On the molecular engineering of graphitic carbon nitride supported on carbon cloths for water remediation

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https://wwwdisc.chimica.unipd.it/multi-functional-material-group/

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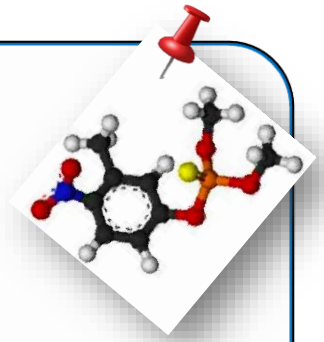
Environmental Concerns

- **Organophosphate compounds used as pesticides, such as Fenitrothion (FNT), represent a serious environmental issue due to their harmful effects on health.**
- **Efficient actions:** Advanced oxidation processes (AOPs) ⇒ **Electro-Fenton (EF) routes are among the most successful AOPs for organic contaminants.**



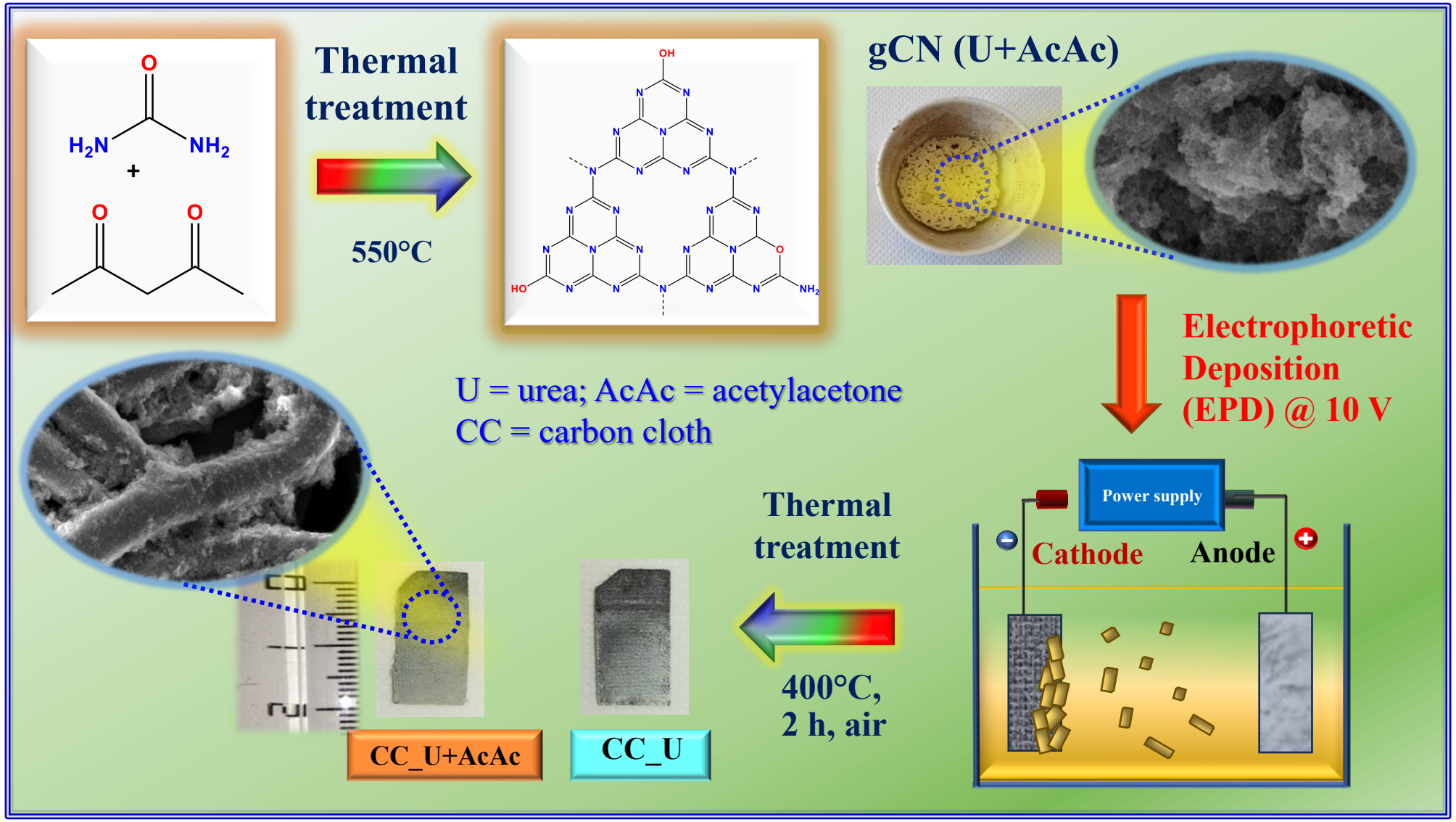
Catalyst Development

- **EF processes** need **low-cost**, **abundant**, **active**, and **metal-free catalysts**.
- **2D materials**, such as **graphitic carbon nitride (gCN)** ⇒ an appealing alternative to precious metal-based systems

gCN Synthesis and Properties

- **gCN is a low-cost semiconductor with very attractive properties for photo(electro)catalysis.**
- **The characteristics of gCN-based materials depend on their *synthesis and functionalization routes*.**

Adopted Synthesis Procedure



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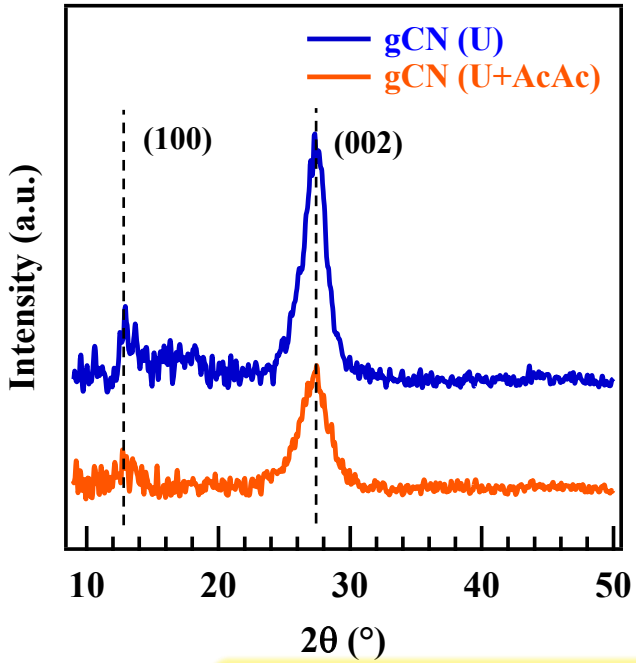
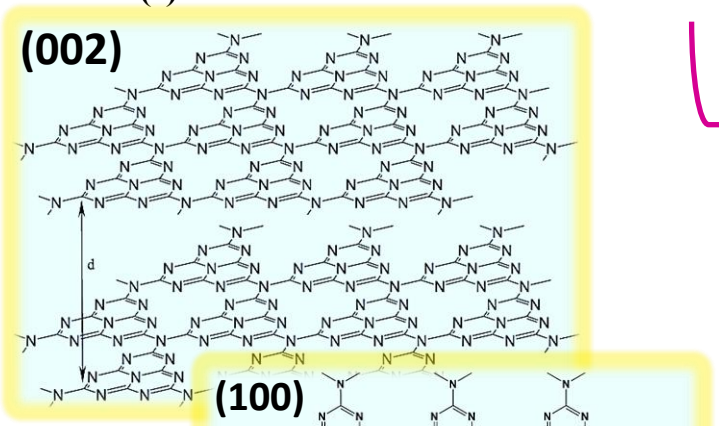
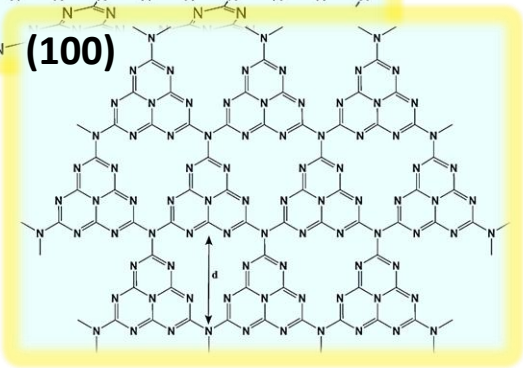
XRD



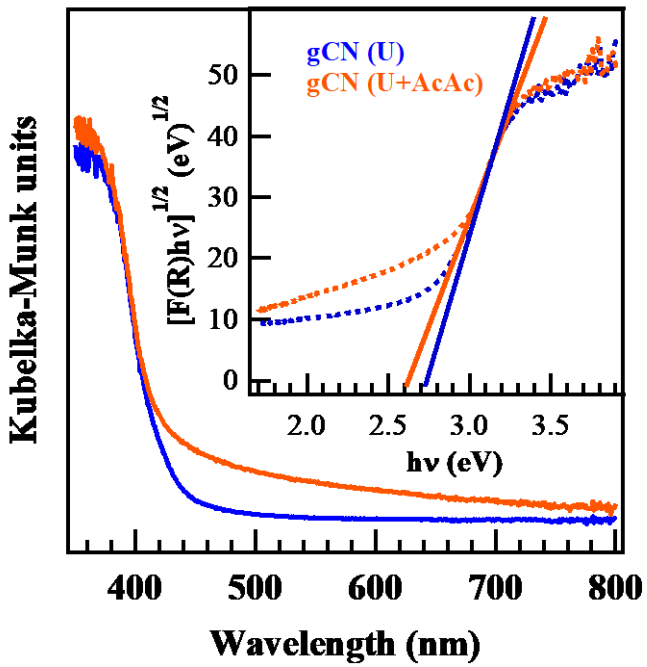
interplanar (002) stacking of gCN sheets



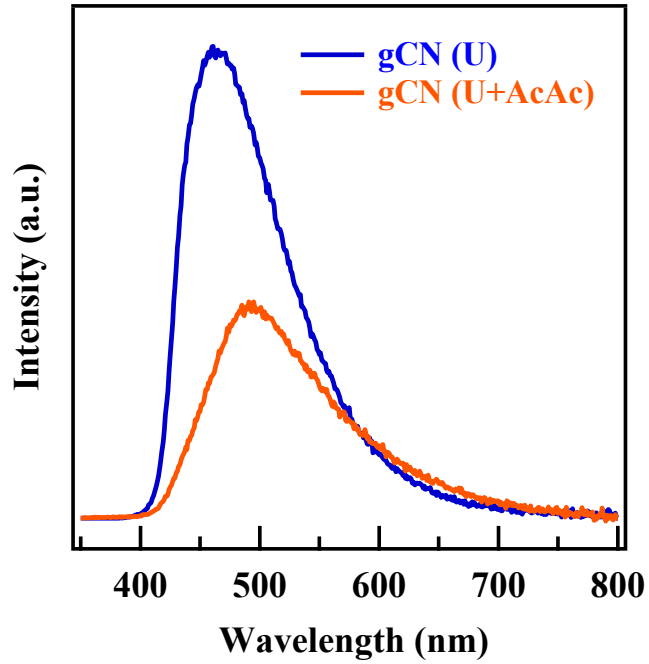
periodic arrangement of tri-*s*-triazine units in (100) planes



UV-Vis

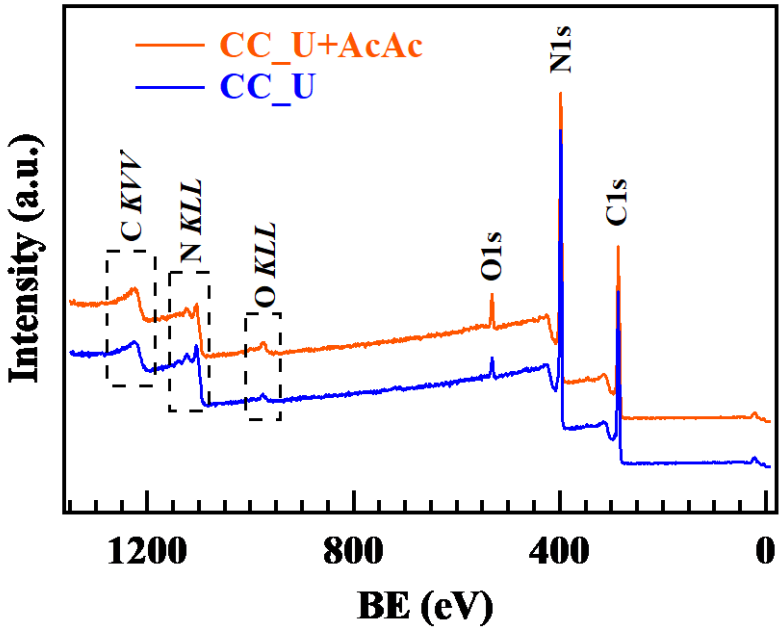


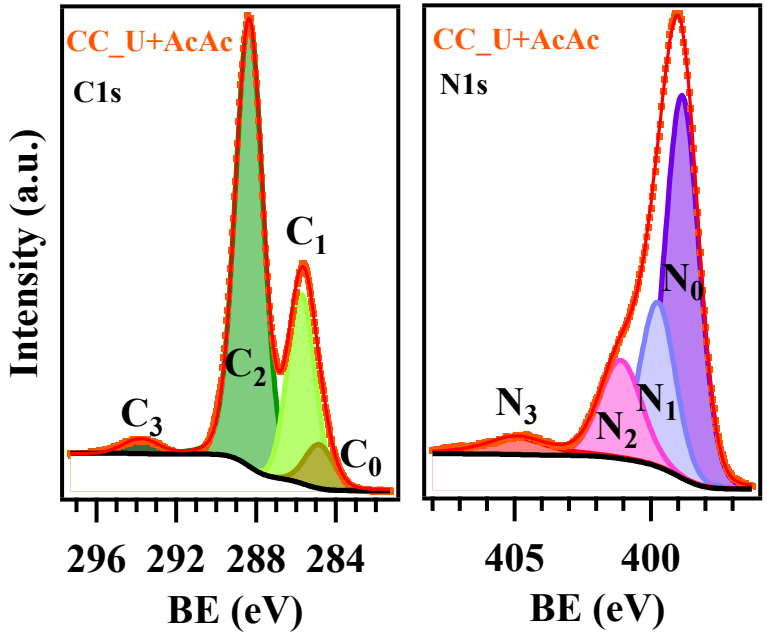
PL

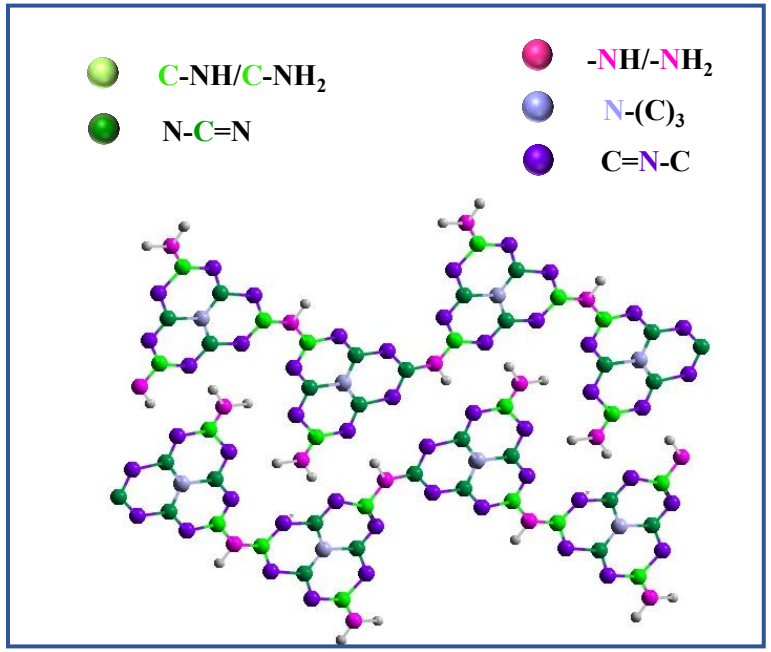


- Lower band gap of gCN (U + AcAc) ⇒ Higher Vis light absorption
- Lower PL intensity of gCN (U + AcAc) ⇒ AcAc functionalization suppresses charge carrier recombination ☺ for the target application

XPS







- Highly pure materials
- AcAc-functionalized specimen shows a high content of defective sites
  (confirmed by the increased intensity of **C_1** and **N_2** components → NH_x groups)

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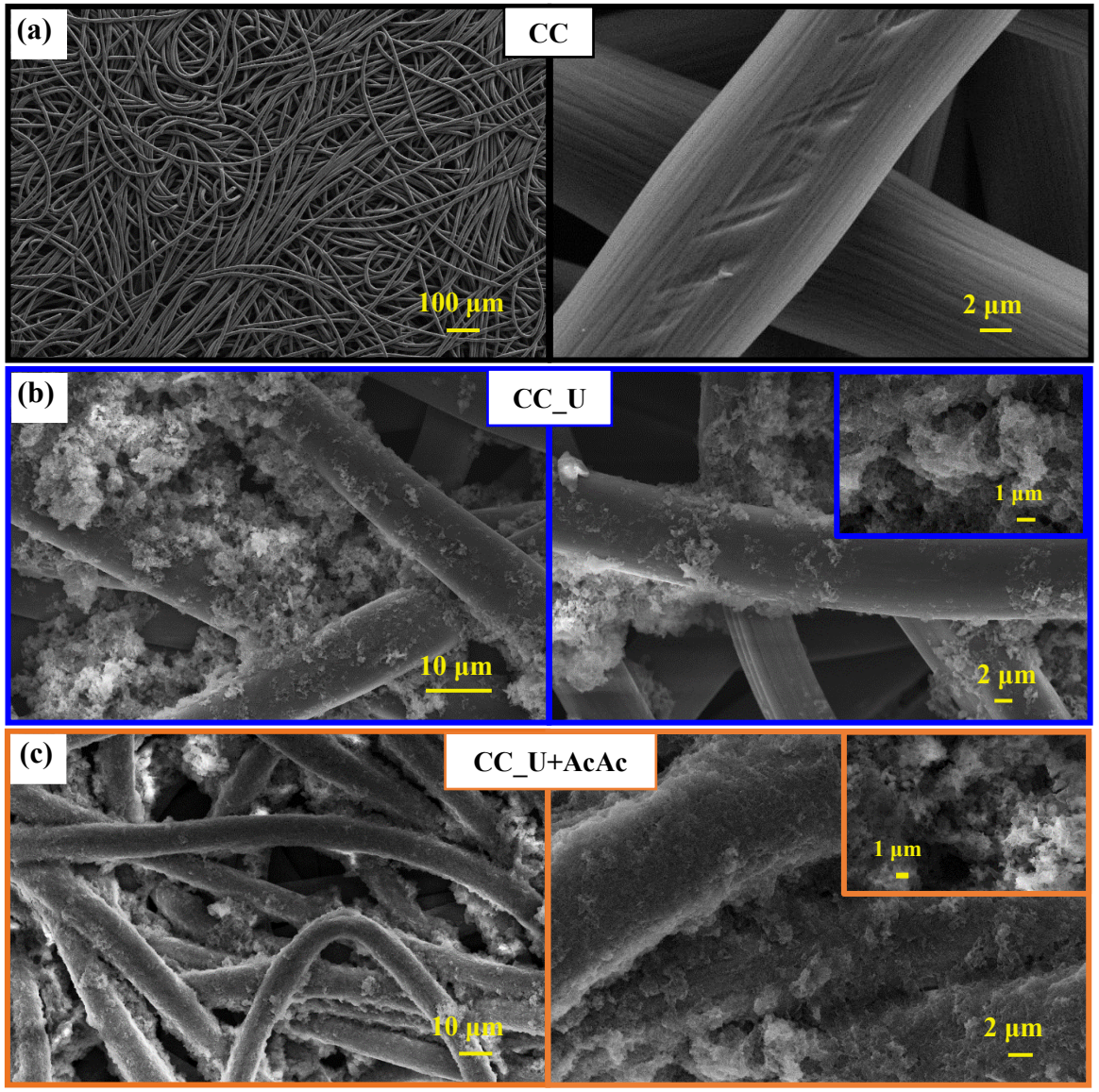
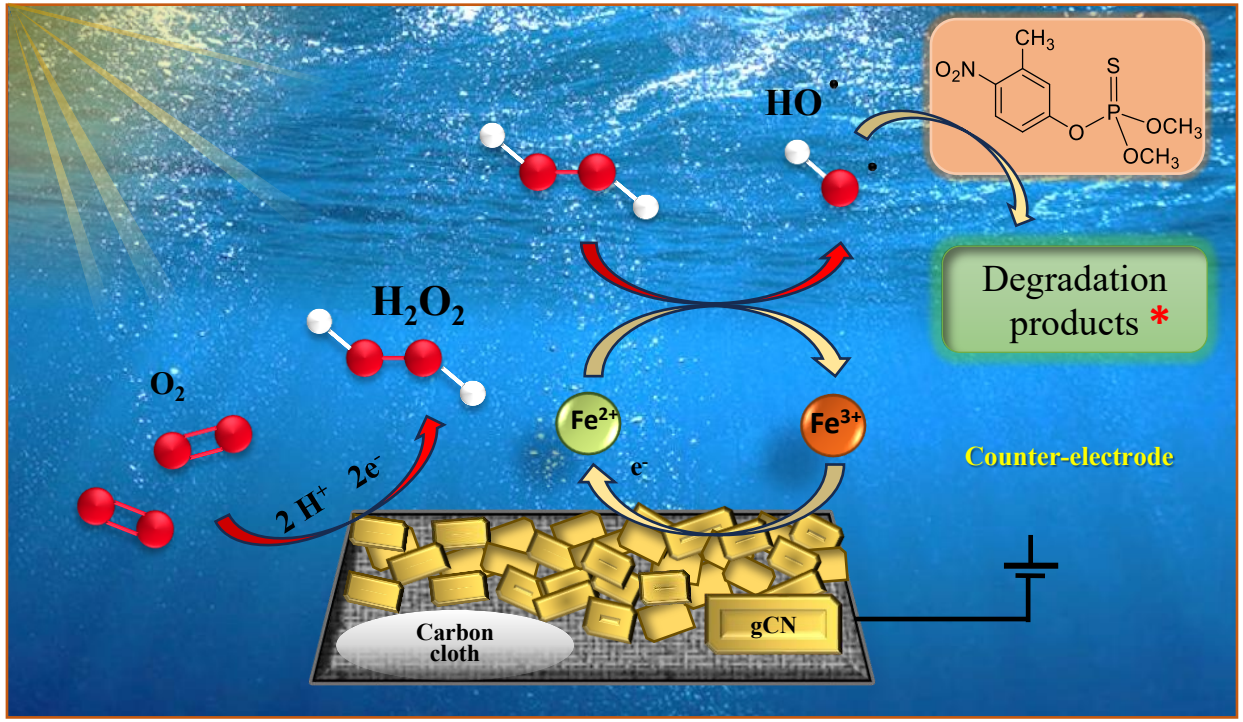
AcAc functionalization is a viable tool to achieve **carbon nitride defect engineering**

FE-SEM

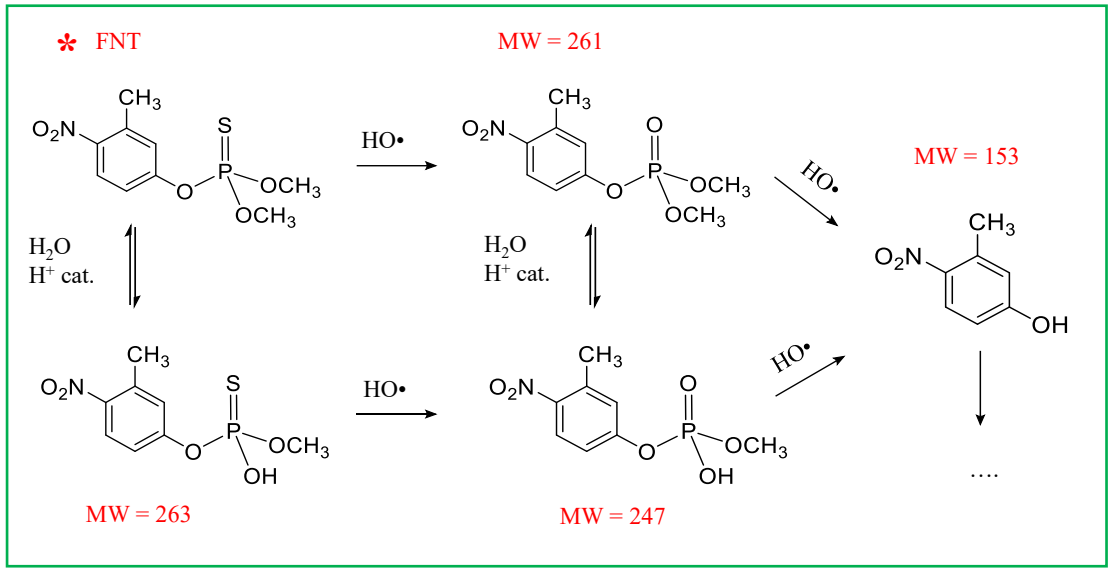


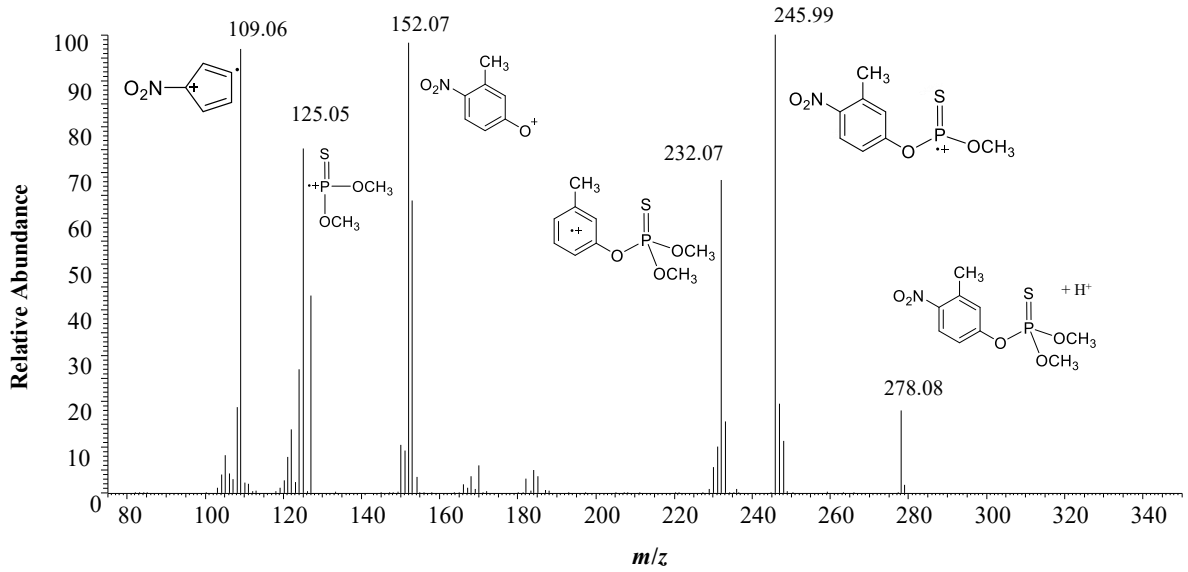
- gCN ⇒ sheet-like aggregates, increasing the active area
- **CC_U**: gCN particles were aggregated in confined areas, leaving some CC regions uncovered.
- **CC_U + AcAc**: Homogeneous gCN dispersion on CC fibers and penetrating the cloth meshes
- **Improved dispersion in CC_U + AcAc ⇒ higher defectivity ⇒ better adhesion to the CC substrate**

Electro-Fenton (EF) Tests



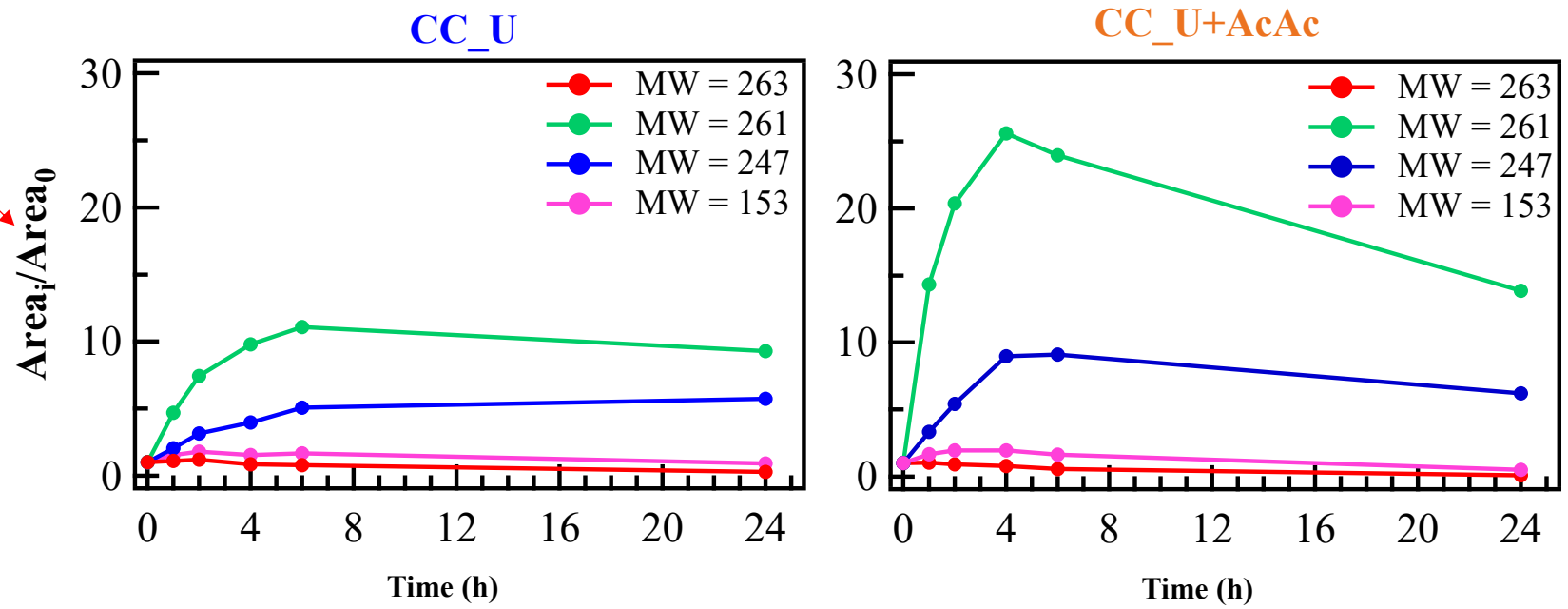
- After starting EF tests **newly generated Reactive Oxygen Species (ROS)** promoted the degradation of different organic species identified by mass spectrometry analyses
- 3-methyl-4-nitrophenol (MW = 153) was the lowest molecular weight product detected
- Further oxidative processes could produce even lighter organic species, which were undetectable by HPLC-MS measurements





Evolution of FNT degradation products during electro-Fenton experiments

$Area_i/Area_0$ ratio was calculated as the ratio between the chromatographic peak areas at the i-th time and at time = 0 h.



- **FNT was not detected by HPLC-MS analysis at any point**
- **Initial adsorption of FNT molecules onto the photoelectrocatalyst surface ⇒ favors a partial FNT degradation directly on the electrode surfaces.**
- The relative concentrations of species with MW = 247 and 261 underwent an increase during the first hours, more significantly in the case of **CC_U + AcAc** ⇒ **demonstrating the beneficial role of defect engineering through AcAc functionalization**

Conclusions & Perspectives

Defect engineering og gCN photoelectrocatalysts, immobilized on carbon cloths by EPD, for FNT decomposition.

The **functionalization with acetylacetone (AcAc) improved**: i) gCN adhesion and distribution on the substrate; ii) reactivity towards FNT degradation, by reducing electron-hole recombination.

Functionalized gCN demonstrated remarkable electrochemical stability.

Results open perspectives for implementing the electro-Fenton technique in **sunlight-activated water purification**.

Further research is needed on formation mechanisms and toxicological effects of FNT-derived products.