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Synthesis of ZnO@Cu2O Core-Shell Nanoparticles by Discharges in Liquid Nitrogen

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Synthesis of nanoparticles (NPs) by discharges in dielectric liquids is an efficient way to process core-shell nanostructures at high rate and very low cost. In this study, attention is paid to the zinc–copper oxides system. Zinc and copper oxides can be used as sensors. They present an appreciable photocatalytic activity and might be good candidates for photocatalysis and solar cells. Their band gaps are ~3.3 eV, 1.2-1.9 eV and ~2.3 eV for ZnO (intrinsic n-type), CuO(intrinsic p-type) and Cu_2 O(intrinsic p-type) respectively. Zinc oxide@copper oxide core-shell nanoparticles have been mostly produced by chemical routes.
The synthesis of ZnO@Cu_2O core-shell NPs by discharges in a dielectric liquid is investigated. With a nanosecond pulse power generator, discharges are created by applying high-voltage (10kV – 200 ns – 10 Hz) between two pin electrodes immersed in liquid nitrogen.
The process is three-step. For example, discharges are run first between two copper electrodes to produce Cu NPs. Next, new discharges are run between two zinc electrodes in the same liquid where Cu NPs, formed during the first step, are present. Zn@Cu core-shell NPs are thus expected to be obtained. To get Cu@Zn NPs, steps 1 and 2 should just be swapped. The last step corresponds to the oxidation of the synthesized core-shell NPs, which occurs after evaporation of liquid nitrogen that leads to air exposure and transformation of metals into oxides.
High resolution transmission electron microscopes (HRTEM), energy-dispersive X-ray spectroscopy (EDX), electron energy loss spectroscopy (EELS) and electron microdiffraction analyses were carried out to characterize the NPs. Surprisingly, regardless of the order in which steps 1 and 2 are done, ZnO@Cu_2O NPs are always obtained. In fact, it turns out that Zn NPs form 2D sheets that either wrap Cu NPs if Cu electrodes were used first or embed Cu NPs if Zn electrodes were used first. This unexpected behavior is the first of its kind ever shown.

Keywords
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