Synthesis and Characterisation of ZnO-Au Bifunctional Nanocomposites

Cristina S. Neves[a], Pedro Quaresma[a,b], Patrícia A. Carvalho[c], Peter Eaton[a] and Eulália Pereira[a]*

a REQUIMTE/Faculdade de Ciências, Universidade do Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal
b CIGMH/Departamento de Ciências da Vida, FCT-UNL, 2829-516 Caparica, Portugal
c Departamento de Engenharia de Materiais, IST, Av. Rovisco Pais 1049-100 Lisboa, Portugal
* Corresponding author: cristina.neves@fc.up.pt

Fluorescent semiconductor nanocrystals, also know as quantum dots(QDs), have evolved over the past two decades from electronic materials science to biotechnological applications, such as luminescence tagging, immunoassay, drug delivery and cellular imaging [1]. As a fluorescent semiconductor material, ZnO can form nanocrystals exhibiting higher chemical stability and safety relative to the toxic Cd-containing semiconductor nanocrystals [2, 3].
The addition of gold to ZnO particles to form bifunctional water-soluble ZnO-Au nanocomposites (NCs) may confer additional useful capabilities. For example, the SPR band of gold in the UV-vis absorption spectrum allows further modes of detection, and in addition, the ease of further functionalisation of gold can simplify the modification of the QDs for sensor applications. In order to develop nanocomposites QDs for biosensor applications, we have been studying the modification of ZnO QDs with gold nanoparticles.

Quantum dots were synthesised by a sol-gel method based on the condensation of zinc acetate [4]. The nanoparticles were characterized by Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), UV-Vis and fluorescence spectroscopy. This was followed by a gold coating procedure using $[AuCl_4]^-$ and sodium citrate. The results show the production of a population of photoluminescent ZnO nanocrystals of approximately 5 to 10 nm diameter, according to hydrodynamic radius measurement by DLS (R_h). Reduction of the gold salt in the presence of the ZnO QDs led to the appearance of the expected surface plasmon resonance (SPR) in the UV-vis spectrum from the Au^0 crystals in solution, along with an increase in R_h from the DLS measurements (see figure 1). TEM results indicated co-existence of semiconductor and metal phases but did not unequivocally prove the binding. Therefore we attempted to extract the gold component of the samples to a new phase to test the Au-ZnO binding.

Quantum dots were functionalized with a non polar thiol (1-decanethiol) and were extracted to an organic phase. This phase was characterized by UV-Vis and fluorescence spectroscopy showing the presence of both fluorescence from the ZnO and the SPR band from the gold which indicates the existence of a bifunctional quantum dot nanostructure.

References:

[1] X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir and S. Weiss, *Science* **307**(5709) (2005) 538.

[2] Y. C. Liu, M. Y. Zhong, G. Y. Shan, Y. J. Li, B. Q. Huang and G. L. Yang, *J. Phys. Chem. B* **112**(20) (2008) 6484.

[3] X. Wang, X. G. Kong, Y. Yu and H. Zhang, *J. Phys. Chem. C* **111**(10) (2007) 3836.

[4] L. Spanhel and M. A. Anderson, *J. Amer. Chem. Soc.* **113**(8) (1991) 2826.

Figures:

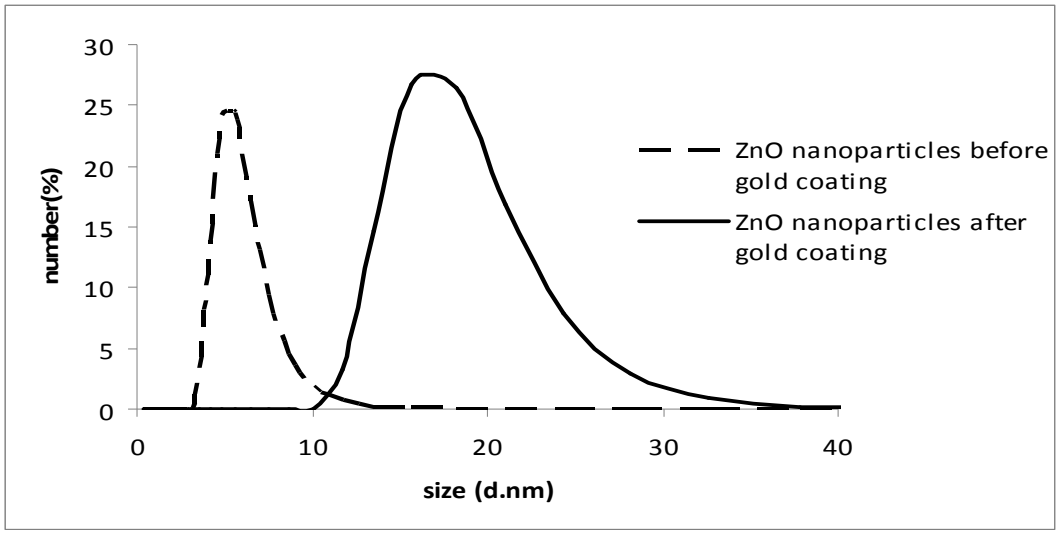

Figure 1 – Dynamic light scattering (DLS) of ZnO nanoparticles before and after gold coating.

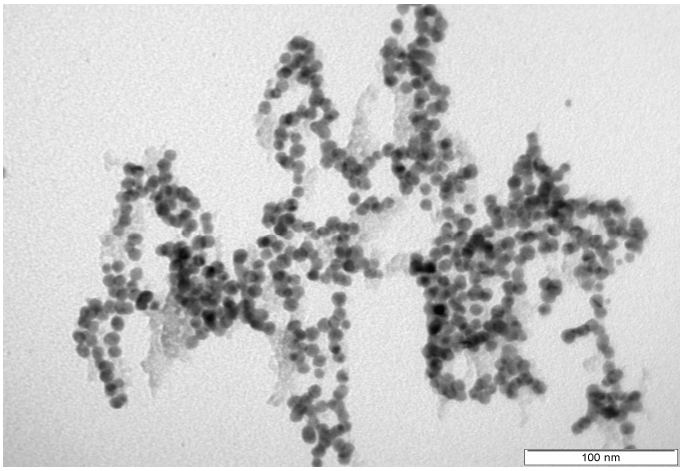

Figure 2 – Transmission electron microscopy (TEM) image of ZnO-Au NCs.

Acknowledgments: Fundação para a Ciência e a Tecnologia, Portugal for financial support through project PTDC/QUI/64484/2006. P. Quaresma thanks FCT for PhD grant SFRH/BD/28209/2006.