Radiolysis Metallization and/or photo reduction of auto-assembled nanostructured polymers

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The formation of nanometric metallic objects is a very promising field of research due to the modifications of solid materials properties. Such modifications can be induced by size reduction when surface effect or confinement effect becomes significant. Depending on the nature of the metal, the size and the shape of the nanoparticle, it is possible to obtain very different optical properties (displacement of the plasma band, nonlinear optical traits) and semi-conductivity...

We developed an innovative method combining the self-assembled properties of organic amphiphilic molecules and the metal reduction to form nano-objects with adjustable functionalities [1,2]. Different shapes can be obtained by using organic structures as molds which are covered by a metallic layer of nanometric thickness. The metal reduction is performed by the radiolysis of solubilized ions (Ag⁺) to the solution or by a photo-reduction procedure. In order to obtain more complex shape and elaborate mixed metallic nanostructures we enlarge the mold to polymers. Indeed, diblock copolymers “hydrophobic-hydrophilic” poly(styrene)-block-pol(acrylic acid) (PS-b-PAA) are used as the organic material. These macromolecules present the advantages with respect to the classic surfactants: First, they have an enhanced surface activity at the air/water interface compared to small surfactant molecules. Second, they allow a fine adjustment of the surface density charge and thus the absorption of metallic ions in the neighborhood of the organic interface by modifying the pH of sub-phase.

We have characterized the structure of the formed organic-metallic nanostructures at the air-liquid interface of the ionic (Ag+) solution sub-phase and we have controlled the adsorption of metallic ions in the neighborhood of the organic interface, by performing simultaneously the grazing Incidence x-ray measurements (GIXD) (figure (a)) and fluorescence (figure (b)) to follow the evolution of the concentration of silver atoms at the interface at different physicochemical conditions as pH sub-phase (acid and basic) and surface density.

Indeed, the GIXD spectras exhibit several diffraction peaks just at basic pH indicating that these nanostructures are formed only in the vicinity of the hydrophilic chains when they are ionized. They composed not only of the metallic silver but also of the silver oxide. In addition, the study of the growth kinetic of each diffraction peak allowed us to understand that the silver oxide grows earlier and more rapidly than the metallic silver. We note also, in the 2D spectra that these diffraction peaks are rings, demonstrating that the formed nano-objects are the colloids. We have obtained a silver wire at the air-liquid interface resulting from the reduction of ions under footprint beam (figure (c))
Figures: (a) GIXD spectra diffraction of inorganic nanostructures formed by irradiating a monolayer of copolymers in the presence of silver ion at pH = 9. (b) Intensity of silver fluorescence (at 3.1 Kev) as a function of time. (c) Photo of silver wire floating on the liquid interface after reduction of Ag⁺ at pH = 9

References