Ni-based films by electrophoretic deposition of $Ni(OH)_2$ nanoflowers and nanoflakes

CSIC

colloidal processing

OBJECTIVE

$Ni(OH)_2$ nanoflakes and nanoflowers have been sonochemically synthesized in aqueous medium. Two different surfactants (PVP and PAA) have been used as synthesis aid and dispersant, respectively, in order to stabilize and control the morphology of the particles. The employment of PVP allows the fabrication of flake-like particles that can be shaped directly in the reaction media creating a thin film. Films obtained have been characterized in terms of surface morphology, growth mechanism and crystallography.

EXPERIMENTAL

Synthesis of β-$Ni(OH)_2$

0.1 M $Ni(NO_3)_2 \cdot 6H_2O$ + 2 M NH_3 → $Ni(NH_3)_x^{2+}$

Ultrasonic horn (24 kHz; 200 W; 65 W/cm²)

Polyvinylpirrolidone (PVP)
M_w ~ 29.000
R=1/100 (PVP/Ni^{2+})

Nanoflakes — *One-pot synthesis and shaping*

Nanoflowers — *Dried, redispersed and EPD*

Polyacrylic acid (PAA)
M_w = 2000

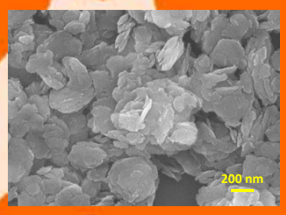
- EPD -

SYNTHESIS

Nanoflakes

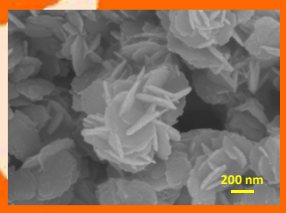
"PVP- protective mechanism":

- ✓ Hydrogen-bond through the oxigen atom of the carbonile group.
- ✓ Complex formation through the nitrogen or oxigen atoms (or both).



Nanoflowers

- ✓ Growth by an Ostwald ripening mechanism.
- ✓ Random aggregation of petal-like particles during growth mechanism favored by the high energy process of ultrasound.

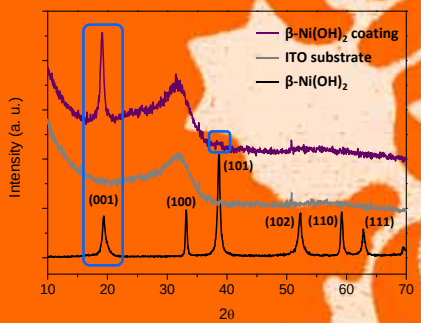


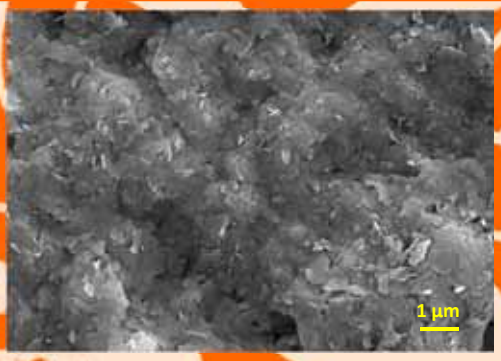
EPD NANOFLAKES

"One-pot synthesis" and direct EPD from the reaction media.

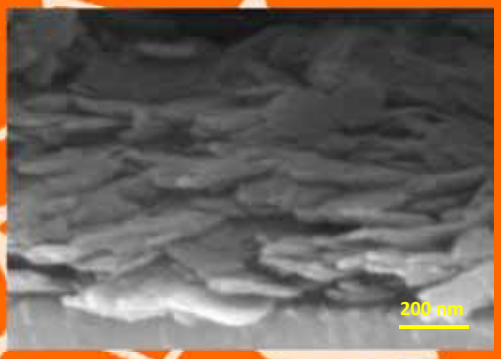
EPD conditions

$[Ni(OH)_2]$ (g/L)	0.1 – 1.0
σ (mS/cm)	0.5 – 4.4
E (V/cm)	0.2 – 1.0
t (min)	10 - 30





SEM image of the top view of the coating: heterogeneous deposits of the nanoflakes.



SEM image of the cross section of of the coating: ITO substrate covered by a stack of orientated β-$Ni(OH)_2$ nanoflakes across the c-axis.

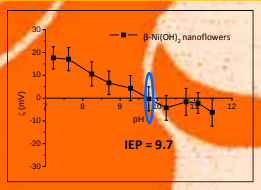
XRD analysis of the β-$Ni(OH)_2$ coating shows an intense peak corresponding to the (001) plane of the nickel hydroxide and a very small one related to the (101) plane. This means that the $Ni(OH)_2$ nanoplatelets are highly orientated within the coating with their higher surface parallel to the ITO substrate.

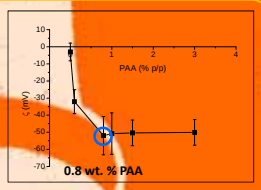
EPD NANOFLOWERS

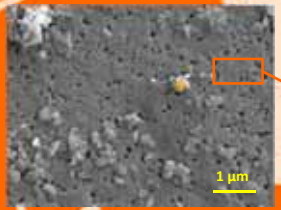
$Ni(OH)_2$ nanoflowers were dried and redispersed in water before EPD: Considering the IEP and that at pH < 7.1 the $Ni(OH)_2$ is dissolved in the medium, the working pH was established at 9.5 where the ζ is slightly positive, what allows the employment of an anionic surfactant (PAA). The optimal PAA concentration to stabilized the particles was found to be 0.8 wt. %.

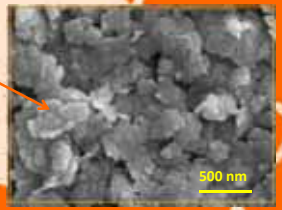
EPD conditions

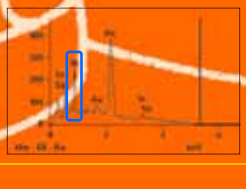
$[Ni(OH)_2]$ (g/L)	0.1 - 10
σ (mS/cm)	$4 \cdot 10^{-3}$
E (V/cm)	0.2 – 2.0
t (min)	10











- Low adhesion capacity of the nanoflower-like particles to the ITO substrate due to the small contact surface between both.
- Electrophoretic deposition of the thinnest fraction of platelet-like particles coming from the synthesis process or the aggregates breakage during the dispersion process.

CONCLUSIONS

- ✓ It is possible to control the morphology of β-$Ni(OH)_2$ particles through the employment of surfactants as synthesis additives.

Nanoflakes:

β-$Ni(OH)_2$ coatings have been obtained with the flake-like particles.

Coatings are formed by highly orientated nanoflakes that stack with their higher dimension parallel to the ITO substrate.

Nanoflowers:

Optimal dispersion conditions for the β-$Ni(OH)_2$ nanoflowers using PAA as dispersion agent have been established (IEP = 9.7, working pH ~ 9.5, optimal PAA concentration 0.8 wt. %), but nanoflowers adhesion should be improved.

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