

## STUDY OF ITO NANOPARTICLES BY SOLID STATE NMR SPECTROSCOPY

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## INTRODUCTION

Recently nanoscience and nanotechnology have sparked a lot of interest in many fields of science and engineering. In the field of plasmonics, noble metal nanoparticles (NPs) exhibit optical properties that differ significantly from those of the bulk. Indeed, they show a strong absorption band in the UV-Vis region due to coherent oscillation of conduction electrons, driven by the electric field of light. This phenomenon is called "Localized Surface Plasmon Resonance" (LSPR) and the position of the resonant peak depends on the size of the metal nanoparticle [1].



Plasmonic NPs are currently object of considerable interest thanks to their wide range of potential applications in the fields of nano-optics, chemical and biological sensing, spectroscopy and molecular imaging. Lately, doped semiconductors, including tin-doped indium oxide (ITO), have been proposed as new cheaper nanomaterials with plasmonic properties. Unlike noble metal NPs, ITO is a near-infrared plasmonic system and the resonant peak can be easily tuned by changing the dopant concentration [2]. In this work we studied four oleyamine-stabilized ITO NPs samples with different doping concentration (**7.5%**, **10%**, **12.5% and 15%**) using high-resolution solid state NMR. We recorded <sup>119</sup>Sn DE/MAS (Direct Excitation/Magic Angle Spinning) spectra to investigate the effect of doping concentration on the structure and electronic properties. In addition <sup>1</sup>H MAS, <sup>13</sup>C DE/MAS and CP/MAS (Cross Polarization/Magic Angle Spinning) spectra were recorded in order to get insights into the arrangement and dynamics of the stabilizer around the nanoparticles.



- <sup>13</sup>C spectra show that oleylamine chains are mobile and in an amorphous conformation. Moreover, the chemical shift of the methyl group (14.6 ppm) suggests that the oleylamine is in a multilayer environment [4].
- The different linewidths of <sup>1</sup>H and <sup>13</sup>C signals of the two samples, as well as the different efficiency in the <sup>1</sup>H-<sup>13</sup>C CP experiment, indicates that in the case of ITO 15% the oleylamine is more mobile.
- <sup>119</sup>Sn spectra with two different recycle delays (D<sub>1</sub>) were recorded. Going from D<sub>1</sub>=2s to D<sub>1</sub>=10s, especially for samples with higher dopant concentration, there is a line broadening and a shift towards lower chemical shift.
- The comparison of  $^{119}\text{Sn}$  DE/MAS spectra (D\_1=10s) shows an increase of  $^{119}\text{Sn}$  spinlattice relaxation time, T\_1, with increasing doping.

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using a 2.5 mm CP/MAS probe. <sup>13</sup>C and <sup>119</sup>Sn experiments were performed at a MAS

frequency of 15 kHz while <sup>1</sup>H experiments at a MAS frequency of 30 kHz.

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