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Tailoring wettability and photocatalytic properties of NiO nanosystems fabricated by plasma-assisted vapor deposition

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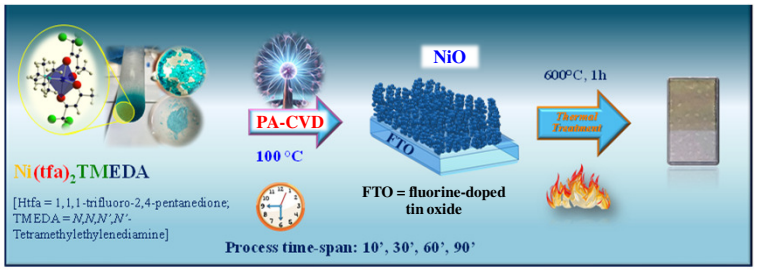
SCAN ME

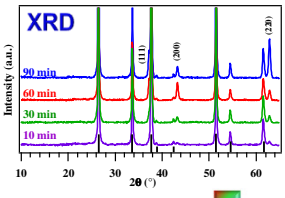
INTRODUCTION & AIM

- **NiO supported nanostructures** are fabricated *via* an original plasma assisted-chemical vapor deposition (PA-CVD) on glassy substrates at temperatures of 100°C, the lowest ever reported for similar processes, starting from a second-generation precursor, $Ni(tfa)_2TMEDA$ **[1-3]**.
- Variations of the sole *process duration from 10 to 90 minutes* allow to **modulate the system morphology**, and, in particular, grain dimensions and deposit thickness. The control of the latter enables to tailor functional performances in terms of **wettability** and **photocatalytic degradation of aqueous diclofenac** {DCF = 2-[2-(2,6-dichloroanilino)phenyl]acetic acid}, *a recalcitrant pharmaceutical pollutant*.

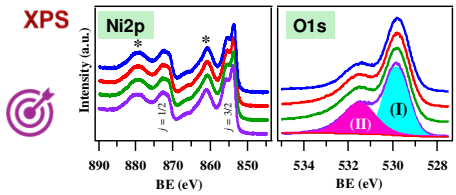
METHOD



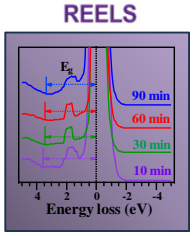
RESULTS & DISCUSSION

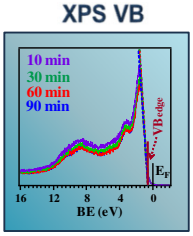


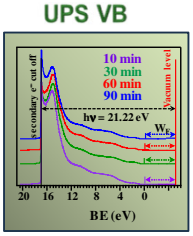
XRD patterns showed:
- **Three signals from (111), (200), and (220) planes of cubic NiO**
- **Preferential orientations along [111] and [220] directions**



- **Ni2p peaks consistent with NiO (* = satellites)**
- **O1s bands ⇒ lattice O (I) and –OH groups adsorbed onto O defects**
- Sn signal from FTO, decreases with longer deposition times **Surface CF_x groups**





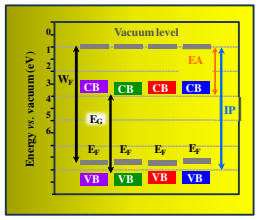


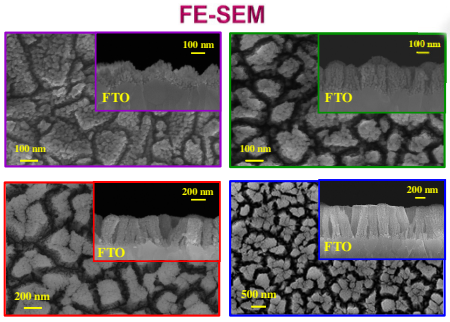
Material electronic structure

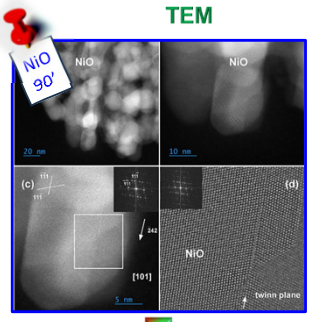
Work function values all close to 4.7 eV

REELS spectra: intense peak at **zero energy loss due to elastically scattered electrons** + **signal below 2 eV due to scattering collisions with H atoms**, whose content ⇑ **at lower deposition times**. ⇑ PA-CVD process duration ⇒ modest E_G decrease of the measured energy gap from 3.6 to 3.3 eV

- Separation between **VB edge** and **Fermi level** slight decrease as a function of the the PA-CVD process duration

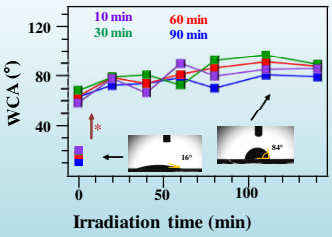






- Nanocolumnar open-area morphology promoted by a hybrid 2D-3D growth mode;
- **Deposit thickness linearly increases with deposition time**
- **Growth control by the sole variation of process duration**

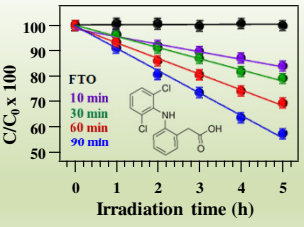
Defect structure, elongated NPs of twinned single NiO nanoparticle along the <111> growth direction of the cubic structure



Wettability: Water contact angle (WCA) measurements

- **These materials evidenced an initially higher hydrophilicity for thicker NiO systems, ascribed to a larger surface area**
- **WCA change over time: increase up to 60-70° after 24 days, and is further promoted upon illumination**

The system hydrophobicity can be fostered by two concomitant factors:
- **The presence of oxygen vacancies promote O_2 adsorption**;
- **The presence of surface CF_x groups helps the maintenance of the hydrophobic behavior upon irradiation.**



- **Photodegradation of aqueous diclofenac (DCF)**
  - **The degradation activity increases as a function of the deposit thickness**
  - **The most hydrophilic sample produced the fastest DCF degradation**
  - **Higher columns larger and NiO grains atop the columns favor a better UV light absorption ⇒ a more efficient charge carrier generation and a faster DCF degradation.**

CONCLUSION

- ✓ **Phase-pure NiO nanosystems** were fabricated *via* **PA-CVD** on glassy substrates at 100°C
- ✓ **Wettability and photodegradation efficiency of aqueous DFC solutions** were directly affected by morphology, with particular regard to grain dimensions and deposit thickness
- ✓ The work demonstrates a straightforward strategy for preparing NiO nanostructures, applicable even to thermally labile substrates
- ✓ Surface hydrophobicity of the system can potentially be used to design **catalysts with improved activity and selectivity**
- ✓ Flexible control over thickness and morphology makes NiO systems promising candidates for photoactivated applications, including water splitting for green hydrogen production

REFERENCES

[1] C. Maccato *et al.*, *Chem. Commun.*, 2025, **61**, 2945; [2] C. Maccato *et al.*, *Surf. Sci. Spectra*, 2025, **32**, 024005; [3] C. Maccato *et al.*, *Dalton Trans.* 2023, **52**, 10677.