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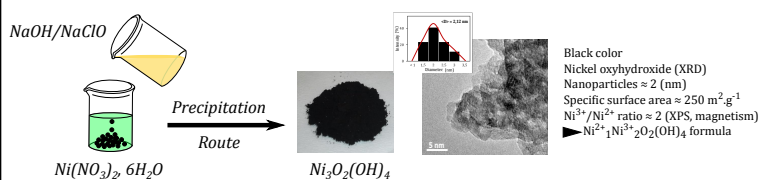
Control of the Ni non-stoichiometry in Ni_{1-x}O nanoparticles : "Core-shell"-like model

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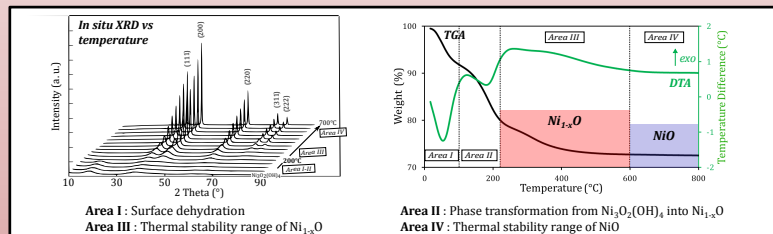
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To improve the performances of p-Dye Sensitized Solar Cell (p-DSSC) [1], the synthesis of modified p-type nickel oxide semiconductor, commonly used as a photocathode in such devices, was initiated using a mixed valent nickel oxyhydroxide Ni₃O₂(OH)₄. The decomposition of this precursor in air at temperatures lower than 600°C leads to non-stoichiometric Ni_{1-x}O nanoparticles (from 2 to 30 nm) with tunable nickel vacancies concentration (up to 25% for 2-3nm particle sizes) [2]. According to our chemical characterizations (XRD, TEM, density, chemical analysis, BET measurement...), the nickel vacancies segregate at the surface of the Ni_{1-x}O nanoparticles to create a "core-shell"-like edifice (similarly to our previous work on Zn-deficient Zn_{1-x}O nanoparticles [3]). This "core-shell" is constituted by a dense stoichiometric NiO coated (or terminated) by an oxygen (hydroxide or carbonate groups) surface layer free from nickel atom. The Ni-free surface layer influences drastically the density of the smaller nanoparticles by decreasing it. When the nanoparticles size increases, the density evolves until reaching the theoretical density of stoichiometric nickel oxide for the bigger particles (≥ 50 nm). Thus, with the control of the particles size, we can also control the Ni non-stoichiometry in Ni_{1-x}O following our "core-shell"-like model.

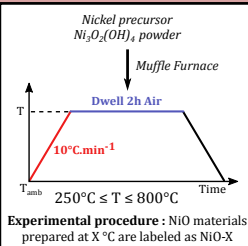
Nickel precursor synthesis & characterizations



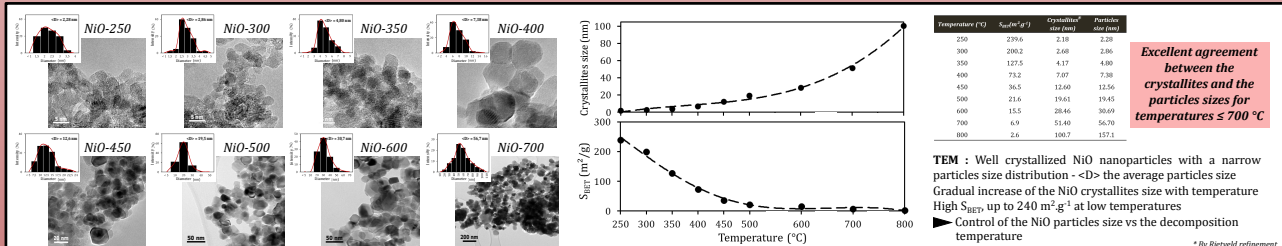
Thermal decomposition in air



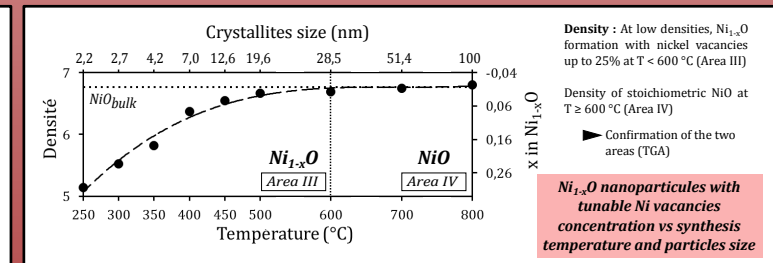
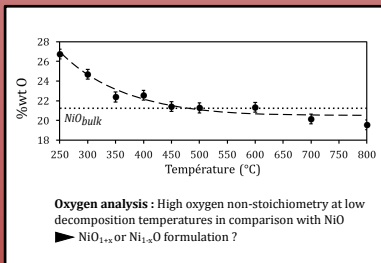
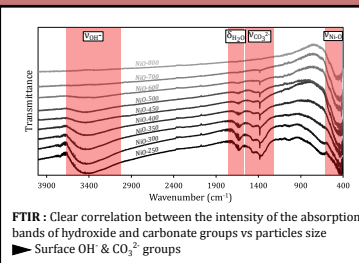
NiO synthesis



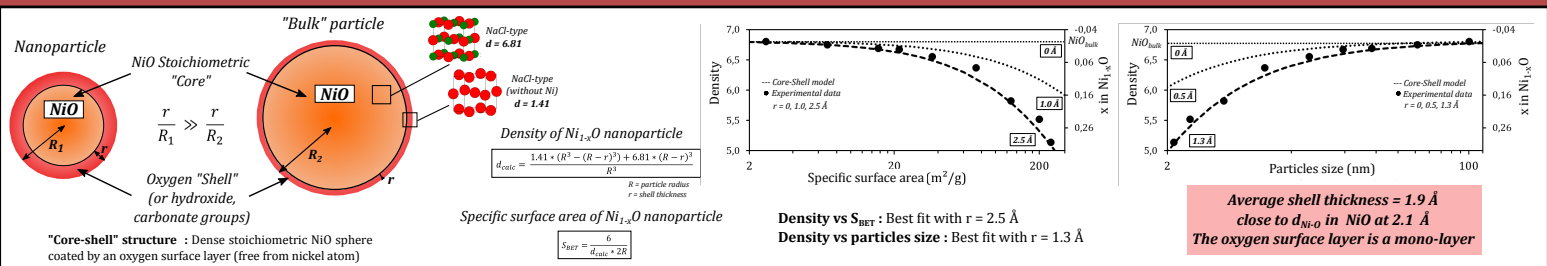
NiO nanoparticles with high specific surface areas



Evidence of Ni_{1-x}O nanoparticles at low decomposition temperatures



"Core-shell"-like model



References

- [1]. F. Odobel, L. Le Pleux, Y. Pellegrin, E. Blart, Acc. Chem. Res., **43**, 1063, (2010). [2]. B. Polteau, F. Tessier, F. Cheviré, L. Cario, F. Odobel, S. Jobic, Solid State Sci., **54**, 37 (2016). [3]. A. Renaud, L. Cario, X. Rocquefelte, P. Deniard, C. Payen, E. Gautron, E. Faulques, F. Cheviré, F. Tessier, S. Jobic, Sci. Rep., **5**, 12914 (2015).