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Growth mechanisms of self-assembled gold nanoparticles in Deep Eutectic Solvent

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Self-assembled metallic nanoparticles are attractive candidates for plasmonic heating, non-linear optical switching [1], bio-analytical, chemical [2], catalytic , and surface enhanced RAMAN scattering (SERS) [3]. These applications are strongly dependent on the shape, size, composition, size distribution and volume fraction of nanoparticles. Here, self-assembly of gold nanoparticles (AuNPs) was obtained by low energy sputter deposition on Deep Eutectic Solvent (DES ; choline chloride and urea) surfaces and elucidated by Small Angle X-ray Scattering (SAXS), Cryogenic Transmission Electron Microscopy (Cryo-TEM) and UV-Vis. Data analysis shows the formation of spherically shaped AuNPs of 5 nm in diameter with narrow size distributions. Moreover, analysis reveals that prolongation of gold-sputtering time has no effect on the size of the particles and only the concentration of AuNPs increases linearly. The growth of the maxima in evaluated structure factor S(q) and the distance distribution function G(r) at higher concentrations of AuNPs is caused by the interference effects. Moreover, it indicates that the particles are not arranged in random but have a self-assembly in short-range order. Prolonged gold-sputtering time leads to increase in the ordering of the AuNPs with strong interactions. It is proposed that the self-assembly of AuNPs is due to the ionic liquid template effects of DES and the balancing physical forces. Moreover, a disulfide based stabilizer bis ((2-Mercaptoethyl) trimethylammonium) disulfide dichloride was applied to supress the self-assembly. The stabilizer even reverses the self-assembled or agglomerated AuNPs back to stable 5 nm individual particles. The templating effect of DES is compared with the non-templating solvent Castor oil. Our results will also pave a way to understand and control self-assembly of metallic and bimetallic nanoparticles.

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