Approaches to maximizing the production yield of ZnS wurtzite nanopowder: Co-precipitation synthesis using a pilot-plant reactor

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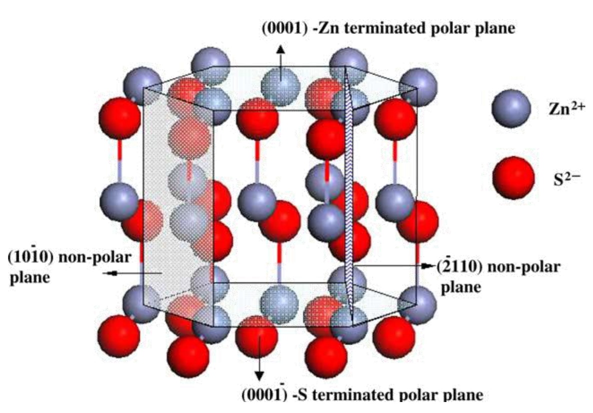
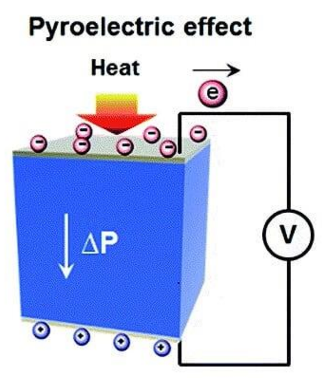




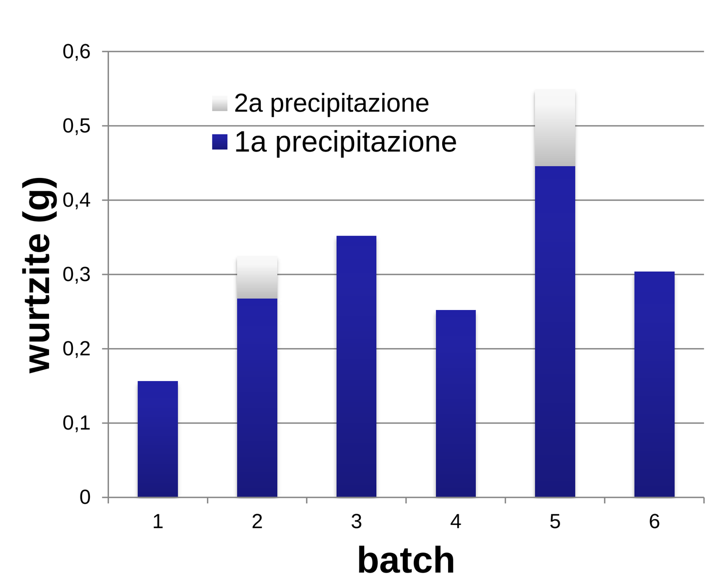
Pyroelectric materials can harvest energy from naturally occurring ambient temperature changes, as well as artificial temperature changes due to exhaust gases or convection and solar energy. Pyroelectric energy harvesting is a highly promising technology for the future of autonomous and self-powered electronic devices (battery free) and could be the right methodology to harvest enormous amount of wasted heat. The current technology can produce electricity in the milliwatt range and further developments are required to maximize power generation.

ZnS is one example of a wurtzite-based material, all of which are low cost, structurally simple pyroelectrics, being non-toxic and eco-friendly, with high chemical and thermal stability, and offering higher thermal conductivities compared to ferroelectrics, allowing them to react faster to temperature changes. We aimed to find a simple, easily scalable synthesis for nanocrystalline wurtzite ZnS production. Purified and dried ZnS nanopowder were characterized by conventional methods (XRD, SEM, TEM, TG, BET, FTIR) and for two samples dielectric measurements were performed. The obtained ZnS nanopowder is intended both as a precursor for pyroelectric ceramics and as a filler for ferroelectric polymer-based composite thin films (PVDF co-polymers), for novel energy harvesting applications.

ZnS Co-precipitation Synthesis

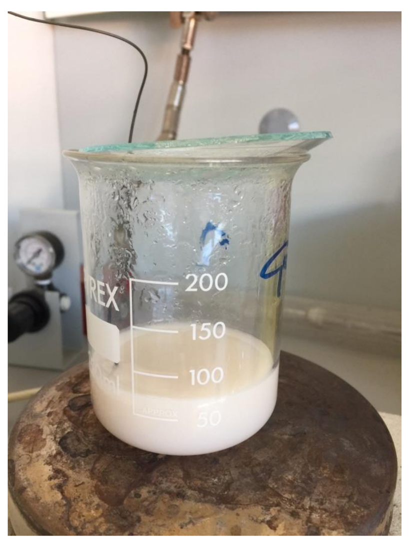
Method: The well-known reaction of ZnCl2, as the zinc source, with thiourea as the sulphur source, dissolved in ethyl-glycol at a carefully controlled, constant molar ratio of precursor Zn and S ions (mMZn/mMS=1) under medium temperature conditions (140°C-150°C).

"Circular synthesis": By recycling a used solvent obtained from previous reactions and topping up the quantity lost, the productivity yield increased 3.5 times.



The amount of solvent remained the same (60 ml of ethyl glycol) by re-using what remained of the solvent used in the previous reaction and topping up the quantity lost. Productivity yields increased over six successive reactions from 156 mg to 549 mg of ZnS nanopowder per batch.

- Hexagonal wurtzite ZnS nanopowder
- Beige colour nanopowder
- Wide band gap (3.77 eV)
- High refractive index (n=2.75)
- Nanoparticles size: 3 to 5 nm
- Specific surface area: 38 $m^2 g^{-1}$
- Ethyl glycol & thiourea decompose at 250°C-290°C



Observed self-alignament of ZnS nanopowder dispersed in ethanol, after being washed several times in acetone and ethanol.

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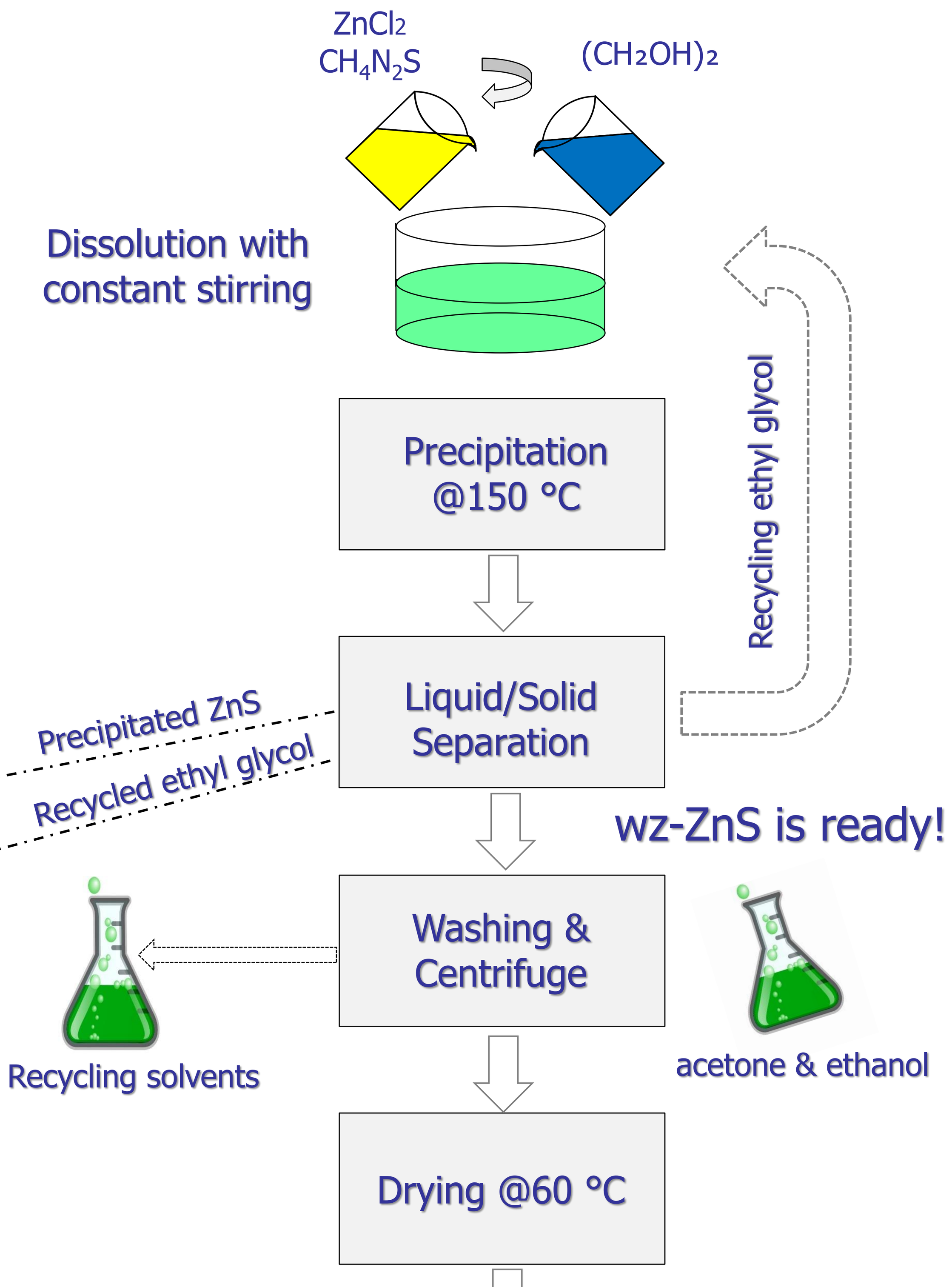
Our pilot plant reactor

Glass cylindrical jacketed reactor (V = 5 l)



TECHNICAL DESCRIPTION

Open glass reactor, capacity 5 L, mechanical stirrer, temperature range 20-200°C, equipped with temperature sensor, stirring velocity controller (rpm) and pH controller.

ADVANTAGES

Commercial items & transparency.

YIELD

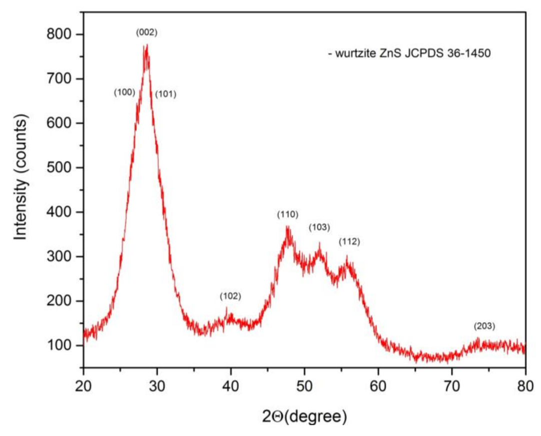
18-20% per batch

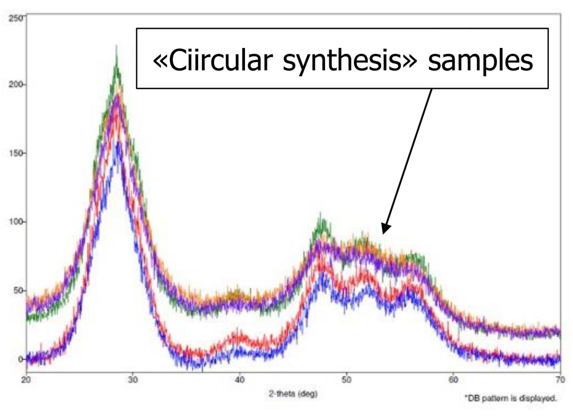
RECYCLING SOLVENTS - 100 %

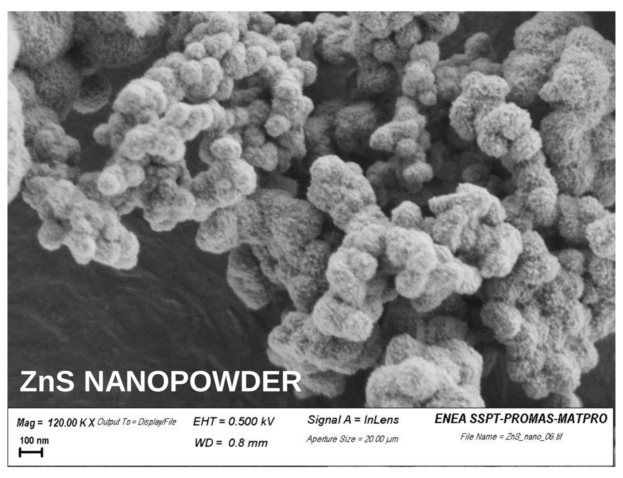
ZnS Nanopowder Characterization

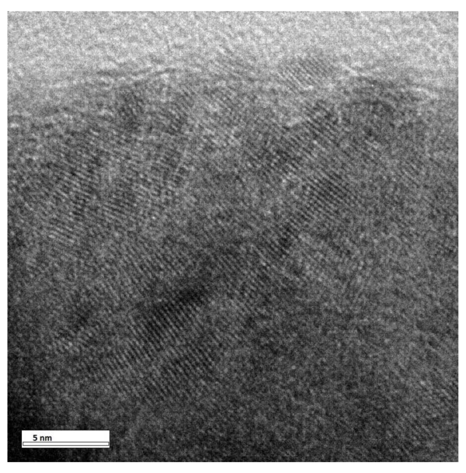
Structural and morphological characterization

The XRD analysis confirmed formation of hexagonal, wurtzite ZnS structure in all synthesized ZnS nanopowders. The "circular synthesis" samples are less crystalline and contain more remnants from the organic part, as confirmed with the TG measurements.





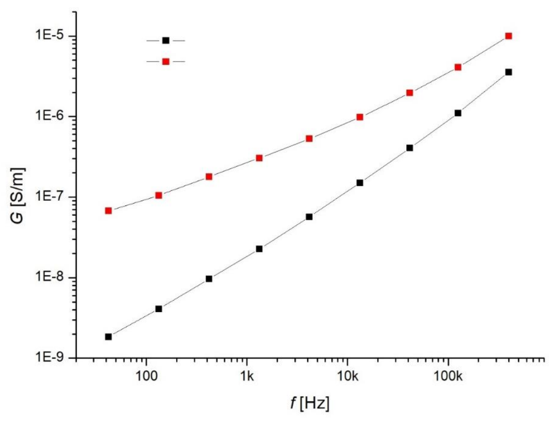




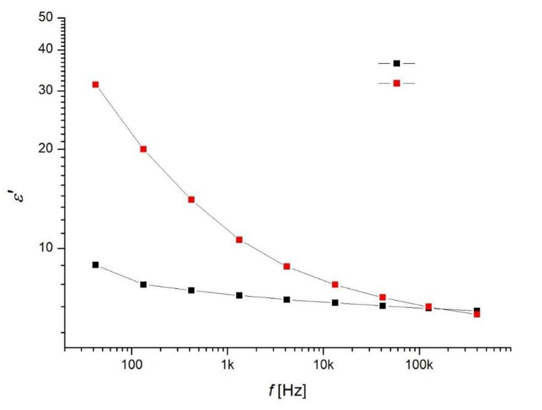
The SEM observations revealed that ZnS nanopowder samples are organized quite uniformly on a large scale in 100-200 nm-size spheres. These spheres are actually big agglomerates of nanoparticles. HRTEM images show that w-ZnS samples are made up of well crystalline nanoparticles of about 3-5 nm in size.

Dielectric characterization

Two samples with different molar concentrations of precursor Zn and S ions in the reactive solution were selected having molar ratio R1= mMZn/mMS = 1.22 (■) and R2= mMZn/mMS = 0.47 (■).
Dielectric measurements were performed in a specially designed cell (3D-printed internally). Our results are in the range of the values presented for ZnS thin films [RSC Adv., 2020, 10, 9549].



Conductance vs. frequency



Dielectric susceptibility vs. frequency

The sample with R1 molar ratio has greater mobility of charge carriers in respect to sample with molar ratio R2. The differences in conductance values observed at lower freq. could be explained as a consequence of the different carriers' mobility. The phenomenon of substantial increase of dielectric susceptibility with the drop in frequency is usually assign to the build-up electricity at the borders of conductive areas (MWS polarization).

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