Synthesis of metal nanoparticles in polymeric films induced by electron beam

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I. Intorduction

Metal nanoparticles are generated by chemical reduction of ion precursors in solution and matrices. The aim of the present work is to synthesize and characterize composites constituted of metal nanoparticles embedded in a polymeric film, both generated without additives *via* a one-step exposure to ionizing radiation. Using electron beam, the process will permit the production of metal nanoparticles exclusively in the irradiated parts of the polymeric films. In this study, the elucidation of formation mechanism in polymeric films was investigated. Also, conditions have been found to radiolytically synthesize stable metal nanoparticles of silver or gold embedded in polymeric films.

II. Experimental

For the synthesis of the films, the solution concentrations in the casting solvent propylene glycol monomethyl ether acetate (PGMEA) were $AgClO_4$ or $KAuCl_4$ at 2×10^{-2} mol L^{-1} and 0.5 mol L^{-1} in poly(styrene) (PS) or poly(methylmethacrylate) (PMMA), respectively. A volume of silver ions and PS or gold ions and PMMA in PGMEA is deposited drop by drop on a quartz plate at the temperature of 80-90 °C, and the solvent is evaporated. The film is then exposed using 75 kV electron beam (EB). The irradiated films are then ready for characterization by optical spectrophotometry, microscopy and XRD.

III. Results and discussions

After an EB exposure, the film is still totally transparent. However, the exposed part of the film acquires the specific yellow color for silver nanoparticles films, which is due to the silver clusters after heating the film. The optical absorption spectra at increasing doses after heating are shown in **Figure 1**. The absorbance maximum is at 410 nm as for the surface plasmon band of silver nanoparticles. The absorbance after heating of the Ag-PS film does not increase much between 80 and 200 $\mu C\ cm^{-2}$. Clearly, the formation of clusters is strictly restricted to the exposed area but the absorbance intensity is too small before the heating step. Interestingly, heat alone is unable to start the reduction in the unexposed area and developable nuclei are provided exclusively by EB irradiation. In AFM images of the film, the individual silver nanoparticles have a diameter of 6 nm (**Figure 2a**). TEM images show also nanoparticles of 5 nm embedded in the film (**Figure 2b)**. In HRTEM images, some clusters are larger and display a pentagonal shape (**Figure 2c**) that we assign to 5 multi-twinned clusters with a fcc structure as shown by the XRS patterns (**Figure 2d**). Thus, conditions have been found to radiolytically synthesize stable metal nanoparticles of silver or gold embedded in polymeric films. Also, direct patterning was attempted using silver nanoparticles.

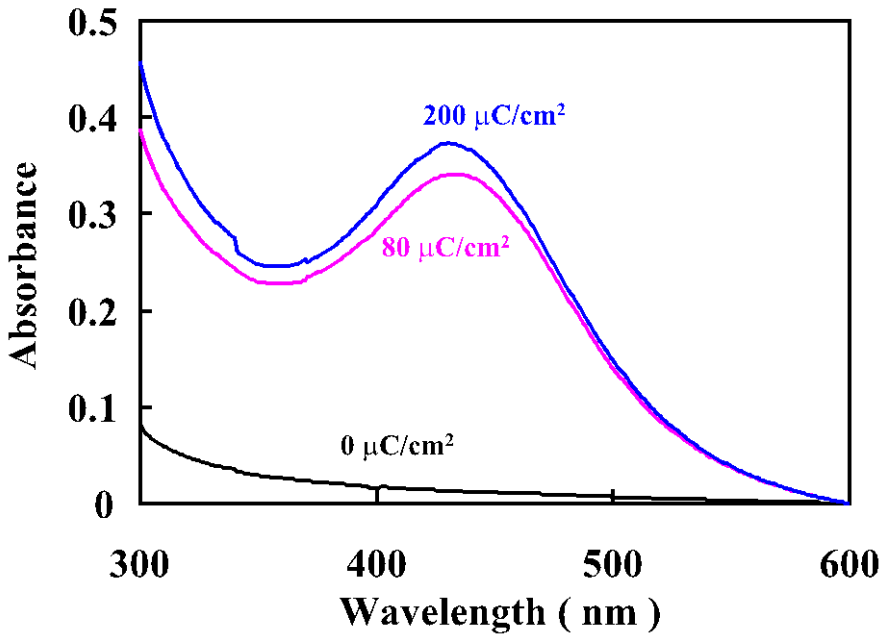

*Figure 1:*Optical absorption spectra of PS films containing $AgClO_4$ at 4% loading, before and after increasing irradiation doses delivered by the 75 keV electron nano-beam then heating at 120 °C for 5 min.

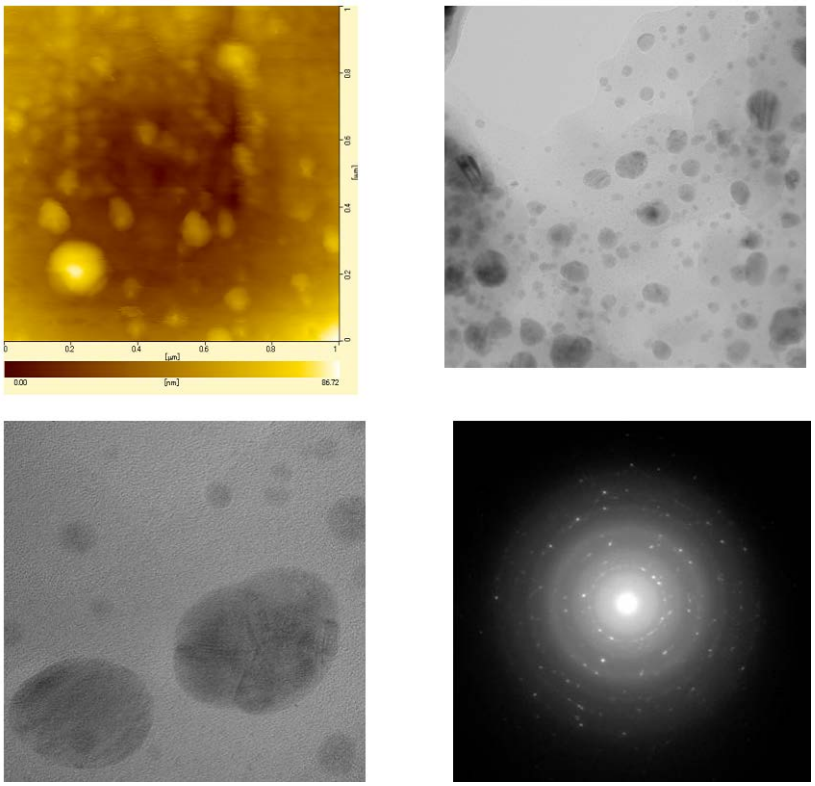

Figure 2 Silver nanoparticles synthesized in PS films irradiated using the 75 keV electron beam (dose : 200 μC cm-2), then heated at 120 °C for 5 min. a- AFM image b- TEM image c- HRTEM image d- XRD pattern.