Poster

PREPARATION OF Ag NANOPARTICLES BY γ–IRRADIATION: APPLICATION TO SURFACE-ENHANCED RAMAN DETECTION OF FUNGICIDES

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Small metal clusters are of great interest because of their optical, electronic and catalytic properties and are useful in wide fields[1-3], including biological labelling[4,5] and photography. Their unique properties are mostly dependent on the size and geometry of the nanoparticles.

Over the recent past, many efforts have been addressed to the preparation of noble metal nanoparticles, such as silver, gold and platinum. Besides the use of conventional chemical and photochemical techniques, γ-radiolysis appears to be a suitable method to form metal colloids in solution.[6,7]

The γ-irradiation has important advantages as compared to the chemical reduction method. It does not require the addition of reducing agents. In fact, the reducing agents are represented by radical species formed by the interaction of ionising radiation with the solvent. In aqueous solutions the formation of two short-lived reducing species, solvated electron (e^-_{aq}) and hydrogen atoms ($^\bullet H$), is obtained together with the $^\bullet OH$, a strong oxidizing radical. Both e^-_{aq} and $^\bullet H$ have reduction potentials capable of reducing metal ions to lower valences and, finally, to metal atoms. From monovalent cations, such as Ag^+ ($E°(Ag^+/Ag^0(aq))$= -1.8 V), metal atoms (Ag^o) are formed according to:

$$Ag^+ + e^-_{aq} \rightarrow Ag^0$$
$$Ag^+ + H^\cdot \rightarrow Ag^0 + H^+$$

Ag nanoparticles were successfully prepared by γ-radiolysis of Ag^+ aqueous solution containing *t*-BuOH or *i*-PrOH (Figure 1). We have seen that the absorbance maximum and the size distribution of particles depends on factors such as: irradiation dose, Ag^+ concentration and the alcohol molecule employed as scavenger of $^\bullet OH$ radicals. Thus the control of all these experimental conditions allow to obtain a metal suspension with a controlled mean size. One of the main advantages of this Ag nanoparticle preparation method is the fact that minimum hindrance from impurities is observed in the SERS spectra. This is an important issue in SERS technique, since many times the presence of impurities coming from other species present in the medium avoids a correct interpretation of the results.

The use of low radiation doses lead to the preparation of Ag nanoparticles which remain stable in suspension during months without any stabilizer of colloids which may introduce further spurious bands in the Raman spectra. In the presence of *i*-PrOH a more intense Ag reduction is induced due to the reducing ability of the derived alcohol radicals, thus increasing the efficiency of the metal reduction. The best experimental conditions to obtain Ag nanoparticles by radiolysis were at a dose of 100 Gy and at a metal concentration of 10^{-4} M (Figure 1B).

The combination of microscopy and SERS allowed to develop a sensitive and more spatially resolved SERS-based method to detect the fungicide thiram and to carry out studies, even at low concentrations, without the overlapping of impurities normally existent in conventional colloidal suspensions of Ag nanoparticles. These studies revealed in more detail the changes occurring in the pesticide structure and its orientation on the metal surface.

References:

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Figures:

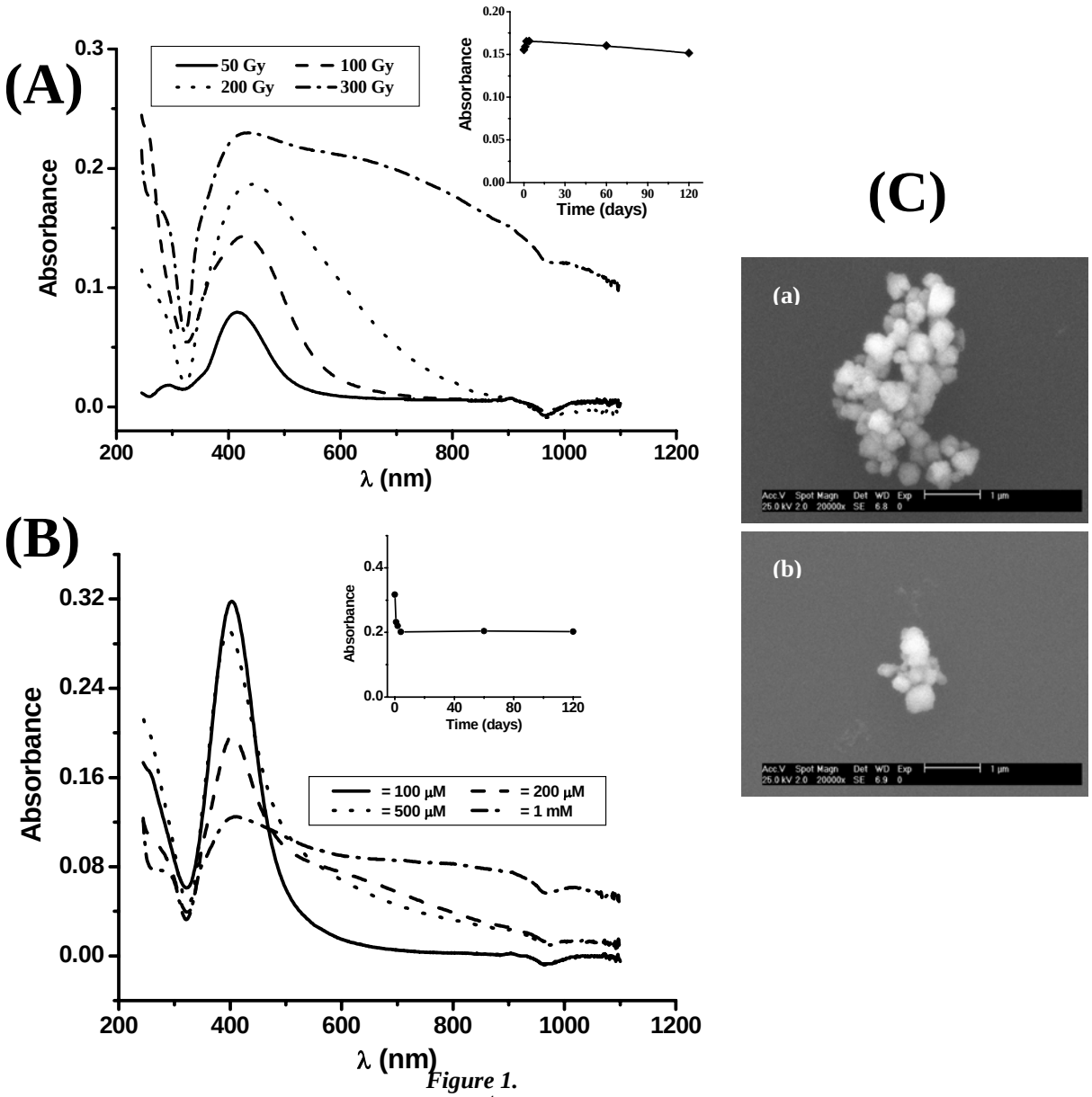

Figure 1.

A: UV-Vis spectra of Ar-purged solutions containing 2×10^{-4} M $AgNO_3$ and 0.5 M *t*-BuOH after γ-irradiation at natural pH; total delivered doses reported in the figure. Inset: time evolution of the 428 nm band absorbance, 100 Gy .
B: UV-Vis spectra of Ar-purged solutions containing different concentrations of $AgNO_3$ (as reported in the figure) and 0.5 M *i*-PrOH after γ-irradiation at natural pH; total dose, 100 Gy. Inset: time-evolution of the 408 nm band, [$AgNO_3$] = 1×10^{-4} M ($Ag_{100x100}$ colloid).
C: SEM micrographs of two aggregates obtained by immobilizing the Ag_0 colloid obtained by a total dose of 100 Gy and 1×10^{-4} M $AgNO_3$ and 0.5 M i-PrOH on a glass substrate.