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Carbon nanotubes/laser ablation gold nanoparticles composites

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ABSTRACT

The production of nanohybrids formed by oxidized multiwalled carbon nanotubes (MWCNTs) and nanoparticles, produced by pulsed laser ablation in liquids process, is described. The use of linkers, obtained by transformation of pyrene-1-butanol, is mandatory to generate an efficient and stable interaction between the two components. Transmission electron microscopy and X-ray photoelectron spectroscopy analysis showed the obtainment of the efficient coverage of the MWCNTs by nanoparticles composed by metal gold and, partially, by oxides.

1. Introduction

Hybrid nanostructured materials formed by carbon nanotubes (CNTs) and nanoparticles (NPs) have attracted the attention of many research groups due to their peculiar chemical–physical properties [1,2], as well as their reactivity, that offer exciting prospective in catalysis [3,4], sensor development[5], gas storage, energy applications [6] and electronic nanodevices [7,8]. The various nature of NPs, ranging from metallic (any noble metal or catalytically active metal) to ceramic, broadens the research area and the scope of the applications [9]. Since the original work by Planeix et al. [10], the literature flourished in a great number of contributions. Such an amount of literature is due also to the variety of methods proposed for the decoration of CNT with NPs. Among the most used approaches, it is possible to cite electrochemical deposition [11,12], electrolytic deposition [13], electroless deposition [14], physical methods (sputtering [15], thermal evaporation [16], electron beam evaporation [17,18]) and dispersion of NPs obtained with chemical methods onto functionalized CNTs.

Pulsed laser ablation in liquids (PLAL) technique, although widely used for the production of NPs [19,20], has found a very limited use in the production of CNT/NP hybrids. This technique uses a pulsed laser beam to ablate a metal target immersed in a solvent. The opportunities offered by this approach are noteworthy: the production of NPs may occur in a variety of solvents, no surfactant is needed to stabilize the colloid, the NPs can be extremely pure and, finally, a fine-tuning of the process allows the production of NPs, which can differ in size and properties [21,22]. Only two previous reports describing CNT/PLAL NPs hybrids are available in the literature. In a pioneering study by Henley and co-workers [23], the authors describe the production of CNT/Pd and CNT/Au NPs obtained by mixing together PLAL-produced metal NPs and oxidized CNTs and applying again the ablation condition to favor CNT–NP interactions. In a very recent report, Parvin and co-workers [24] produced CNTs/Pd NPs nanohybrids in a "one step" procedure by using the laser ablation of the Pd target in the presence of a dispersion of pristine CNT in water. However, the interaction between PLAL-produced NPs and CNTs is not a spontaneous process, and the partial degradation of CNTs induced by the laser beam is, in both studies, claimed to be necessary to obtain the nanocomposites.

In this work, a different approach is described. Indeed, we found an optimal interaction between PLAL Au NPs and CNTs when it is mediated by a linker, namely, a pyrene derivative, bearing an alkylthio or an alkylamino group. The preparation of the final nanocomposites proceeds through mixing, in the following order: (i) oxidized and purified multi-walled carbon nanotubes (from here on referred as ox-MWCNTs), (ii) pyrene linkers and, finally, (iii) preformed PLAL Au NPs, in order to tune the ratio of the components and obtain nanocomposites whose composition is known and reproducible.

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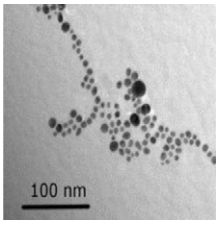
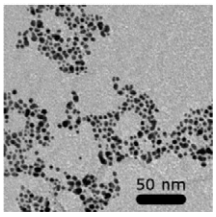
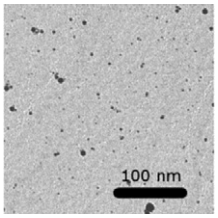
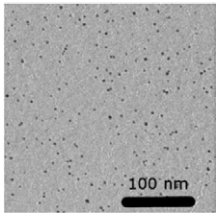
Table 1
Mean size, distribution and TEM images of Au NPs produced at different wavelengths in water or acetone.

Sample	Wavelength (nm)Solvent	Average diameter (nm)	σ_+/σ_- (nm)	Au conc. (mg/L)	NP/mL	TEM images
1	1064Water	7	$\sigma_+ = 3$ $\sigma_- = 2$	63	9×10^{12}	
2	532Water	3	$\sigma_+ = 2$ $\sigma_- = 1$	25	3×10^{13}	
3	1064Acetone	4	$\sigma_+ = 4$ $\sigma_- = 2$	48	2×10^{13}	
4	532Acetone	3	$\sigma_+ = 1$ $\sigma_- = 1$	46	1×10^{14}	

2. Material and methods

We prepared AuNPs by laser ablation of a gold target in liquid environment with the fundamental (1064 nm) or the second harmonic (532 nm) of a mode-locked Nd-YAG laser (EKSPLA PL2143A: rep. rate 10 Hz, pulse width 25 ps at 1064 nm and 20 ps at 532 nm). The laser beam was focused with a lens having 20 cm focal length. The target was placed in a 1 cm × 1 cm quartz cuvette and was kept 2 cm in front of the focal plane. The diameter of the laser spot on the target was fixed at 1.4 mm. The pulse energy was 15 mJ. The ablation process was monitored by measuring in situ the visible spectra with an Avantes fiber spectrophotometer and a deuterium-tungsten lamp. The sampling beam was perpendicular to the ps laser beam and crossed the quartz cuvette 0.5 cm above the bottom of the cell. The gold target was purchased from Goodfellow (high purity: 99.95%). AuNPs suspensions were prepared in deionized water (18.2 MΩcm @ 25 °C) or acetone (Carlo Erba > 99.8%). The volume of the solvent used for the ablation and post-irradiation tests was 2 mL, corresponding to a 2 cm-high liquid column.

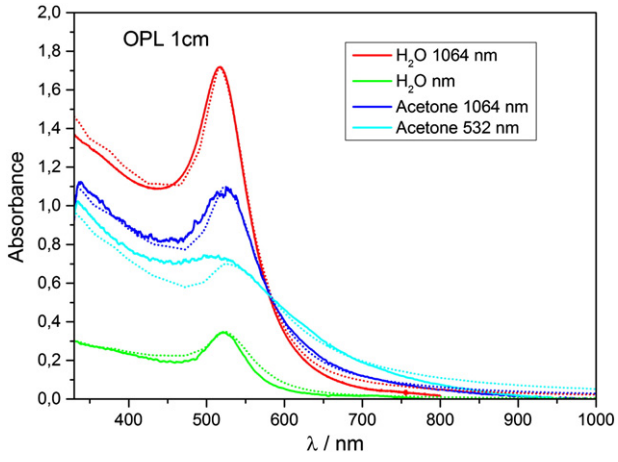


Fig. 1. UV experimental spectra (solid lines) and their Mie fit (dotted lines) of the four colloidal dispersions listed in Table 1.

Transmission electron microscopy (TEM) samples were obtained by dropping a small amount of colloid onto carbon-coated copper grids and letting it to evaporate. The images were recorded with a Philips CM12, 120 kV. Particle mean diameter and dispersivity were determined by fitting the measured statistical distributions with a lognormal function. This permits the calculation of particle concentration by fitting the experimental ultraviolet-visible (UV-Vis) spectra of the colloids with a homemade computer code, based on first order Mie Scattering theory [25]. Subsequently, Au concentration in the colloids can be evaluated by calculating the number of Au atoms per mL under the assumption that Au radius in small AuNPs is 159 pm [26].

The ζ-potential of the colloids was measured, in water, with a Zetasizer Nano ZS90, Malvern Instruments. In this apparatus, the ζ-potential is automatically calculated from the electrophoretic mobility on the basis of the Helmholtz–Smoluchowski relation.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a non-monochromated Mg-Kα X-ray source (1253.6 eV) and a VSW HAC 5000 hemispherical electron energy analyzer operating