoparticles homogeinity increase. By this, two step Ni and Ag deposition trough polystyrene nanospheres (100,300,500,700,900 nm), the various Ag surfaces were obtained. Ni layer formation in the first step of deposition enabled more precisions controlling of Ag film deposition and thus final Ag surface morphology. Prepared substrates were tested as active surfaces in SERS application. The best SERS signal enhancement was observed at 500 nm Ag nanocavities with normalized thickness Ni layer  $\sim$  0.5. Enhancement factor has been established at value 1.078x10<sup>10</sup>; time stability was determined within 13 weeks; charge distribution at nanocavity Ag surfaces as well as reflection spectra were calculated by FDTD method. Newly prepared nanocavity surface can be applied as in SERS analysis, predominantly.

#### Keywords: colloidal lithography; Ni/Ag nanocavities; SERS; electrochemical deposition

#### 1. Introduction

Some of the important features by metal nanomaterials are the ability of interacting with light [1], nanoscale size, at which much of biology occurs [2], a high degree of bio-compatibility [3], not complicated procedures for bio-functionalization [4] and elevated surface to volume ratios [5,6]. Nano scale of materials is more important than size, the shape, surface treatment and internal structure of these nanosystems are responsible for the cited properties [7–9]. The fabrication of SERS substrates, which can offer the advantages of strong Raman signal enhancement with good reproducibility and low cost, is still a challenge for practical applications [10]. A wide variety of metal nanostructures is were reported in literature, with shapes ranging from simple spheres, to more complex and sometimes exotic architectures, which include

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