Controlling the Morphology of Silver Nanoparticle Films formed by Laser-induced Deposition from Liquids

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Photoreduction of silver has been widely used to prepare and modify nanoparticles in solution. [1] However, relatively few investigations have addressed laser-induced photodeposition of silver directly on solid substrates.[2,3,4,5] Here we show that a thin coating of (3-aminopropyl) triethoxysilane (APTES) dramatically improves the density of silver nanoparticle films deposited on glass by laser induced deposition from liquids. Additionally we show that the deposit's structure varies dramatically with illumination intensity. Increased density and structural control could be important for direct material patterning, deposition of Ag seeds for subsequent processing, surface-plasmon resonance (SPR) and surface-enhanced Raman spectroscopy (SERS).

A soda lime glass slide in contact with an aqueous solution containing 1 mM sodium citrate ($NaC_6H_7O_7$) and 10 mM silver nitrate ($AgNO_3$) is illuminated with a 532 nm wavelength continuous wave laser. The reagent concentrations were selected from 9 trial combinations to optimize deposit density. A range of illumination intensities were investigated with a maximum of 80 W/cm^2. For coated samples, the slide was immersed in a 10 wt.% aqueous solution of APTES for 30 minutes and subsequently washed. A previous study showed that this coating procedure yields approximately three molecular layers of APTES.[6]

At near neutral pH, the APTES becomes positively charged[7] and may nucleate, attract, and/or stabilize the newly formed, negatively charged silver particles. The APTES coating increases film density greatly as shown in Figures 1 and 2 where coverage increases from 34% to nearly 100%. Using this method it is also easier to notice that different illumination intensities form differently shaped nanoparticles. Nanoparticles formed with the highest intensities tend to be more spherical, and ones formed with lower intensities are plate-like and grow normal to the substrate. Under the conditions studied thus far, these differences appear to depend only on the incident intensity and not on the total dose.

In conclusion, an improvement in laser-induced silver deposition has been obtained by coating the substrate with a thin APTES layer. A correlation has been found between illumination intensity and structure of the silver deposits.

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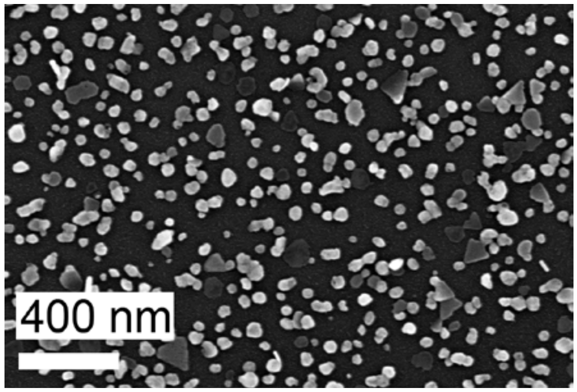

Figure 1: Deposition without APTES: Silver nanoparticles made with an illumination of 5 minutes at an intensity of 66 W/cm^2. It can be seen that the particles are spread and they do not form a continuous film.

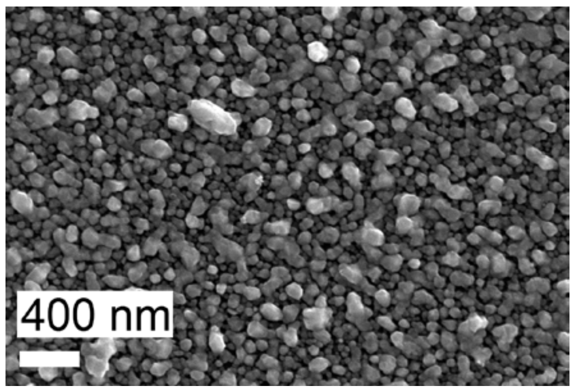

Figure 2: Deposition with APTES: Silver nanoparticles made with an illumination of 5 minutes at an intensity of 73 W/cm^2. It can be seen that, compared to the particles shown in figure 1, these particles are closer to each other, larger and they make an almost continuous film.

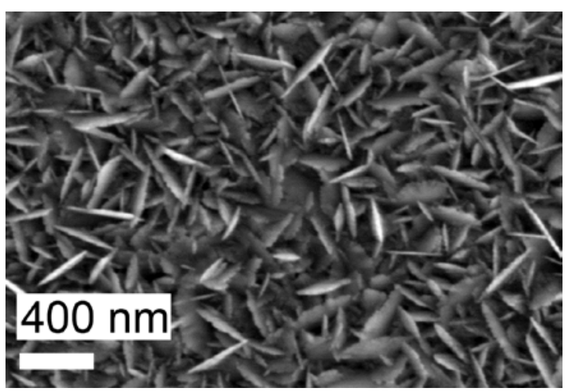

Figure 3: Deposition made with low Intensity: Silver nanoparticles made with an illumination of 16 minutes at an intensity of 17 W/cm^2. It can be seen that the particles are plate like and also form a continuous film.