

Direct Determination of Carrier Parameters in Plasmonic Indium Tin Oxide Nanocrystals Exploiting Magnetoplasmonic Modulation

A. Gabbani^{1,2*} E. Della Latta,² X. Li,³ A. Scarperi,² F. Martini,² F. Biccari,⁴ M. Kociak,³ M. Geppi,² S. Borsacchi,⁵ F. Pineider,^{2,4}

¹Department of Chemistry “Ugo Schiff”, University of Florence, Italy

²Department of Chemistry and Industrial Chemistry, University of Pisa, Italy

³Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, Orsay, France

⁴Department of Physics and Astronomy, Università degli Studi di Firenze, via Sansone 1, Sesto Fiorentino, FI, Italy

⁵Institute of Chemistry of Organometallic Compounds, Italian National Research Council (ICCOM-CNR), via G. Moruzzi 1, 56124 Pisa, Italy

*corresponding author: alessio.gabbani@unifi.it

Abstract: Tin-doped indium oxide nanocrystals are promising candidates for optoelectronics and active plasmonics in the NIR. Here, an integrated approach was developed involving magneto-optics and single particle spectroscopy to directly determine experimentally the carrier parameters as a function of tin doping, which is challenging in such small nanosystems.

Indium Tin Oxide (ITO) is the prototype conductive oxide, which has recently gathered interest in nano-optics,¹ owing to the excellent plasmonic properties displayed by ITO nanocrystals (NCs) in the infrared spectral region. Unlike noble metals, the plasmonic resonance frequency in spherical ITO NCs can be tuned synthetically by controlling the tin content.² Nanostructuration typically introduces several challenges in the characterization of electronic parameters in NCs, hampering advanced material design. Indeed, while films of doped oxides are routinely studied through electrical experiments, these cannot be reliably applied to NCs, since the insulating ligand layer forces charge hopping and results in a complex (albeit interesting) behaviour. Moreover, the surface potential creates a depletion region near the surface, which typically requires core@shell models with a purely dielectric shell to fit the extinction spectrum.³

In this work,⁴ we present an integrated approach (Figure 1) based on magneto-optics, single-particle Electron Energy Loss (EELS) spectroscopy and ¹¹⁹Sn Solid State Nuclear Magnetic Resonance (SSNMR) spectroscopy to extract the fundamental electronic parameters of a series of ITO NCs with variable tin doping. Our methodology overcomes the limitations of standard fitting approaches based on extinction spectroscopy, which can only determine the ratio between carrier density and mass. Conversely, exploiting concepts from magnetoplasmonics^{5,6} we determined the carrier effective mass directly on the NCs, discarding the use of literature values. We found that mass values depart appreciably from those measured on thin films; consequently, we found carrier density values that are different from reported literature values for similar systems. The effective mass was found to deviate from the parabolic approximation at high carrier density. This approach can be generalized to other plasmonic heavily-doped semiconductor nanostructures and represents, to the best of our knowledge, the only method to date to characterize the full Drude parameter space of 0-D nanosystems.

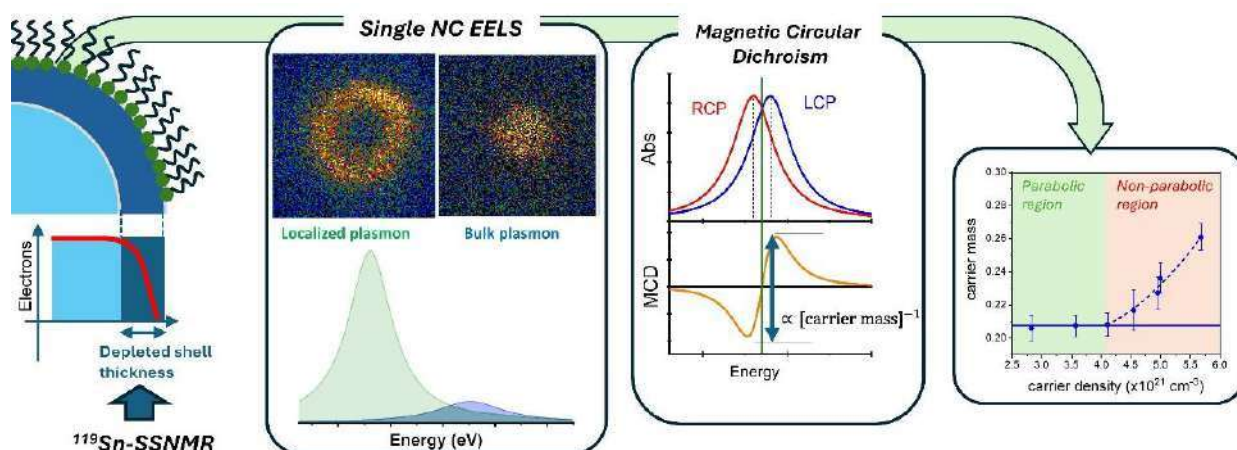


Figure 1: Scheme of the multitechnique approach employed in this work to extract the relation between carrier mass and carrier density in a series of chemically prepared ITO NCs with variable Sn content.

Italian MUR is acknowledged through PRIN 2022 PNRR project P20229723Z (CUP: B53D23025560001).

References

1. A. Agrawal, *et al.*, Chem. Rev. 2018, 118 (6), 3121–3207.
2. A. Mazzotta, *et al.*, ACS Appl. Mater. Interfaces 2022, 14 (30), 35276–35286.
3. S. L. Gibbs, *et al.*, Acc. Chem. Res. 2019, 52 (9), 2516–2524.
4. A. Gabbani, *et al.*, ACS Nano 2024, 18, 15139–15153.
5. A. Gabbani, *et al.*, Nano Lett. 2022, 22 (22), 9036–9044.
6. A. Gabbani, *et al.*, J. Appl. Phys. 2021, 129 (21), 211101.