Synthesis and characterization of doped SnO_2 and TiO_2 nanoparticles and hybrid composites for technological applications

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INTRODUCTION

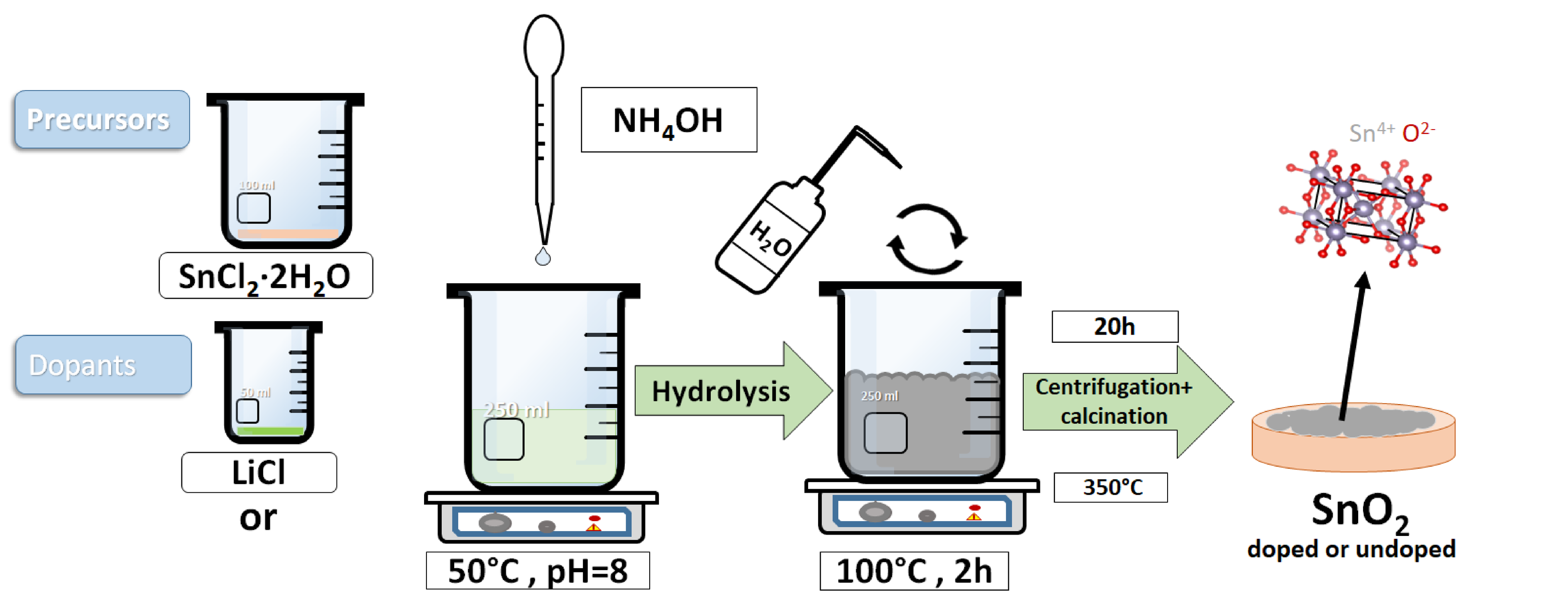
Wide bandgap semiconducting oxides, such as **SnO_2** and **TiO_2**, in form of **nanoparticles** have demonstrated potential applicability in numerous fields of technology such as optoelectronic devices, catalysis, gas sensing or energy storage. A higher control of the dimensions and doping of these nanoparticles can lead to enhanced performance.
Hybrid composites are emerging as low-cost materials with reported applications in photovoltaic and energy storage devices, among others [1]. In addition to the characteristic properties of the organic and inorganic compounds, these materials can exhibit new synergetic properties.

AIMS

- Synthesis via co-precipitation method based on hydrolysis of both anatase **TiO_2** and rutile **SnO_2** nanoparticles doped with **Li** or **Ni**, with variable cationic concentrations.
- Structural, compositional and luminescent characterization of the obtained nanoparticles.
- Fabrication of a **composite** via spin-coating technique combining the nanoparticles with PEDOT:PSS and measurement of **photovoltaic** properties.
- Assembly and measurement of different **anodes** for ion-Li batteries.

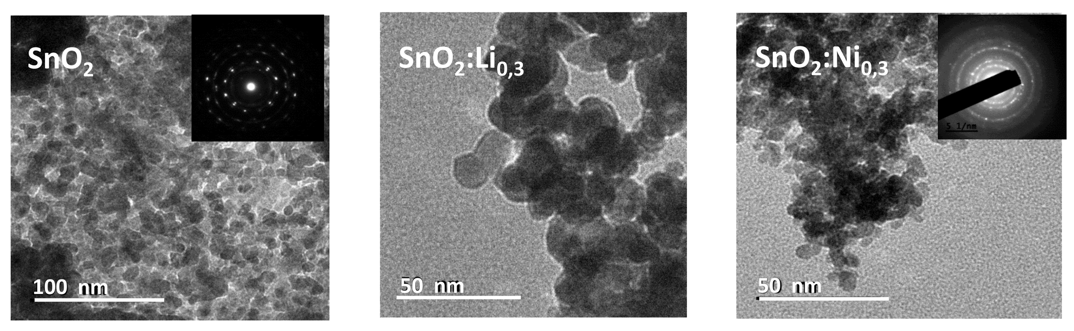
SnO_2

Synthesis



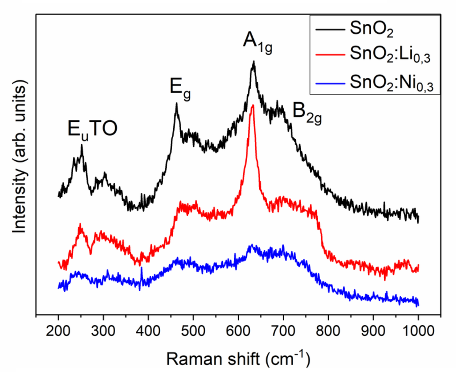
Characterization

Transmission Electron Microscopy (TEM)



TEM analysis confirms the presence of SnO_2 nanoparticles with dimensions 4 – 20 nm, in accordance with XRD analysis. SnO_2:$Ni_{0,3}$ nanoparticles show the lowest dimensions.

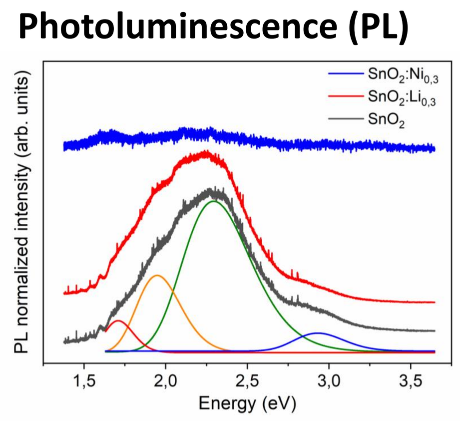
Raman Spectroscopy



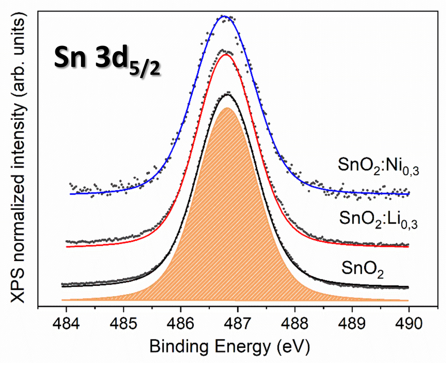
The presence of dopants modifies the SnO_2 vibrational modes (mainly E_g and A_{1g} modes).

PL spectra show common SnO_2 emissions [2]
The presence of Ni^{3+} is known to strongly decrease the luminescence ("killer effect").

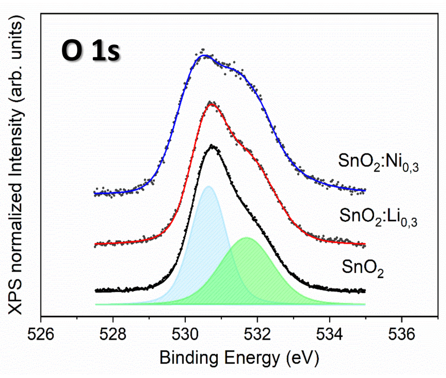
Photoluminescence (PL)

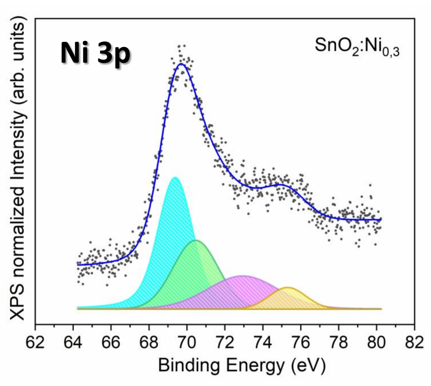


X-ray Photoelectron Spectroscopy (XPS)



Only Sn^{4+} in both undoped and doped nanoparticles was detected. However, both Ni^{2+} and Ni^{3+} were detected in samples doped with nickel.





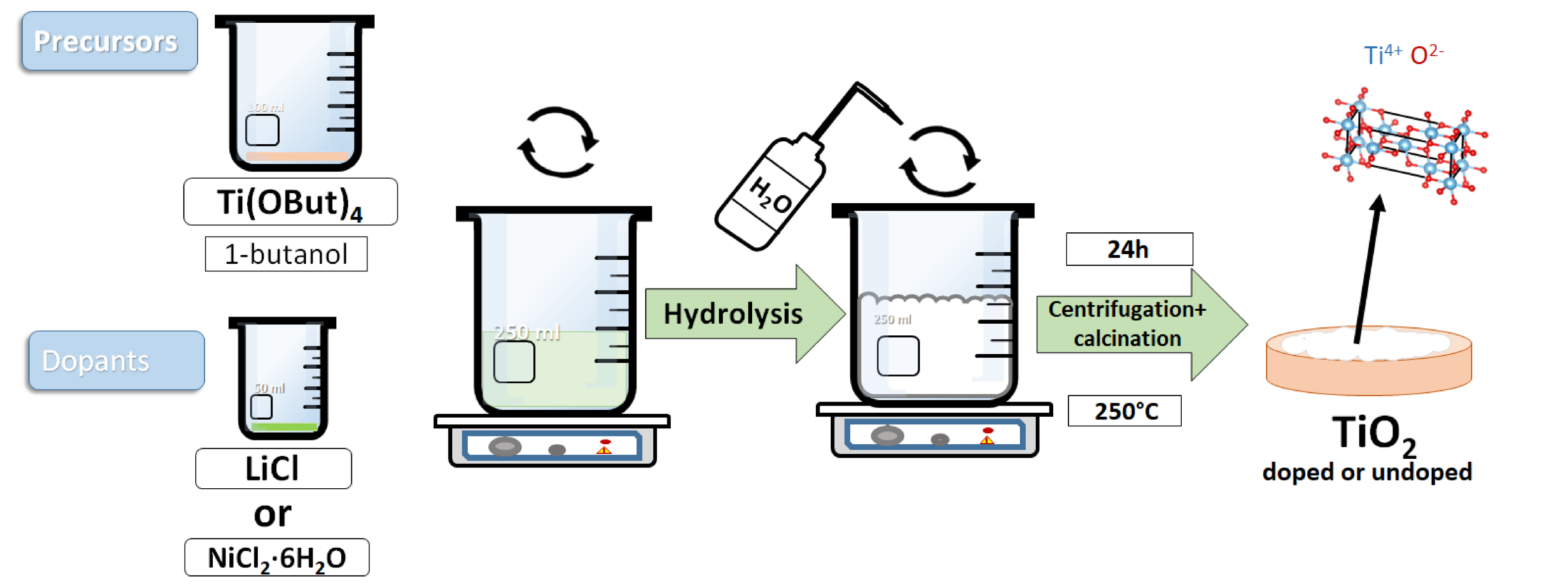
Compositional analysis

EDS		ICP-OES	
dopant conc.	% at.	dopant conc.	% at.
Ni 0,3	3,9±0,3	Li 0,3	0,95±0,02
Ni 0,2	0,5±0,1	Li 0,2	0,06±0,03

The amount of Ni in the nanoparticles is below 4 % at., according to EDS measurements.
Li is incorporated in the SnO_2 lattice in concentrations below 1 % at, as detected by ICP-OES.

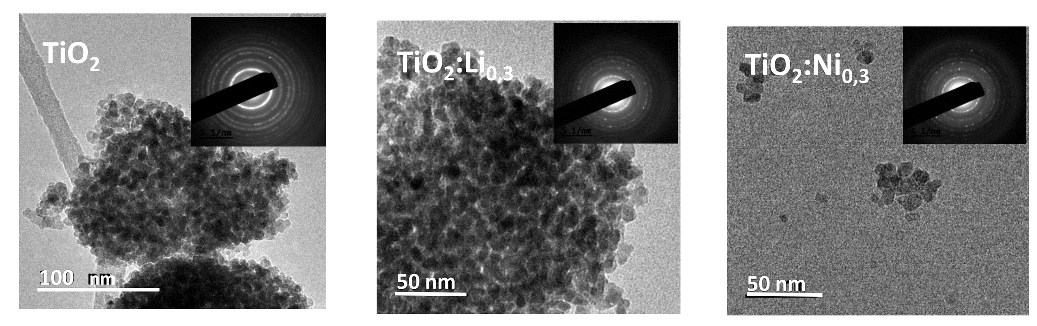
TiO_2

Synthesis



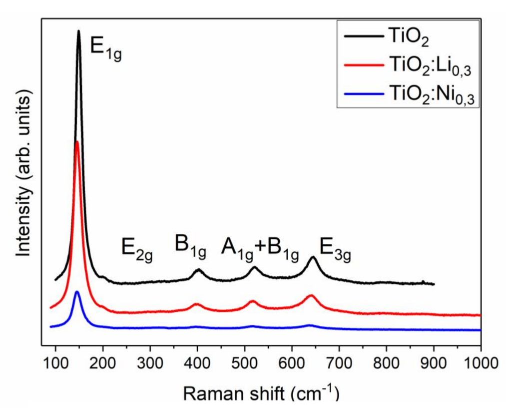
Characterization

Transmission Electron Microscopy (TEM)



SAED patterns confirm the presence of anatase TiO_2 with dimensions 4 – 15 nm.
Doped nanoparticles show reduced dimensions, according to TEM analysis.

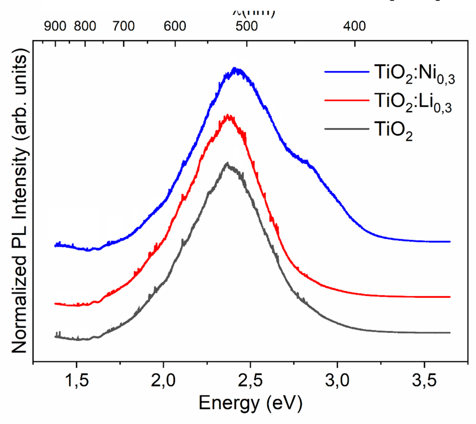
Raman Spectroscopy



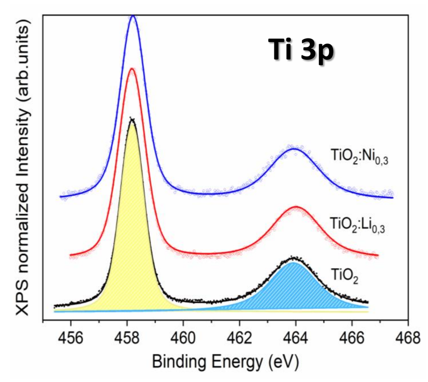
Small variations have been observed in the anatase TiO_2 vibrational modes due to the presence of dopants.

A broad emission centred in 2,36 eV related to oxygen vacancies dominates the PL spectra. Ni doped nanoparticles also exhibit an emission at 2,78 eV [3]

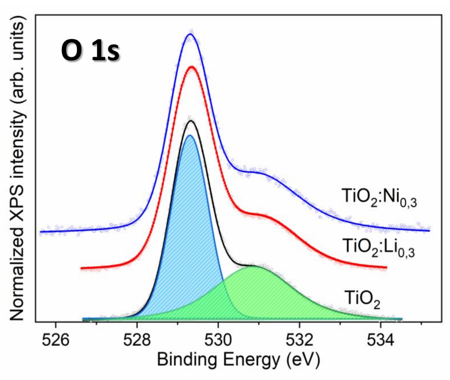
Photoluminescence (PL)

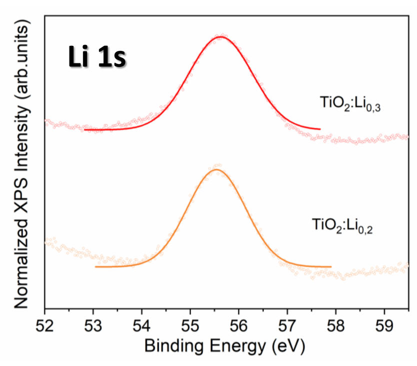


X-ray Photoelectron Spectroscopy (XPS)



XPS indicates that Ti is present only as Ti^{4+} in both undoped and doped nanoparticles.





Compositional analysis

EDS		ICP-OES	
dopant conc.	% at.	dopant conc.	% at.
Ni 0,3	1,5±0,2	Li 0,3	0,65±0,02
Ni 0,2	1,4±0,1	Li 0,2	0,50±0,02

Concentrations below 1,5 at. % have been estimated for Ni and Li, respectively. Slight variations in the at. % have been observed for both dopants.

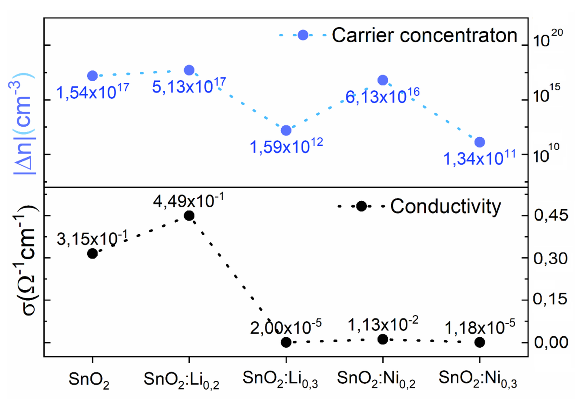
BATTERIES

FABRICATION

Anodes Li- ion batteries were fabricated combining SnO_2 with active material and binder in different concentrations, for wich carbon black and PAA were selected.

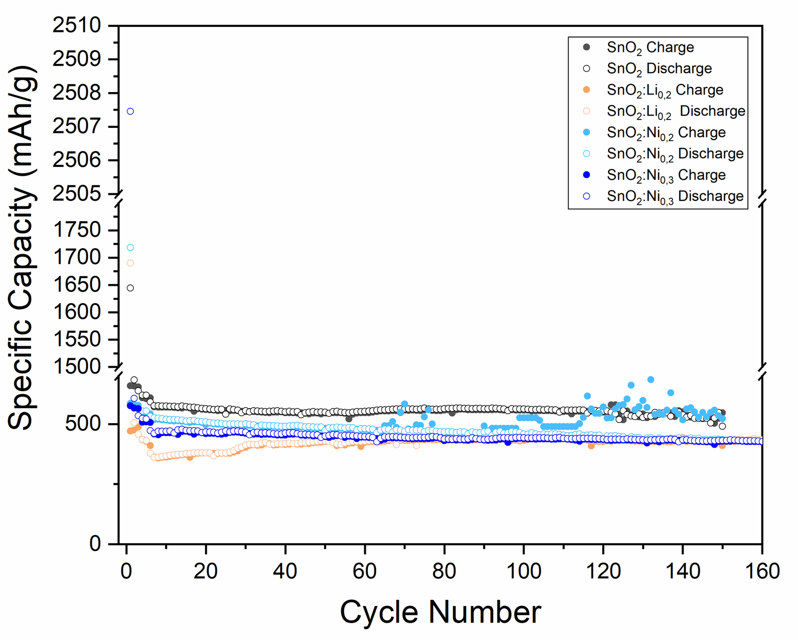
Electrical measurements

SnO_2:$Li_{0,2}$ shows an increase of conductivity and carrier density.
However adding nickel decrease both parameters, specially for higher concentrations.



CHARACTERIZATION

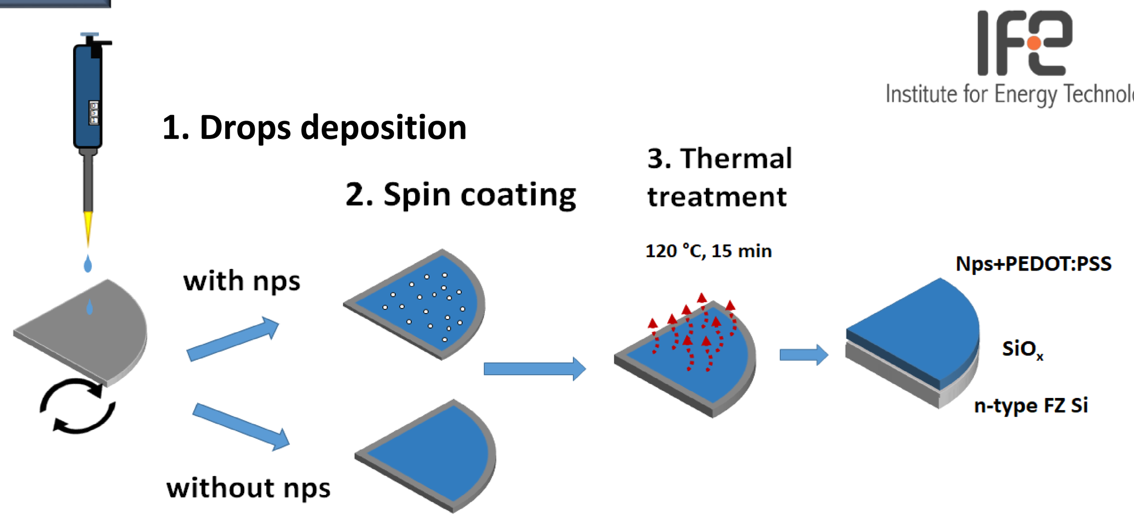
After **100** cycles, SnO_2 sample shows a specific capacity of 562mAh/g. Doped ones show great stability over time.



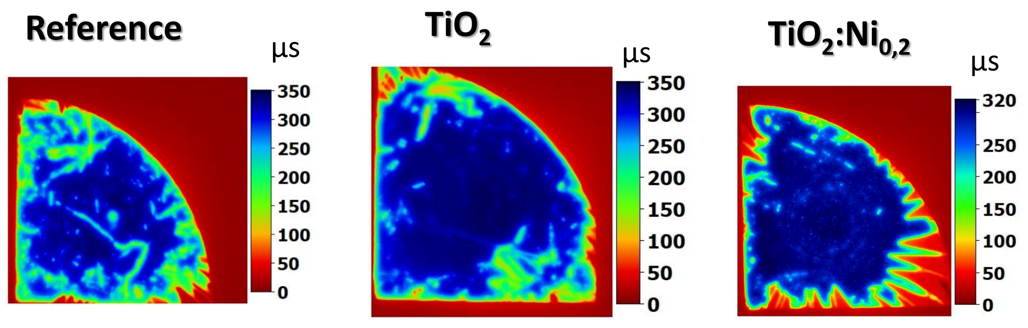
HYBRID COMPOSITE

FABRICATION

Composites were fabricated via **spin coating**. Mixture of PEDOT:PSS, organic solvents and nanoparticles were deposited over n-type silicon



CHARACTERIZATION



Bare PEDOT:PSS samples show lifetimes arround 320µs.
Slight improvements of lifetime were observed in the samples with the addition of TiO_2.

CONCLUSIONS

- SnO_2 and TiO_2 nanoparticles, undoped and doped with Li or Ni, were synthesized using the hydrolysis method.
- Homogeneity in the dimensions and crystalline structure of the nanoparticles have been achieved.
- The dopant inclusion into the lattice does not modifies the chemical structure of the SnO_2 and TiO_2 nanoparticles but it does modify the Raman modes and luminescence.
- Anodes for ion-Li batteries were fabricated with SnO_2 as an active material, showing promising results on specific capacity for electrodes with SnO_2
- Hybrid composites were fabricated by mixing PEDOT:PSS and TiO_2 showing good lifetime results for samples with TiO_2 and TiO_2:$Ni_{0,2}$

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[1] M García-Tecedor, S. Zh Karazhanov, G.C. Vásquez, H. Haug, D. Maestre, A. Cremades, M. Taeño, J. Ramírez-Castellanos, J.M. González-Calbet, J. Piqueras, C.C. You, E.S. Marstein. *Nanotechnology,* **29**, 035401 (2018)
[2] M. A. Peche-Herrero, D. Maestre, J. Ramírez-Castellanos, A. Cremades, J. Piqueras, J. M. González-Calbet, *CrystEngComm*, **16**, 2969, (2014)
[3] G. C. Vásquez, M. A. Peche-Herrero, D. Maestre, B. Alemán, J. Ramírez-Castellanos, A. Cremades, J. M. González-Calbet, J. Piqueras, *J. Mater. Chem. C* ,**2**, 10377–10385, (2014).

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