



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

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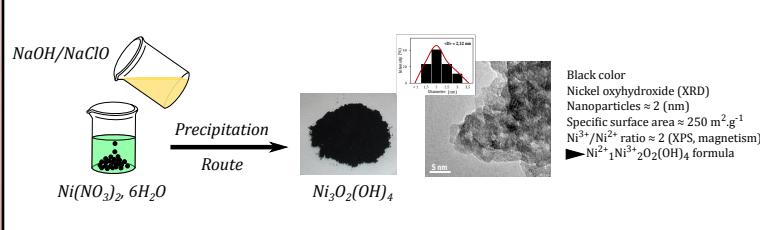
Baptiste Polteau ^a, Franck Tessier ^a, François Chevire ^a,
Laurent Cario ^b, Stéphane Jobic ^b

^a Institut des Sciences Chimiques de Rennes (UMR CNRS 6226), Université de Rennes 1, France

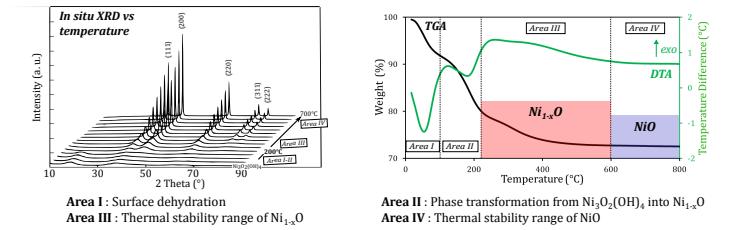
^b Institut des Matériaux Jean Rouxel, (UMR CNRS 6502), Université de Nantes, France

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 $\text{Ni}_3\text{O}_2(\text{OH})_4$. 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.

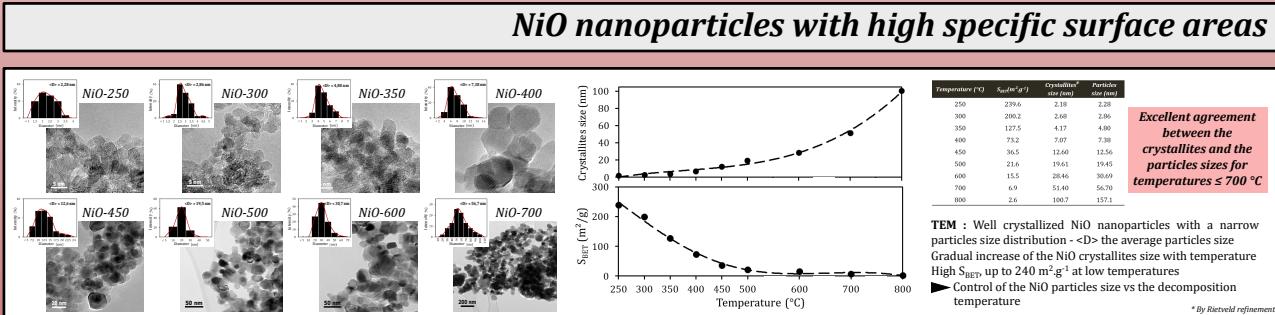
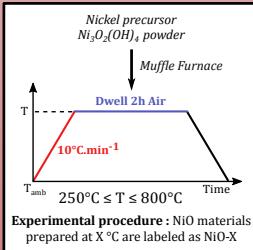
Nickel precursor synthesis & characterizations



Thermal decomposition in air



NiO synthesis

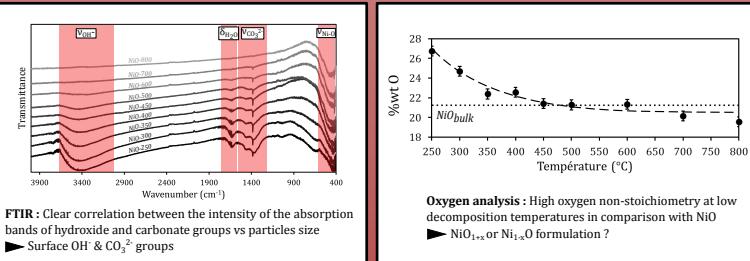


Excellent agreement between the crystallites and the particles sizes for temperatures $\leq 700^\circ\text{C}$

TEM : Well crystallized NiO nanoparticles with a narrow particles size distribution - \rightarrow the average particles size Gradual increase of the NiO crystallites size with temperature High S_{BET} , up to $240 \text{ m}^2 \cdot \text{g}^{-1}$ at low temperatures ► Control of the NiO particles size vs the decomposition temperature

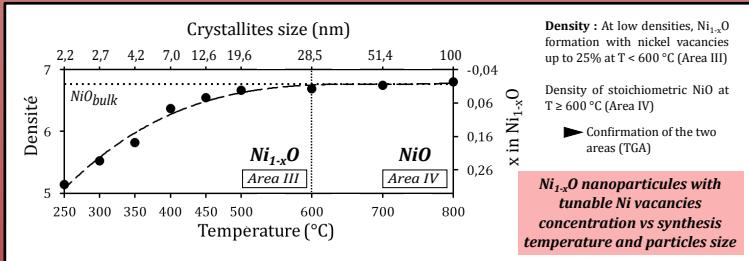
* By Rietveld refinement

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



FTIR : Clear correlation between the intensity of the absorption bands of hydroxide and carbonate groups vs particles size
► Surface OH⁻ & CO₃²⁻ groups

Oxygen analysis : High oxygen non-stoichiometry at low decomposition temperatures in comparison with NiO
► NiO_{1+x} or Ni_{1-x}O formulation ?



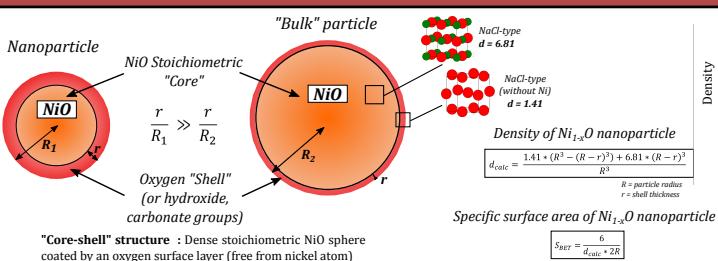
Density : At low densities, Ni_{1-x}O formation with nickel vacancies up to 25% at $T < 600^\circ\text{C}$ (Area III)

Density of stoichiometric NiO at $T \geq 600^\circ\text{C}$ (Area IV)

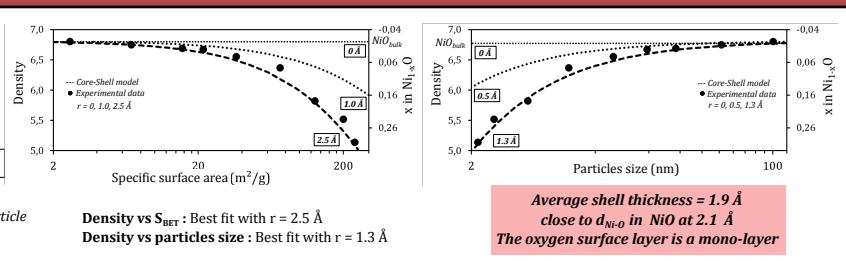
► Confirmation of the two areas (TGA)

Ni_{1-x}O nanoparticles with tunable Ni vacancies concentration vs synthesis temperature and particles size

"Core-shell"-like model



"Core-shell" structure : Dense stoichiometric NiO sphere coated by an oxygen surface layer (free from nickel atom)



Average shell thickness = 1.9 \AA
close to $d_{\text{Ni-O}}$ in NiO at 2.1 \AA
The oxygen surface layer is a mono-layer

References

- [1] F. Odobel, L. Le Pleux, Y. Pellegrin, E. Blart, Acc. Chem. Res., **43**, 1063, (2010). [2] B. Polteau, F. Tessier, F. Chevire, 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. Chevire, F. Tessier, S. Jobic, Sci. Rep., **5**, 12914 (2015).