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Controlling the Deposit of Gold Nanoparticles and Area Coverage on Glass Substrates by a Multistep Method

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Gold nanoparticles (GNPs) had been used extensively in surface-enhanced Raman spectroscopy (SERS) substrates; the methods for substrate preparation include: electrochemically modified electrodes, colloids, island films, particles grafted on silanized glasses and regular particle arrays [1]. Here we present a simple reliable method for the deposit of GNPs on a commercial amine-functionalized glass substrate for their application as SERS probe. For the GNPs synthesis, 80µl of 0.25M chloroauric acid solution was added to a sodium citrate tribasic dehydrate solution (80 ml, 3mM) boiling under vigorous magnetic stirring. After 10 minutes boiling, the solution turned ruby red color indicating the presence of spherical gold nanoparticles [2]. Amino-functionalized microscope slides (Luminano, Ted Pella Inc.), 5 pieces of 25x8mm, were cut and washed with MilliQ water under sonication and submerged overnight in 3ml GNPs solutions. The unbounded GNPs were removed from the slides by washing three times with MilliQ water, after that, four of the substrates were submerged in 1,3-propanedithiol (3ml, 5mM) for 6 hours and rinsed plenty with methanol and MilliQ Water. By submerging the slides overnight again in the colloidal solutions, more GNPs were deposited onto the surface of the substrates due to the functionalization with thiol groups. This process was until we obtained substrates with 1 to 5 cycles of GNPs deposited. Figure 1A shows the UV-Vis extinction spectra of the as synthesized GNPs and the corresponding substrates labeled as S1 to S5. The GNPs spectrum presented a single extinction band located at 517.5nm; when GNPs are deposited in the amino-functionalized substrate the extinction band red shifted to 534nm due to the change of refractive index of the surrounding medium. As more GNPs deposit cycles were performed the extinction band broadened and shifted to longer wavelengths, and its optical extinction increased.

SEM analysis revealed quasi-spherical GNPs with a 17±3nm mean size, see Figures 1B and 2A (JEOL, JSM-7800F, operating in gentle beam mode at 1kV and 3mm working distance, 250 NPs measured). Representative SEM images of samples S1 to S5 are presented in figure 2B to 2F; with each GNPs deposit cycle the area covered increased, this was measured using ImageJ software tools [3]. SEM images were contrast enhanced, followed by background subtraction, binarization and area fraction calculation; five SEM images were analyzed for each substrate and the area analyzed was 1200x900nm. The covered area fractions are expressed as percentages in figures 2B-F; we observed that in samples S4 and S5 the deposit is no longer a monolayer of GNPs.

For the SERS assay, all the substrates were immersed overnight in a 1µM 4-aminothiophenol (4-ATP) solution and then rinsed three times in water and air dried. The SERS spectra were acquired using Renishaw InVia microscope Raman spectrometer (785nm excitation source, 4mW, 20x optical objective, 4x4 mesh, 20µm distance between points) for all substrates (Fig. 1C). Samples S1 and S2 showed only glass luminescence. Substrate S3, the monolayer substrate with the highest area coverage, had the maximum intensity for the 4-ATP Raman peaks [4]. For substrates S4 and S5, the not monolayer substrates, the 4-ATP Raman signal was detected but it was lower than the signal for substrate S3; demonstrating that monolayer substrates with high area coverage perform better as SERS probes.

We have demonstrated a simple reliable method for the deposit of GNPs on glass substrates that allows controlling the area coverage by a multistep process and their application as efficient SERS substrates.

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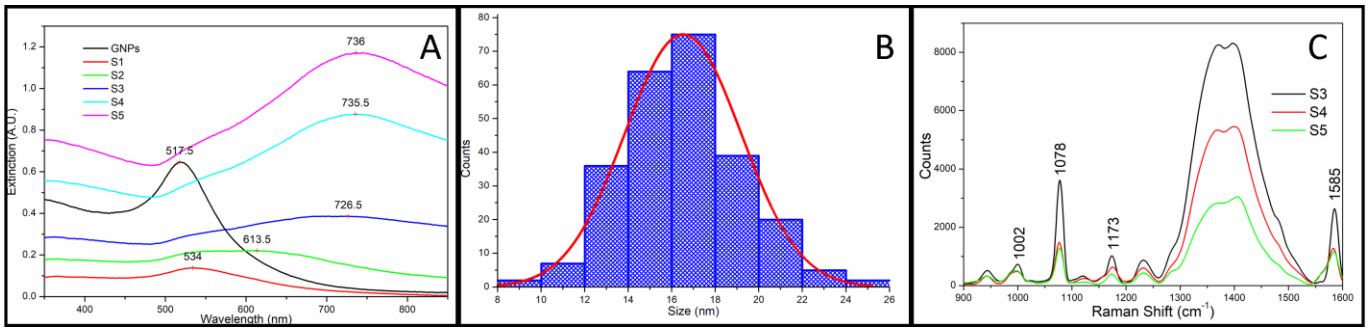

Figure 1. UV-Vis extinction spectra of the GNPs and the substrates S1-S5 (Panel A), GNPs size distribution as measured by SEM (B), and 4-ATP SERS spectra recorded in substrates S3, S4 and S5.

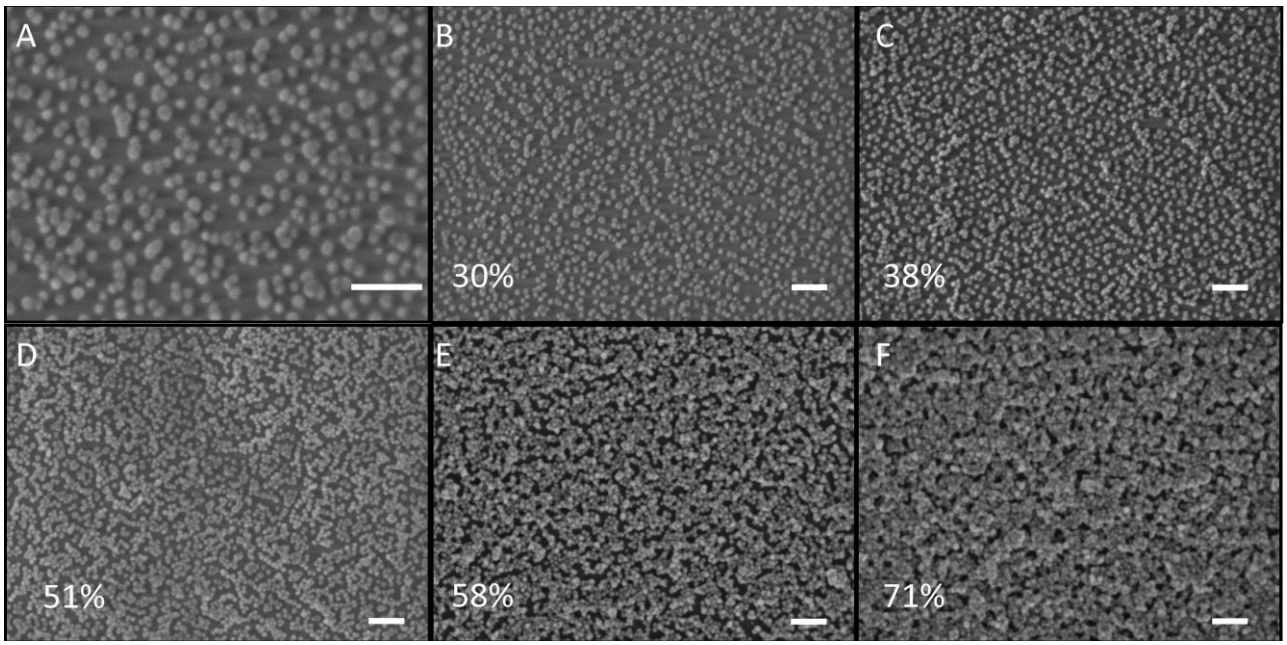

Figure 2. SEM images of the GNPs deposited on the glass substrates. Panels **A** and **B** correspond to the substrate S1 and panels **B-F** correspond to substrates S2 to S5 respectively. Scale bar is 100nm for all cases.

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