THE ROLE OF AFM, HRTEM, SAXS AND OPTICAL SPECTROSCOPY IN SIZING Cu, Ag, Fe AND Ni NANOPARTICLES GENERATED BY ULTRAFAST LASER ABLATION OF SOLID TARGETS IN DIFFERENT LIQUID MEDIA

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This work deals with the generation of Cu, Ag, Fe and Ni nanoparticles (NPs) by femtosecond laser ablation in different media and the characterization of their structures, configurations and sizes using Atomic Force Microscopy (AFM), High Resolution Transmission Electron Microscopy (HRTEM), Optical Extinction Spectroscopy (OES) and Small Angle X-Ray Scattering (SAXS). Colloidal suspensions receive nowadays considerable attention due to their attractive physicochemical properties, which boost applications in catalysis, optics, electronics and biomedical areas based on their unique size-dependent optical, electrical and magnetic properties. Over the last few years, we have carried out a systematic work in producing, by top down methods, noble-metal (Cu and Ag) metallic NPs colloids [1], [2] and more recently magnetic NPs such as Fe and Ni [3]. In laser ablation, energy is deposited in a bulk material at a sufficient fast rate so that it breaks up and forms particles in the nanometric scale. The structure of the so-produced colloids includes a variety of morphologies like bare-core, core-shell and hollows NPs as well as aggregates including fractals. AFM appears as a suitable tool for 3D characterization with sub-nanometric resolution. AFM and TEM characterize dried samples while OES and SAXS characterize the NPs structuring in the colloid state. The observation of isolated NPs is shown in Fig. 1 for Ag. The formation of fractal structure is shown in Fig. 2 for Fe colloid. Self-similarity property is observed for Ag colloid through the invariance under scale transformation comparing AFM (inset in the lower panel of Fig. 3) with optical microscopy images shown in Fig. 3. Self-similarity was analyzed by applying box-counting method to the AFM images. Complementarily, TEM technique images a hollow Ni NP, as shown in Fig. 4. The size distribution and composition of the colloidal suspensions were derived from OES by fitting experimental extinction spectra using Mie theory, taking into account specific modifications of the complex metal dielectric function with size for free and bound electron contributions, as shown for Cu colloid in Fig. 5. We discuss the advantages, limits and complementarity of AFM and TEM techniques with OES optical spectroscopy and SAXS to characterize nanometric size colloids produced by femtosecond laser ablation.

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FIGURES

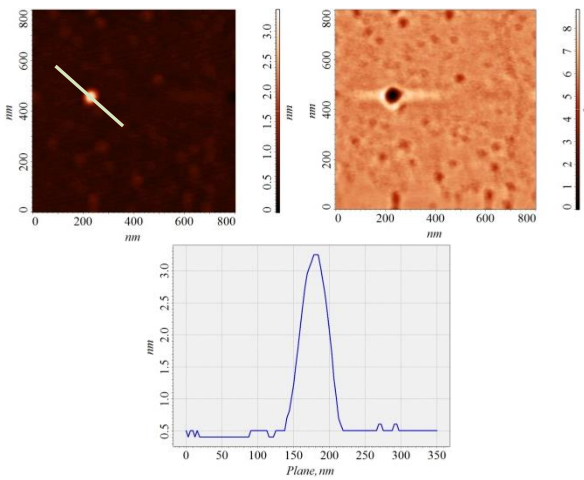

Fig. 1: AFM data analysis of a single Ag nanoparticle of 2.7 nm diameter. Upper panel height profile of topographic image. Left: semicontact topography image. Right: second pass phase contrast image.

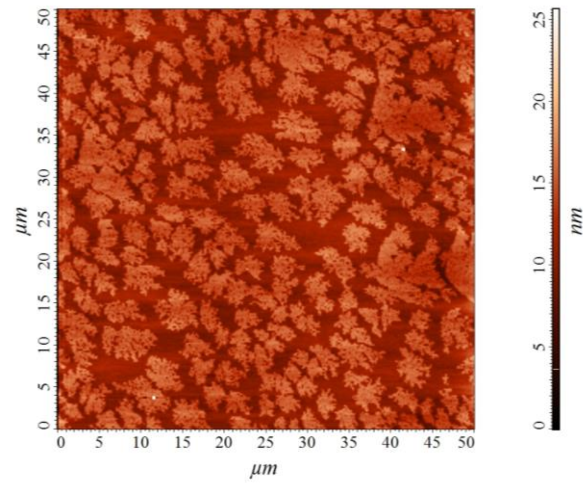

Fig. 2: 50 x 50 μm AFM image of Fe fractal structure acquired using semicontact mode over mica. Right bar color scale from 0 to 25 nm.

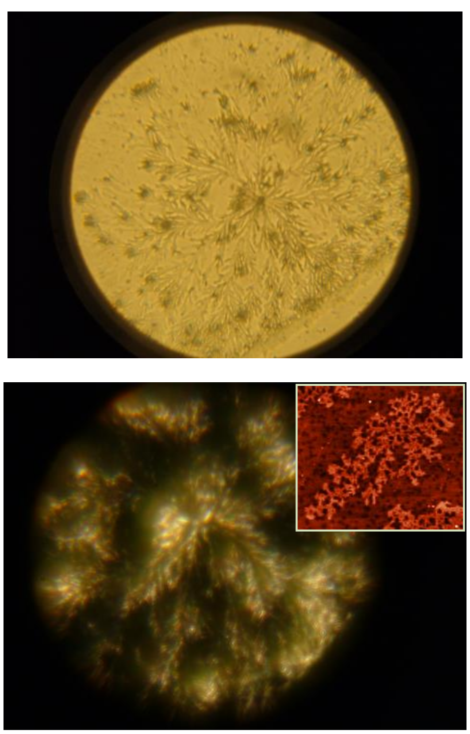

Fig. 3: Upper panel: optical microscopy bright field image of a fractal structure produced dropping Ag colloid into a glass slide. Lower panel: dark field image of other region of the same sample. Field of view diameter: 200 μm. Inset: 12 x 10 μm AFM image of Ag fractal structure acquired using semicontact mode over mica substrate. Color scale from 0 (dark) to 5.5 nm (white).

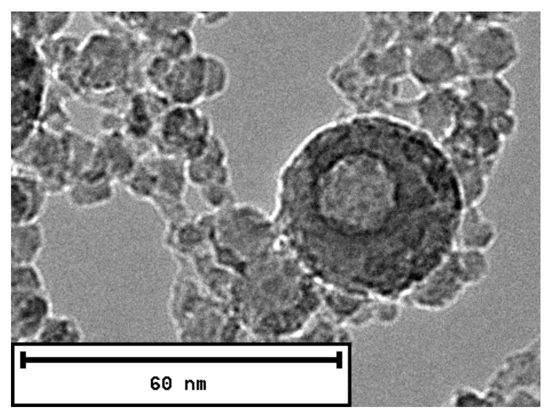

Fig. 4: TEM image of hollow Ni nanoparticle.

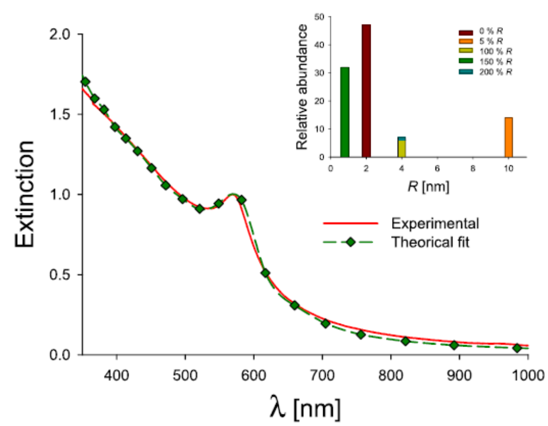

Fig. 5: Experimental spectra and theoretical fit of colloidal suspension fabricated in acetone with pulse energy E = 500 mJ. The fit is based on a combination of Cu bare-core and Cu-Cu_2O structures.