Synthesis of inorganic functional materials in innovative solvents: a joyful game of structure, shape, and properties

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One of the fields where DES and ionic liquids, some of the most interesting and widely studied solvent systems developed in the last decades show remarkable added values, is the synthesis of inorganic materials, in particular nanoparticles. In this field, the inherent and highly tunable nano-homogeneities of DES structure give origin to a marked templating effect, a precious role that has led to the recent bloom of a vast number of studies exploiting these new synthesis media to prepare nanomaterials and composite structures of various shapes. In this contribution, newly developed synthetic strategies based on Deep Eutectic Solvents will be described and some remarkable examples of metal oxide nanoparticles preparations employing Lewis Acids DES (LADES) will be discussed and compared with alternative syntheses carried out in ionic liquids. All the prepared materials have nanometric dimensions, and possess different topologies, ranging from globular to flower-like aggregates of nanoplates [1], depending on the type of liquid media employed.
The materials reported in the presentation feature varied properties of technological interest and possess various compositions. A pivotal role is played by zinc oxide NPs, that can be used in a large number of applications. In one of the most recent investigations, they were employed as photoanodes, the active light-harvesting part of photovoltaic (PV) devices, where they govern charge injection and transport processes. In this context, ZnO proves to be a particularly promising candidate, owing to its high electron mobility and exciton binding energy, often surpassing those of TiO_2 while maintaining a comparable bandgap. Dye-sensitized solar cells (DSSCs) made with ZnO photoanodes synthesized using the DES method achieve a remarkable 1.8% efficiency (Fig 1a), placing them in the top tier for devices of this type (non-TiO_2), with the additional benefit of their high transparency, a coveted feature when use as photovoltaic window material is envisaged. Moreover, ZnO can be synthesized through several green and unconventional approaches, which are carried out at low temperature, and do not require energy-intensive post-treatments like calcination, or use of conventional organic solvents.
Another field where ZnO excels due to its fluorescent properties is sensoristics, where it can be employed to prepare chemosensors for a large number of molecules, the most notable being toxic chlorinated pesticides. The mechanism of detection implies the modulation of fluorescence signal, either as quenching or enhancement, through the interaction between the oxide, acting as extrinsic fluorophore, and the pesticide molecule. Our recent studies reveal that the fluorescence properties of oxide nano powders largely depend on the compound morphology. If the synthesis (precipitation) is performed in the highly templating medium (DES), 2D nanoplatelets (20x100 nm) are obtained, that give origin to orange fluorescence, whereas if the ionic liquid choline nitrate is used, 0D rounded nanoparticles (20 nm) endowed with yellow luminescence are formed (Fig 1b). [2] A similar templating behavior exerted by DES can be found in other similar preparations, including CuO and NiO.
Following the line of DES-assisted synthesis of oxide nanoparticles, recent achievements in the field of nano-sized photocatalysts will be discussed. In this respect, tin oxides play a very important role as photocatalysts in water remediation methods, thanks to their electronic properties, which feature high or very high bandgap values, namely, 2.7 eV for SnO and 3.6 eV for SnO_2. A new, simple synthetic approach to tin oxides based on DES that refines the method reported in the literature for SnO, and extends it to the preparation of SnO_2 by adding readily available and low-cost oxidizing additives (e. g. sodium percarbonate or hydrogen peroxide) to the eutectic mixture, will be showcased. The appropriate selection of reaction conditions leads to pure SnO, SnO_2 or their blends. The nanoparticles obtained possess different shapes, namely ice-cream scoops in SnO

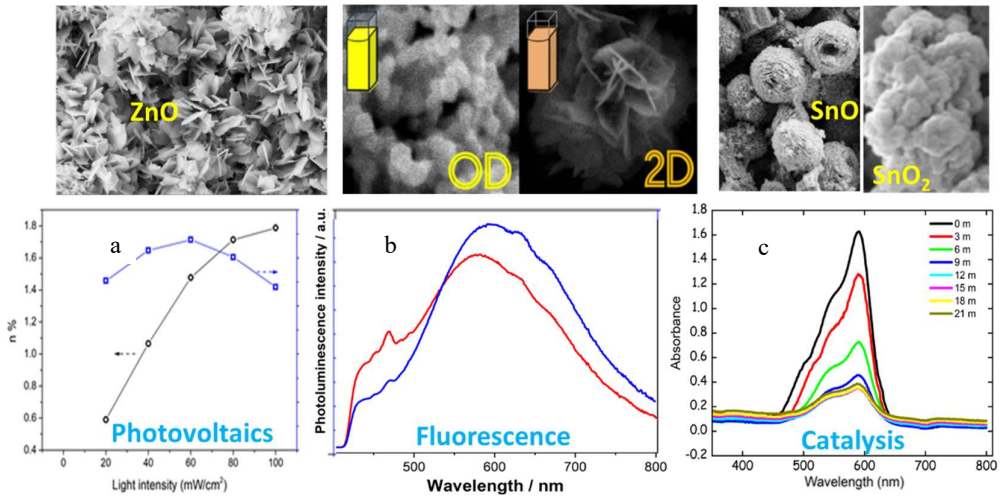

Figure 1 – Examples of metal oxide nanoparticles synthesized in Deep Eutectic Solvent media. Top row: SEM images – ZnO from DES, left panel, ZnO from choline nitrate (ionic liquid), middle left panel; ZnO from DES, middle right panel, tin oxides, right panel (SnO left, SnO_2, right). Bottom row: Photovoltaic Efficiency of ZnO nanoplatelets, left panel; Fluorescence spectrum of ZnO from choline nitrate (red) and from DES (blue), middle panel; Crystal Violet UV-Vis Absorbance spectrum, at different UV-light exposure times (SnO)

(Fig 1c, left) and nanopillars in SnO_2 (Fig 1c, right). Both systems can (photo)catalyze the degradation of crystal violet (a prototypical polluting textile industry dye) in various illumination conditions, obtaining very promising results in terms of degradation times, remarkably shorter than literature values, and achieving an impressive 95% of removal after only 20 min of UV light exposure with nano-pillared SnO_2.[3] The very large specific surface area of the prepared tin oxides also grants them significant adsorption properties, namely 0.07 mg and 0.13 mg of dye per mg of catalyst powder for SnO and SnO_2, respectively.

REFERENCES

[1] Gontrani L, Donia DT, Bauer EM, Tagliatesta P, Carbone M, (2023) "Novel synthesis of zinc oxide nanoparticles from type IV deep eutectic solvents". *Inorganica Chimica Acta*, 545, 121268. DOI 10.1016/j.ica.2022.121268

[2] Gontrani L, Casoli L, Russina O, Bauer EM, Carbone M, (2025) "Templating effect travelling on the edge between an ionic liquid and a DES: the case of fluorescent ZnO nanostructures in choline nitrate". *Materials Advances*, 6, 2154-2159. DOI 10.1039/D5MA00030K

[3] Gontrani L, Cotirlan FA, Lembo A, Bauer EM, Carbone M, (2026) "Household chemicals as key ingredients: the addition of sodium percarbonate to tin chloride in deep eutectic solvents leads to SnO_2 nanoparticles very efficient for dye photocatalytic degradation". *Inorganic Chemistry Communications*, 187, 116347. DOI 10.1016/j.inoche.2026.116347