# Structural properties of Ag/Cu/O based nanocomposites obtained by pulsed laser ablation in water

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Nanoparticles (NPs) of coinage metals represent an important class of nanomaterials, due to their perspective applications to several fields, including catalysis, medical diagnostic, sensing, drug delivery and development of smart materials, such as fabrics or paintings [1]. In this framework, bifunctional metal or metal/oxide NPs are attractive structures, which are expected to combine the nanoscale properties of two different materials. For example, Cu/Ag bifunctional nanoparticles could provide the well known Raman enhancing efficiency of copper and silver in a wider spectral range of laser excitations and, at the same time, the catalytic and bactericide properties of both metals. In principle, by using such structures, it would be possible to catalyze and monitor by Raman spectroscopy a chemical reaction directly to the single NP level.

Although current chemical methods permit a high degree of versatility concerning size, morphology, composition and surface functionalization of the NPs, the presence of contaminants and reaction by-products can impair applications to several fields, where high purity is a major concern. In this sense, physical preparation protocols, such as pulsed laser ablation in liquid environment, can provide a convenient alternative. However, while laser ablation has been widely investigated for the case of homogeneous NPs, its potentialities in the production of bifunctional nanocomposites has been seldom considered [2].

A fast and easy one-pot synthesis procedure has been recently proposed by some of us, allowing production of Ag/Cu or Pd/Cu nanocomposites by using a ps laser emitting at 1064nm. Such structures are obtained by irradiating a Cu target immersed in aqueous solutions of $AgNO_3$, $AgNO_2$ or $Pd(NO_3)_2$ [3]. The formation mechanism is based on the redox process taking place among Cu clusters extracted from the target and Ag or Pd ions dissolved in the liquid environment. In principle, it can lead to different structures, ranging from core-shell NPs, to alloyed NPs or to bicomponent clusters. In this sense, thorough understanding and control of the process through the tuning of the preparation parameters require careful structural analysis of the obtained products.

This contribution is aimed at describing the structural properties of Ag/Cu/O nanocomposites obtained with the above mentioned procedure, in order to elucidate the relation among fabrication parameters and composition of the final products. For this purpose, XRD, XPS and HRTEM results will be compared with UV-Vis spectroscopy, $\zeta$-potential characterization and Raman tests performed after particle functionalization with organic ligands.

We prepared the NPs by using different concentrations of $AgNO_3$ in water (from 1.2 mM down to 0.01mM) and different energies per pulse (ranging from 3 mJ up to 50 mJ), which, in our focusing conditions, correspond to fluences of 0.1÷3 J/cm$^2$. In the most favourable cases, which correspond to the best trade-off between Cu(0) rate of extraction from the target and concentration of Ag(I) in the liquid, the samples were stable for weeks and exhibited a strongly positive value of $\zeta$-potential (>40 mV), indicating a positively charged particle surface. While typical surface charge of AgNPs in water is strongly negative, the sign change has to be attributed to the presence of Cu [4]. Analysis of UV-Vis spectra also agrees with a model consisting of AgNPs surrounded by a Cu-based layer.

In order to get deeper information on the structures of the nanocomposites and on the oxidation states of the metals, we performed XRD, XPS and HRTEM characterizations. XRD spectra are

dominated by the signal of highly crystalline Ag in its fcc phase, while the bands of crystalline Cu are absent. In contrast, beyond the bands belonging to residual $AgNO_3$, some bands are visible, which could be assigned to different phases of Cu oxides or Ag/Cu/O alloys [5]. HRTEM, (Jeol JEM3010 operated at 300 kV, point resolution of 1.7 Å at Scherzer defocus) micrographs (Fig 1a) were analysed following the procedures suggested by Ruijter [6]. Ag having fcc structure (2.353 Å {111}) together with metallic Cu (2.13Å {111}) and CuO (tenorite, 2.551Å (-111), 2.323Å (111)) are found. This is confirmed by XPS analysis (Fig 1b). The fitting of the core transaction spectrum requires the use of at least two functions (curves blue and red in figure 1b) representative of copper in different chemical environments. Although the interpretation of these spectra is not straightforward, it is reasonable to attribute them to metallic copper and copper oxides. Even though the nature of these species is still under evaluation, the intense shake-up satellites peaks confirm the presence of copper oxides in the sample.

As a final test, we verified the bifunctional nature of Ag/Cu colloids by adsorption of 1,10-phenanthroline (phen) and subsequent Raman tests. These experiments, beyond confirming the Raman enhancing activity of the nanocomposite, also confirmed the presence of both Cu- and Ag-surface adsorption sites.

*References*


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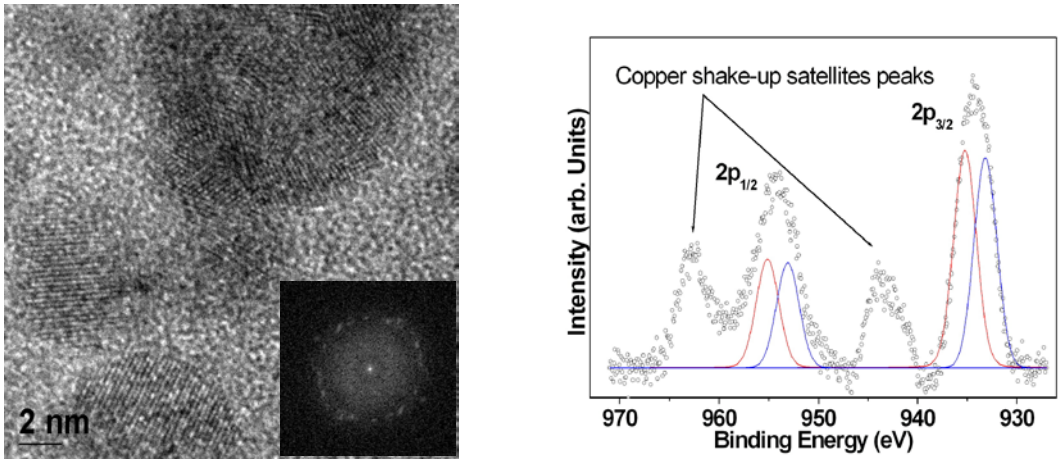


***Figure 1.*** *HRTEM (a) and Cu 2p core level XPS spectra (b) of a Ag/Cu sample obtained in a 0.5mM $AgNO_3$ solution, with 25mJ per pulse and 1400 shots. The inset in (a) is the Hanning masked FFT. The circles in (b) show the experimental data after background subtraction, while red and blue lines represent the fitting functions*