

SELF-ORGANIZED ORIENTED AG NANOCOLUMNS: STRUCTURE AND OPTICAL PROPERTIES

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Metal nanoparticles exhibit unique size and shape dependent optical properties, which make them ideal candidates for the development of new nanoscale electronic and optical devices. Much of this interest is stimulated by the possibility of generating large electromagnetic field enhancement via Surface Plasmon Resonance (SPR). However, practical application of nanocomposites containing metal nanoparticles requires in most cases a fine control of the size, shape and orientation of the nanoparticles.

Among the different methods used to produce metal nanostructures pulsed laser deposition (PLD) has proved its potential for the production of nanoparticles not only on surfaces, but also embedded in complex matrices such as oxides with a nanometer control of their in-depth distribution and reduced size dispersion. In earlier works we have successfully used PLD to produce metal nanoparticles in amorphous hosts such as amorphous Al₂O₃, the nanoparticles being organized in layers whose separation can be easily controlled.¹ This technology has been extended to produce self-assembled Ag nanocolumns,² shown in Fig.1a, by reducing the separation between consecutive layers of nanoparticles, allowing the synthesis of oriented nanostructures having a diameter of 2.7±0.2 nm and a height of 6.7±0.2 nm (aspect ratio ≈2.5). In this work we explore the limits of the deposition technique in order to produce nanocolumns with larger aspect ratios (up to 20) by optimizing the synthesis sequence. High resolution electron microscopy shows the production of Ag nanocolumns having diameters in the range 2.5-3.0 nm and an aspect ratio of 6-7 (Fig.1b). However, a partial loss of the alignment of the nanocolumns is observed when trying to produce nanocolumns with even larger aspect ratios (Fig.1c). Optical extinction spectra of the embedded nanocolumns show the presence of two SPR modes which correspond to the transverse and longitudinal modes of the nanocolumns (Fig.2). These SPR modes are well separated, thus confirming large aspect ratios. When increasing the aspect ratio the transverse mode shows, as expected, a clear blue-shift, while the longitudinal SPR does not present any significant red-shift, as opposite to what is predicted by theoretical models. This behaviour is correlated with the loss of order of the nanocolumns and the possible breaking of nanocolumns having large aspect ratios.

References:

- [1] J.-P. Barnes, A.K. Petford-Long, R.C. Doole, R. Serna, J. Gonzalo, A. Suarez-Garcia, C.N. Afonso, D.E. Hole, *Nanotechnology*, **13** (2002) 465.
- [2] J. Margueritat, J. Gonzalo, C.N. Afonso, A. Mlayah, D.B. Murray, L. Saviot, *Nanoletters*, **6** (2006) 2037.

Figures:

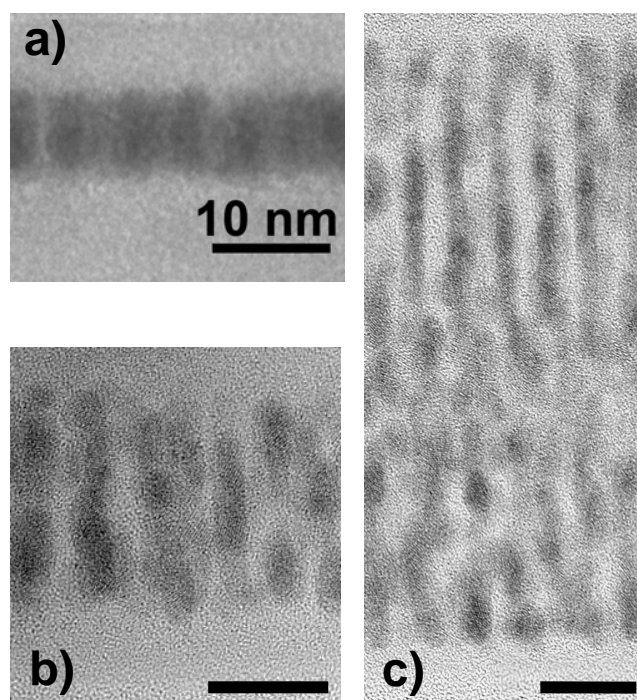


Figure 1. Cross-sectional HREM images of nanocomposite samples containing Ag nanocolumns with increasing aspect ratios: (a) 2.5, (b) 6-7 and (c) 20. The scale corresponds in all cases to a length of 10 nm. Note that (c) is in a different scale.

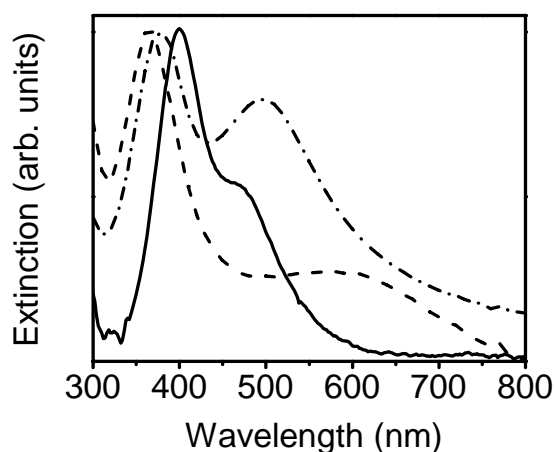


Figure 2. Extinction spectra of nanocomposite samples containing Ag nanocolumns with increasing aspect ratios: (continuous line) 2.5, (dashed line) 6-7 and (dash-dot line) 20. The spectra are shifted on the vertical axis for clarity.