Synthesis of Ni-poor NiO nanoparticles for DSSC-p applications

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Over the last decade, p-type semiconductors (SC) have known a renewed interest. Indeed these materials may have potential applications for light-emitting diodes, transistors, solar cells, etc. Since the achievement of the first Dye Sensitized Solar Cells (DSSC) by Grätzel [1] in 1991 a new generation of solar cells has been developed [2] where the n-type SC is replaced by a p-type one. This leads to the photo-injection of holes instead of electrons in the circuit. To date nickel oxide (NiO) is the reference p-type semiconductor. However yields are still far from those of n-DSSC and many studies aim to replace NiO by other systems such as $CuAlO_2$, $CuGaO_2$, $CuCrO_2$ or $NiCo_2O_4$ nanoparticles. Following our recent synthesis of N doped ZnO with stabilization of p-type charge carriers [3], we focus now on the preparation of N doped NiO nanoparticles to improve the p-type conductivity of NiO. We study here the chemical reactivity of a nickel oxyhydroxide precursor under air and ammonia that conducts to nanostructured Ni-poor NiO [4].

p-DSSC performances

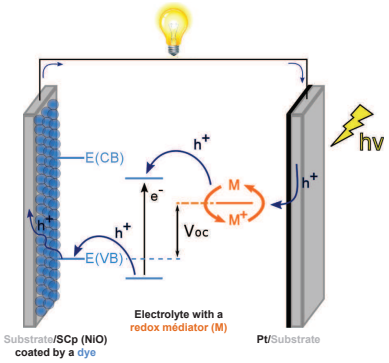


Photo-injection of holes from the excited dye to the valence band of the p-type semi-conductor

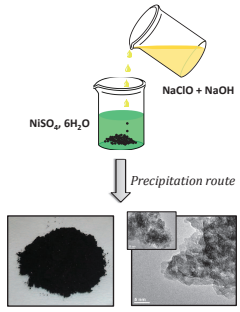
⇨ **Specifications for SC-p :**

- **Nanoparticles (high specific surface area)**
- **High mobility of charge carriers (holes)**
- **Low energy valence band**

Conversion efficiency :
Energy difference between VB (SC-p) and redox potentiel (mediator)→ Voc

Problematics :
Quest of new materials

Nickel precursor synthesis & characterizations

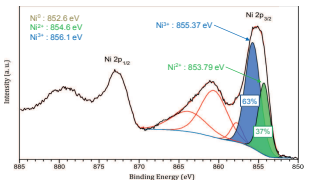


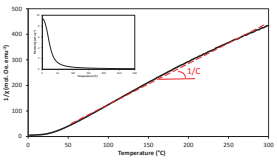
Black color
Nickel oxyhydroxide (XRD)
Agglomerated nanoparticles ≈ 2-3nm (TEM)
Specific surface area ≈ 230 m^2/g (BET)

⇨ XPS Ni(2p) :

- Ni^{3+} $2p_{3/2}$ binding energy (855.8 eV) with surface area 63 %
- Ni^{2+} $2p_{3/2}$ binding energy (854.3 eV) with surface area 37 %

⇒ Ni^{2+}/Ni^{3+} ratio ≈ ½





⇨ Magnetism :

- Curie Constant = 0.63 SI units
- $\mu_{eff} = \sqrt{(8*C)} = 2.24\ \mu_B$

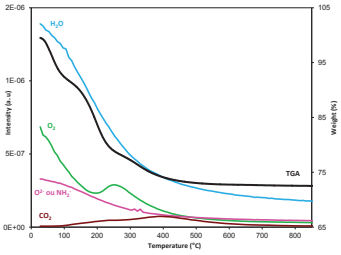
with $\mu_{eff}(Ni^{2+}) = 3.2\ \mu_B$, $\mu_{eff}(Ni^{3+}) = 1.7\ \mu_B$

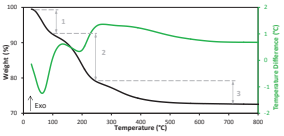
⇒ Ni^{2+}/Ni^{3+} ratio ≈ ½

Oxyhydroxide $NiO_x(OH)_y$ formulation ?

$NiOOH_{1.33} = Ni_3O_3(OH)_4 = Ni^{2+}{}_1Ni^{3+}{}_2O_2(OH)_4$

Thermal decomposition under air atmosphere



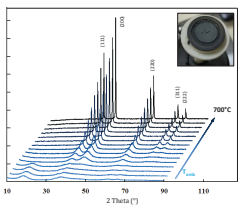


⇨ TGA/TDA/Mass spectroscopy :

1- T_{amb}-110°C → Surface dehydration (desorption of H_2O molecules)

2- 110-200°C → Elimination of OH^- groups in water form without oxygen loss - Formation of Ni-poor NiO

3- 200-500°C → Elimination of O_2 groups excess - Transformation of Ni-poor NiO into stoichiometric NiO



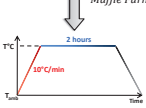
⇨ In situ XRD patterns :

- Cubic NiO structure (NaCl type) formation at 150 – 200°C
- Higher crystallinity with temperature

Experimental procedure

Nickel oxyhydroxide precursor

Muffle Furnace

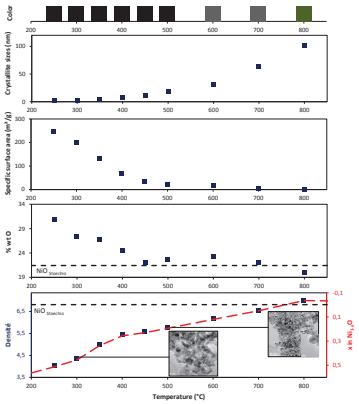


Thermal decomposition
250°C ≤ T ≤ 800°C

Characterizations

Specific surface area, TEM, crystallite sizes, density and oxygen analyses

Evidence of Ni-poor NiO nanoparticles

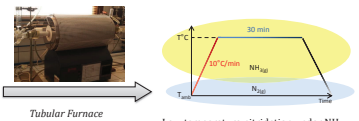


⇨ Physicochemical characterizations :

- Black NiO nanoparticles at temperatures ≤ 500°C and green stoichiometric NiO at high temperatures
- Very small crystallite and particle (TEM) sizes for low temperature decomposition
- High specific surface area ≥ 200 $m^2.g^{-1}$ at 250 and 300°C in agreement with particle/crystallite sizes
- Strong oxygen excess in NiO nanoparticles → NiO_{1+x} or $Ni_{1-x}O$ formulation ?
- Low NiO densities at low temperature → high Ni non-stoichiometry

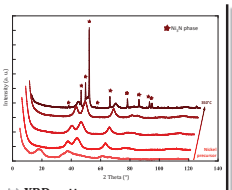
Thermal decomposition under ammonia atmosphere

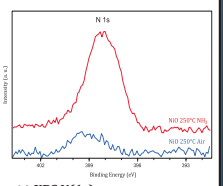
Experimental procedure



Low temperature nitridation under NH_3
200°C ≤ T ≤ 350°C

Nitrogen doping in NiO ?





⇨ XRD patterns :

- Cubic NiO structure (NaCl type) at T ≤ 250 °C
- No influence of temperature on NiO stucture crystallinity
- Hexagonal Ni_3N structure formation at T ≥ 300 °C

⇨ XPS N(1s):

- Absence of N 1s signal in NiO at T = 250°C under air
- N 1s peak at 398.2 eV in NiO at T = 250°C under ammonia ⇒ N^{3-} insertion

Synthesis of nitrogen doped nickel oxide (NiO:N)

Conclusion

⇨ Synthesis of an original nickel precursor with very small particle sizes and high specific surface area. The determination of the Ni^{2+}/Ni^{3+} ratio is leading to the exact formulation $Ni_3O_2(OH)_4$
⇨ Decomposition of $Ni_3O_2(OH)_4$ under air at temperature lower than 500°C forms strong non-stoichiometric NiO nanoparticles with high nickel vacancy concentration
⇨ Stabilization of nitrogen doped NiO by decomposition of $Ni_3O_2(OH)_4$ under ammonia atmosphere at 250°C
⇨ Characterization of Ni-poor NiO and NiO:N nanoparticles in p-DSSC in progress

References

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[4] B. Polteau, F. Tessier, F. Cheviré, L.Cario, S. Jobic, F. Odobel (2015) to be published.