NANOSCALE IMAGING OF PLASMON-EXCITON COUPLING IN Au-ZnO TETRAPODS

Giovanni Bertoni1, Filippo Fabbri2, Marco Villani3, Laura Lazzarini3, Stuart Turner4, Gustaaf Van Tendeloo4, Davide Calestani3, Silvija Gradečak5, Andrea Zappettini3 & Giancarlo Salviati3 *

1 CNR-NANO c/o UNIMORE, Via Giuseppe Campi, 213, 41125 Modena MO, Italy
2 CNR-NANO c/o Scuola Normale Superiore, Piazza San Silvestro 12 - 56127 Pisa, Italy
3 CNR-IMEM, Parco Area delle Scienze 37/A, 43124 Parma, Italy
4 EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium.
5Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA (USA).
**giancarlo.salviati@cnr.it*

We show nanoscale spectroscopy and mapping of plasmon-exciton coupling in Au/ZnO nanostructures by STEM-EELS and STEM-CL. Interestingly, the Au plasmon resonance is localized at Au/vacuum interface, while the ZnO signal is localized inside Au nanoparticle.
Keywords: STEM-EELS/CL, ZnO TPs

1. Introduction

It has recently been shown that the electromagnetic plasmonic-photonic coupling in metal/semiconductor nanostructures may enable the development of several device types. For instance, a significant improvement of the internal quantum efficiency is measured when Ag or Al layers were deposited 10 nm above an InGaN light-emitting layer [1]. In addition, when GaAs NWs are coupled with gold nano-antennas, they display interesting non-linear optical properties because of the resulting electromagnetic coupling [2]. Nanoparticles (NPs) can easily be conjugated to semiconducting nanocrystals (e.g., Si, ZnO, TiO2 …) to enhance band edge emission of the semiconductor [3]. For instance the modification of the electronic properties of nanostructured interfaces between Ag and ZnO has been attributed to an electromagnetic coupling between excitons and plasmons [4]. All these results can be considered as indirect proofs of an exciton-plasmon coupling. EELS investigations can be complemented by STEM-Cathodoluminescence (CL) spectroscopy and imaging to study the optical emission. As a result both high energy and high spatial resolution maps can be obtained, to get information on the excitation and radiative de-excitation of the metal/semiconductor system.

2. Results

Here we experimentally visualize the effect of electromagnetic coupling on the spatial localization of excitons from ZnO nanotetrapods (TPs), after conjugation with Au NPs (Figure 1), and of the plasmon resonance from Au NPs. That is done by aberration corrected STEM-EELS imaging, STEM-CL-spectroscopy and mapping, and numeric simulations in the Mie framework [5]. We provide a direct imaging of plasmon and exciton signals and the effect of their interaction. The effect of coupling is confirmed by an enhancement of the Au LPR intensity, and by the decrease and blue-shift (0.13 eV) of the ZnO TPs NBE emission, as found by STEM-CL spectroscopy. A further evidence is given by spatially resolved STEM-EELS mapping with probe aberration correction showing that the Au nanoparticles act as lenses for the ZnO excitations which spatially enter the Au NPs. As a consequence, the Au localized plasmon resonance is confined toward the nanoparticles/vacuum interface, as confirmed by the simulations (Figure 2).

3. Figures

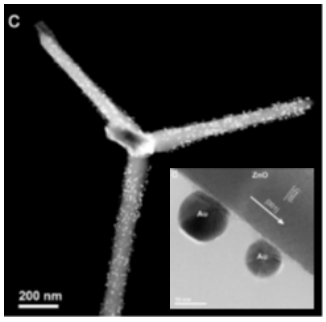

Figure 1: A representative Au NPs/ZnO TP as seen in HAADFSTEM. The inset shows an HRTEM image of two Au NPs in close contact with the ZnO arm surface.

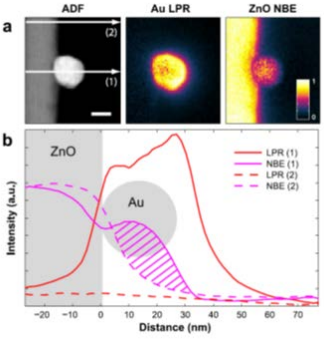

Figure 2 (a) HAADF image of the Au/ZnO interface (scale bar 20 nm), together with the Au plasmon (LPR) component and the ZnO near band edge (NBE) component. The LPR is localized towards the Au/vacuum side, while a signal of the ZnO NBE extends clearly inside the Au NP, as confirmed by the shaded region in the integrated linescans in (b).

4. References

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