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Direct Observation of Plasmonic Enhancement of Emission in Ag-nanoparticle-decorated ZnO nanostructures

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The interactions between surface plasmon resonances (SPRs) in metals and photon emission in semiconductors open a wide range of tuning and enhancement applications in nanostructured devices [1,2]. Optical techniques, such as photoluminescence (PL), have been used extensively to study these effects, but do not have the ability to map out their nanoscale behavior. Scanning transmission electron microscopy (STEM) combined with cathodoluminescence (CL) spectroscopy provides us with a tool to map and analyze plasmon and exciton behavior with nanoscale precision.

ZnO has been a prominent material in nanoscale optoelectronics due to its stable ultraviolet band-edge emission and highly-tunable visible defect emission. We combine emitting ZnO nanowires with an insulating MgO shell, and decorate the surface of the nanowire with Ag nanoparticles, shown in Figure 1a and 1b. The result is a versatile optical workbench, ideally suited for studying the way in which SPRs from the Ag nanoparticles enhance and interact with the exciton emission in the ZnO nanowires.

The structure is first studied macroscopically through PL, as a function of MgO spacer thickness, shown in Figure 1c. The overall PL enhancement is dominated by cavity resonance effects, corresponding to Fabry-Perot and the combination of Fabry-Perot and whispering gallery mode resonances at 20 and 60 nm thicknesses, respectively [3]. However, by comparing the PL enhancement factor of the nanowires with nanoparticles to the ones without, we can see that there is a significant enhancement due to the presence of the plasmons that cannot be explained by cavity resonance effects.

We turn to STEM to shed light on the plasmonic enhancement of the ZnO/MgO nanowires. We can observe the direct enhancement of the ZnO emission by comparing and contrasting annular dark field (ADF) imaging and CL imaging. Figure 2a and 2b show ADF and CL images of the same bare nanowire (a nanowire with no MgO shell). We horizontally sum and normalize the intensities of the nanowire in both images, Figure 2c, and observe that the peaks corresponding to the nanoparticles in CL are much broader than the peaks corresponding to the nanoparticles in ADF.

Peaks in ADF correspond to the actual size of the nanoparticles, while the CL peaks correspond to the emission due to the nanoparticle. Hence, a CL peak from a plasmonic nanoparticle that is broader than the corresponding ADF profile of the same nanoparticle indicates plasmon-enhanced emission. However, we also know that plasmons are excited non-locally by the electron beam, and indeed the

width of the CL peak extends past the ADF profile normal to the nanowire. There is no ZnO here, so the detected emission can only be from surface plasmons in the silver nanoparticle excited non-locally. We must therefore distinguish between non-local plasmon excitation and plasmon-enhanced ZnO emission.

To this end we compare the horizontal and vertical ADF and CL profiles of a large nanoparticle at the top of the wire. In Figure 2d we see the horizontal CL profile is 20 nm broader than the ADF profile, showing the maximum range of non-local plasmon excitation. Figure 2e, on the other hand, shows a vertical CL profile 50 nm broader than the ADF profile, demonstrating enhancement beyond the range of non-local plasmon excitation. Hence, the presence of the plasmonic nanoparticles directly enhances the emission from the ZnO nanowires, even well away from the nanoparticles themselves [4].

References:

[1] P. K. Jain, S. Eustis, and M.A. El-Sayed, J. Phys. Chem. B **110** (2006) 18243
[2] A. Manjavacas, F. J. G. de Abajo, and P. Nordlander, Nano Lett. **11** (2011) 2318
[3] D. C. Mayo *et al*, Thin Solid Films **553** (2014) 132
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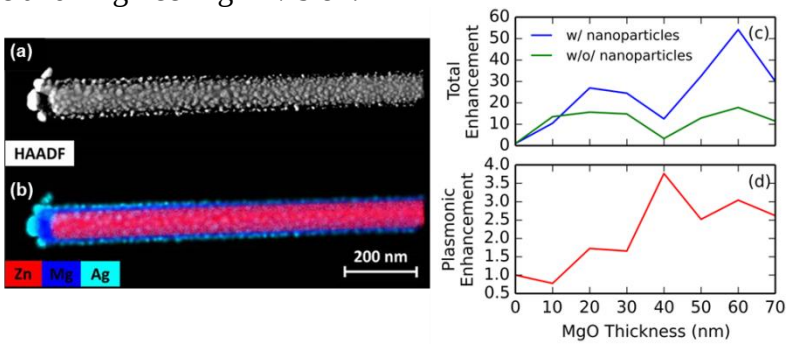

Figure 1. Plasmonic enhancement in Ag decorated ZnO/MgO core/shell nanowires. (a) HAADF and (b) EDAX images of the nanostructures demonstrating their composition and size. (c) Measured PL enhancement due to Fabry-Perot cavity resonances for structures with and without nanoparticles. (d) The enhancement factor due to the presence of the plasmonic Ag nanoparticles.

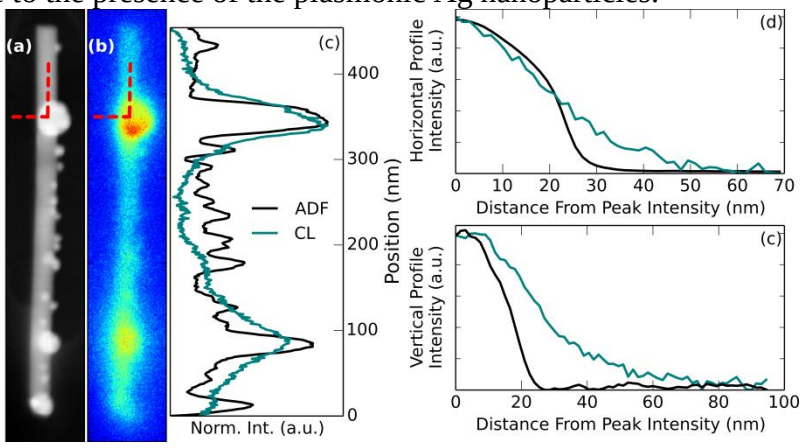

Figure 2. Direct observation of plasmonic enhancement. (a) ADF and (b) CL images of 'bare' nanowire. (c) The normalized intensity of the ADF and CL signals showing broad CL peaks. (d) Horizontal and (e) vertical line profiles of ADF and CL image. Demonstrating that the enhanced emission does not originate from non-local excitation of plasmon, and comes from the ZnO core.

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