Metal-organic frameworks for advanced electro-Fenton treatment of wastewater at near-neutral pH: Preparation of heterogeneous catalysts and enhancement of H_2O_2 production

——Research Plan

Candidate : Lele Zhao

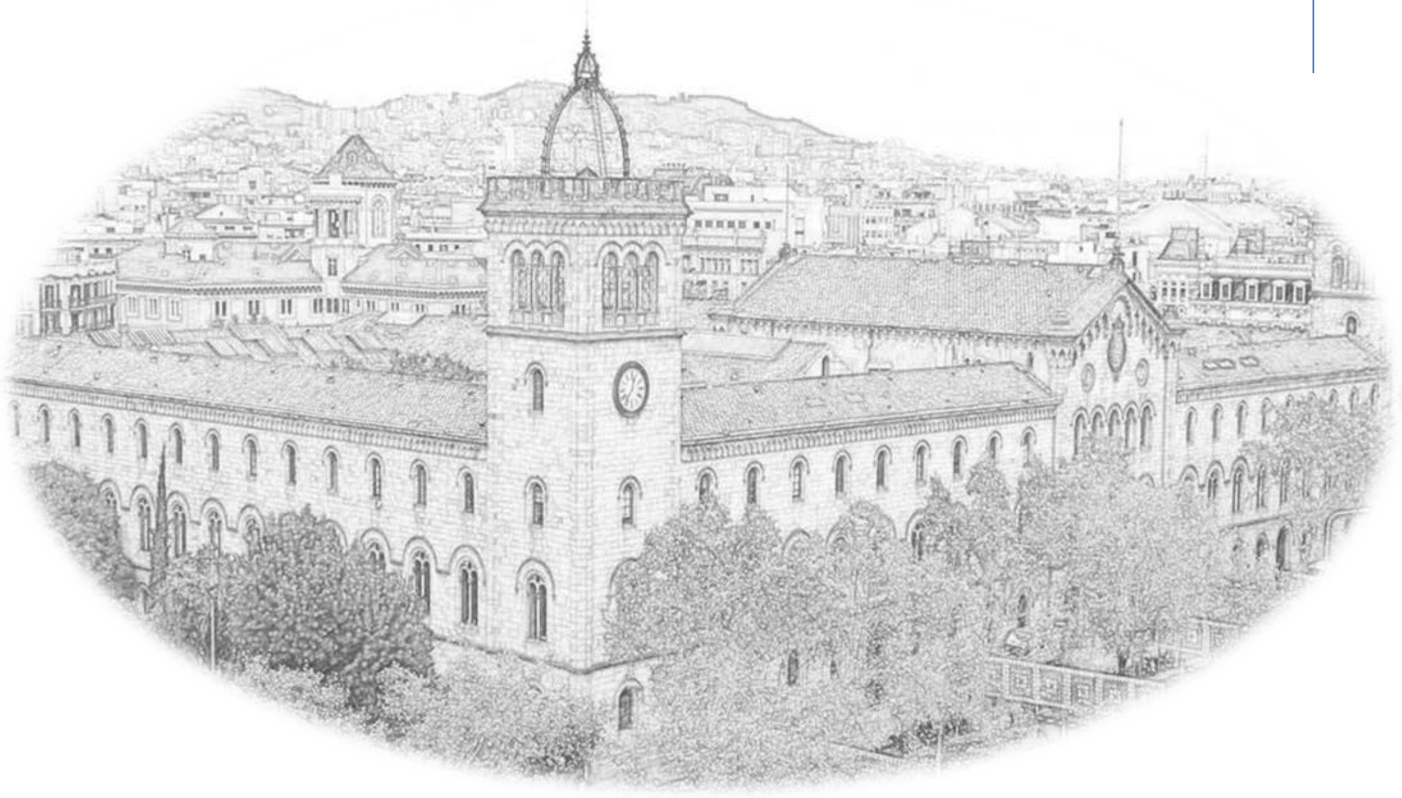
Supervisor : Dr. Ignacio Sirés Sadornil

Tutor : Dr. Pere Lluís Cabot Julià

Research group : LEMMA (UB)

UNIVERSITAT DE BARCELONA

Contents



UNIVERSITAT DE BARCELONA

1、Introduction: Motivation & State-of-the Art

Conventional wastewater treatment technologies are intimately related with the substantial progress in health and environment protection. In spite of this, the diversity and amount of organic pollutants are so vast that water quality has been negatively affected, with conventional treatments becoming less effective to ensure sufficient water decontamination. Within this context, the technologies based on the in-situ promotion of a strong oxidant like the hydroxyl radical (•OH) have emerged with a leading role.

Dyes

Industrial additives

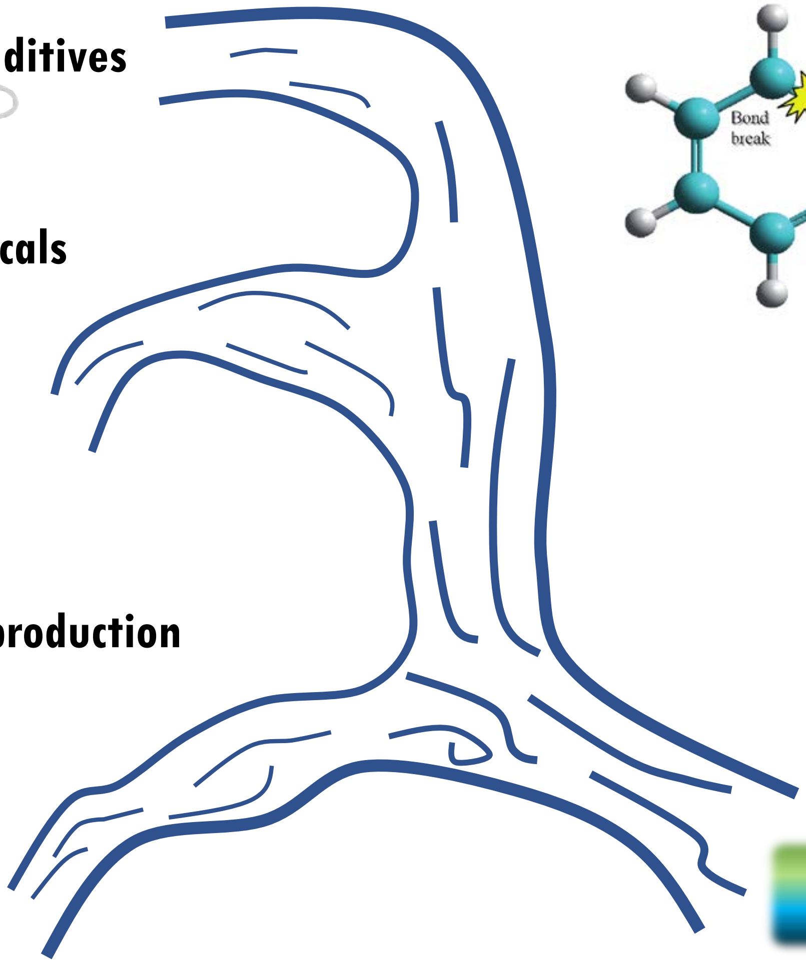
Pharmaceuticals

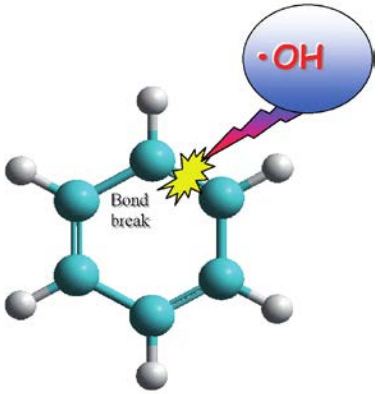
Pesticides

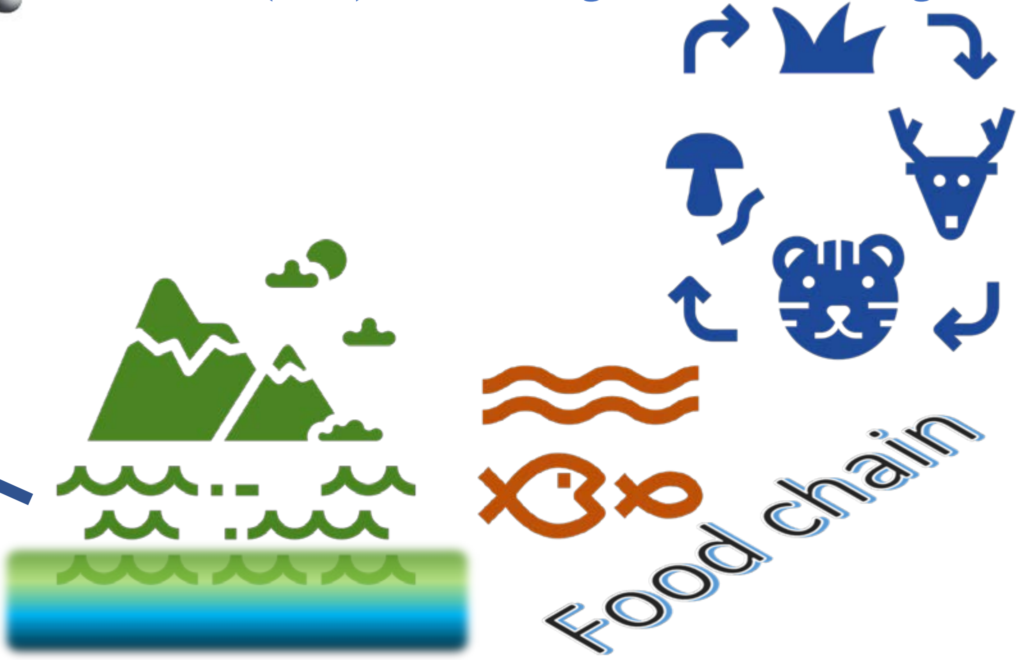
Agriculture production

Healthcare

....







1、Introduction: Motivation & State-of-the Art

Electro-Fenton

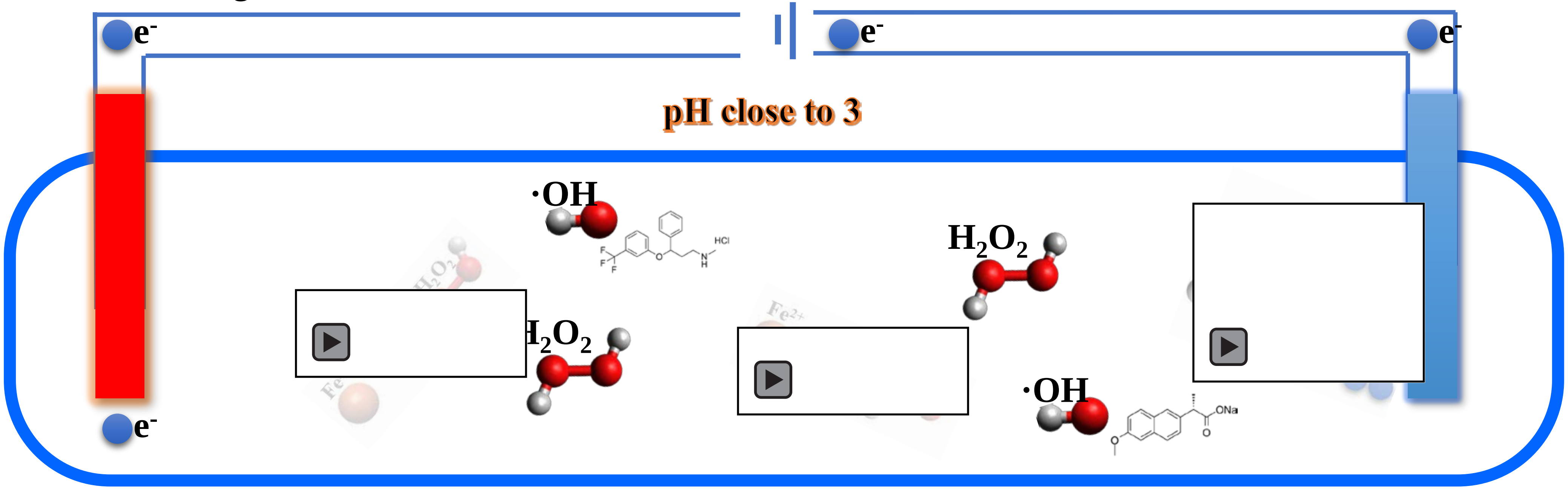
Two key characteristics

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$

It allows a quick and complete destruction of target pollutants, owing to the massive production of ${}^{\bullet}OH$ in the bulk solution through Fenton's reaction.

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

The H_2O_2 needed as reactant is generated on site from the O_2 reduction reaction occurring at the cathode surface



UNIVERSITAT DE BARCELONA

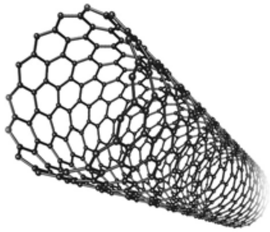
1、Introduction: Motivation & State-of-the Art

Electro-Fenton

But

Urban wastewater effluents is close to neutral pH

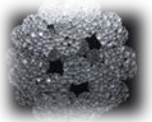
The iron catalyst precipitates



Hence

Several materials have been employed as heterogeneous catalysts in EF

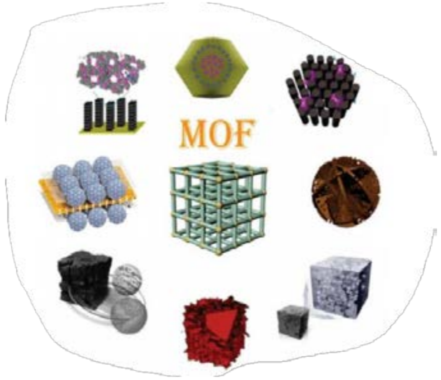
High catalytic activity, stability and recyclability



UNIVERSITAT DE BARCELONA

1、Introduction: Motivation & State-of-the Art

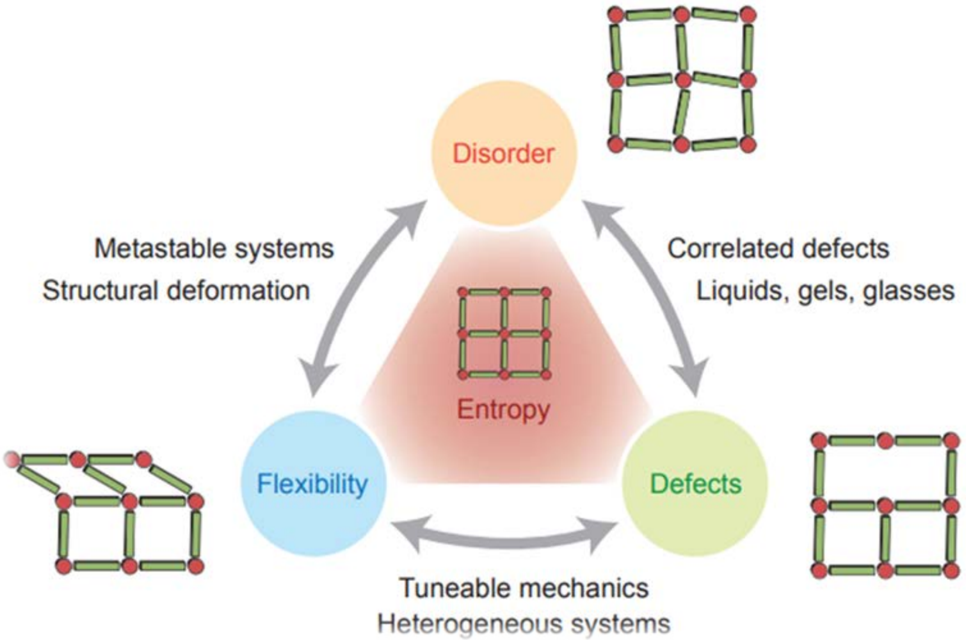
Metal-Organic Frameworks (MOFs)



MOFs are highly ordered and porous crystalline structures synthesized from metal ion/clusters and multidentate organic linkers

Large porosity **Chemical tunability**

Despite the evident advantages of MOFs in model aqueous solutions, their structural <u>instability</u> and other shortcomings have been revealed, thus limiting their scale-up for water treatment. Some researchers have modified the synthesis routes, aiming at obtaining more stable materials.



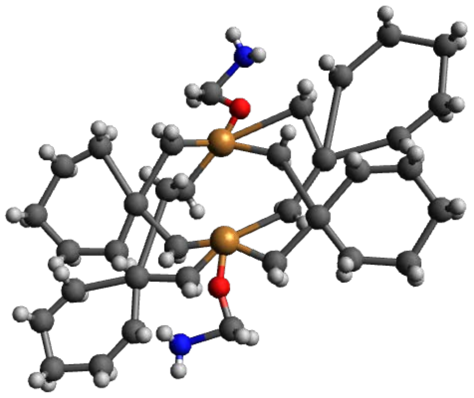
Bennett T D, Cheetham A K, Fuchs A H, et al. Interplay between defects, disorder and flexibility in metal-organic frameworks. *Nature chemistry*, 2017, 9(1): 11.

1、Introduction: Motivation & State-of-the Art

Cu-MOFs

Copper, as an Earth abundant transition metal, is considered as one of the most important iron-free Fenton-like catalysts. The $^{\bullet}OH$ can be generated from the reaction between H_2O_2 and the Cu(II)/Cu(I) redox species.

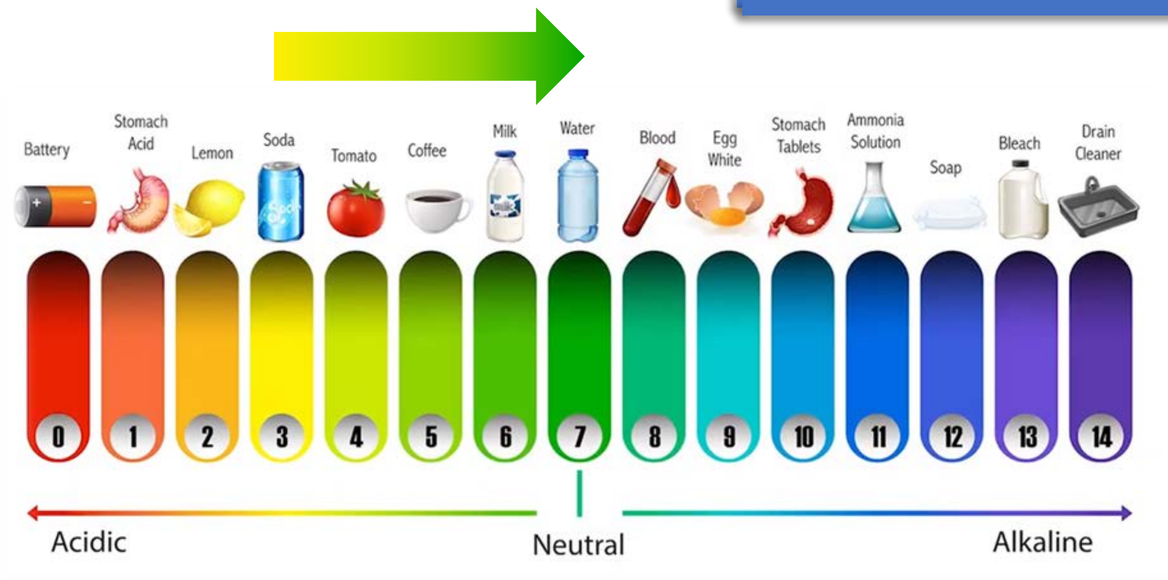
Note that, unlike iron species, leached Cu^{2+} is predominant as $[Cu(H_2O)_6]^{2+}$ at neutral pH, which presumably favors the operation of Cu-based EF over a wider pH range.



UNIVERSITAT DE BARCELONA

2、Objectives

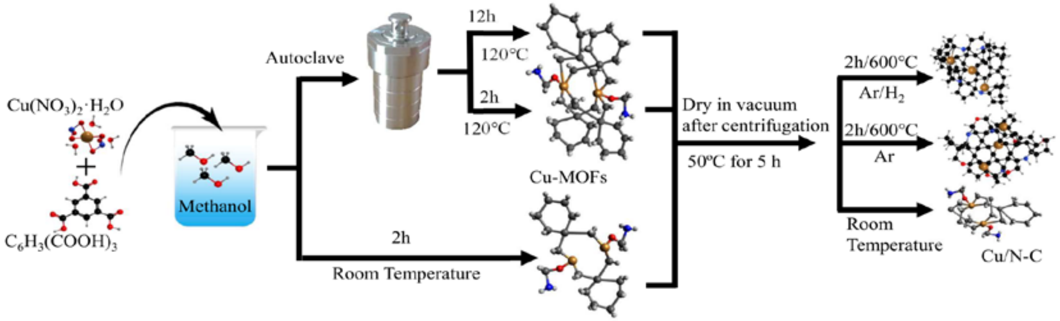
1 As heterogeneous catalysts with high activity, stability and performance within a wide pH range



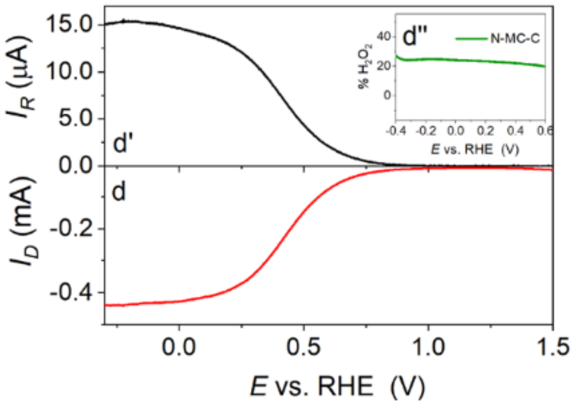
2 As precursors of doped porous carbons further employed to prepare GDEs with high electroactivity for H_2O_2 synthesis

3、Methods & Characterization

The MOF-derived carbons will be obtained under different pyrolysis conditions and then, they will be employed to manufacture the GDEs by spraying the catalyst layer on porous layers

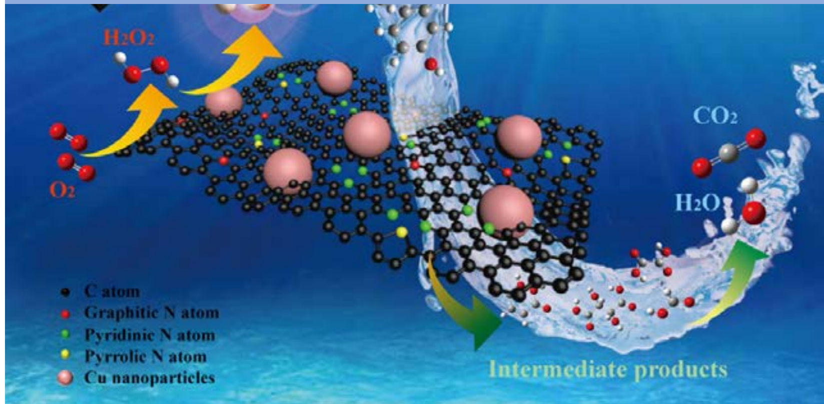


The electroactivity (number of electrons involved in the ORR) of these carbons will be evaluated by rotating disk electrode (RDE) and rotating ring disk-electrode (RRDE) techniques



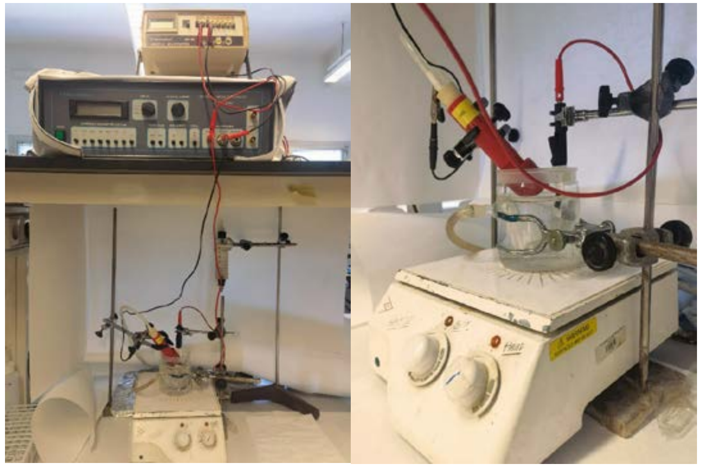
- ✓ Viability of the heterogeneous catalysts and GDEs: pollutant concentration decay and solution mineralization (i.e., TOC removal);
- ✓ Identification of intermediate compounds and their toxicity;
- ✓ Elucidation of reaction pathways of target organic pollutants (preferentially pharmaceuticals) spiked into the wastewater matrices.

Wang Y, Xue Y, Zhang C. Copper embedded in nitrogen-doped carbon matrix derived from metal-organic frameworks for boosting peroxide production and electro-Fenton catalysis. *Electrochimica Acta*, 2021, 368: 137643.



UNIVERSITAT DE BARCELONA

3、Methods & Characterization



Laboratory scale reactor

Flow cells

Electrochemical characterization

TOC analyzer

HPLC

HPLC-MS

UNIVERSITAT DE BARCELONA

3、Methods & Characterization

Autoclave

Hydraulic hot press

Tubular furnace

TEM

DLS

BET

UNIVERSITAT DE BARCELONA

4、Work plan and Schedule

Activity/Term (4 months each)	1	2	3	4	5	6	7	8	9	10	11	12
1. Get familiar with lab, general learning and state-of-the art	X	X										
2. Synthesis, characterization and application of magnetic and photoactive Fe-based MOFs			X	X	X	X	X					
3. Synthesis, characterization and application of novel (non-Fe)-MOFs		X	X	X			X	X	X			
4. MOF-derived carbons, and GDEs (H_2O_2)		X	X	X	X	X						
5. MOF-derived carbons, and GDEs (water treatment)			X	X			X	X	X			
6. Treatment of wastewater at coupling the heterogeneous catalysts and GDEs						X	X	X	X	X		
7. International stay								X				
8. Attendance to conferences		X			X	X		X	X		X	X
9. Writing articles and defense of PhD Thesis			X		X		X		X		X	X

UNIVERSITAT DE BARCELONA

5、Preliminary results

Cu-MOFs

Synthesis

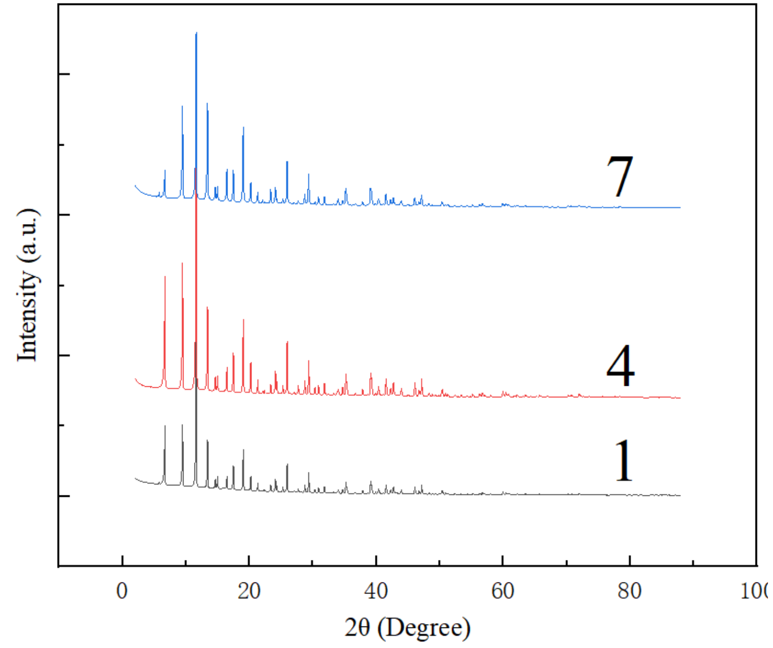
Centrifugation

Pyrolysis

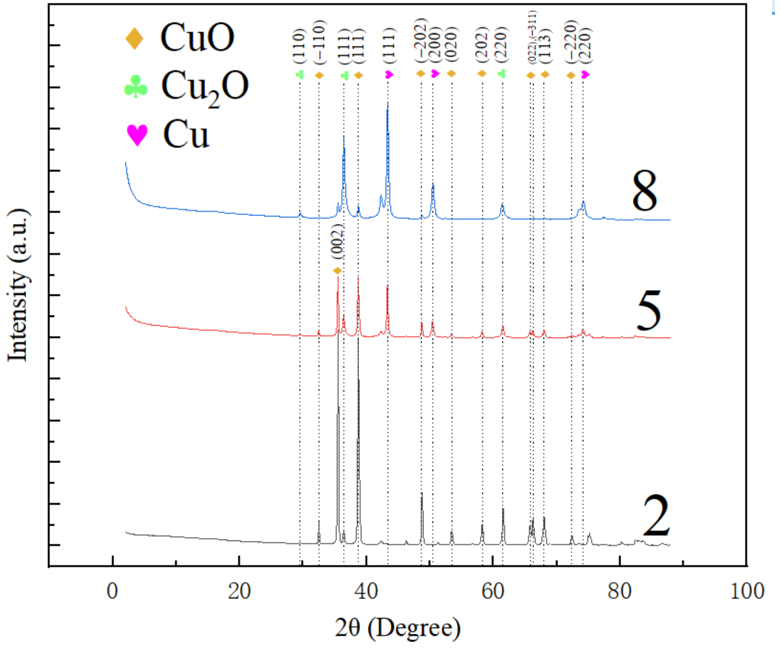
Optimum conditions (from XRD analysis):

- ☻ 2 h, 120 °C in autoclave
- ☻ Pyrolysis carried out in Ar/H_2 atmosphere

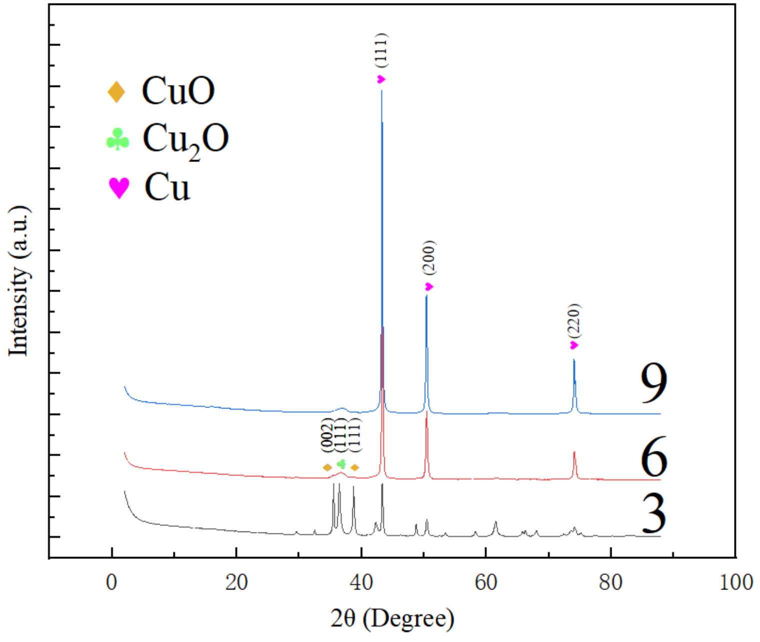
Legend	Room T	600 °C, Ar	600 °C, Ar/H_2
Beaker	1	2	3
Autoclave – 12 h	4	5	6
Autoclave – 2 h	7	8	9



Cu-MOF



Pyrolysis at 600 °C, **Ar**



Pyrolysis at 600 °C, **Ar/H_2**

6、References

[1] E. S. Bernhardt, E. J. Rosi, and M. O. Gessner, Synthetic chemicals as agents of global change, *Front. Ecol. Environ.*, 15 (2017) 84–90.

[2] R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. Gunten, B. Wehrli, The challenge of micropollutants in aquatic systems, *Science*, 313 (2006) 1072–1077.

[3] A. Christou, P. Karaolia, E. Hapeshi, C. Michael, and D. Fatta-Kassinos, Long-term wastewater irrigation of vegetables in real agricultural systems: Concentration of pharmaceuticals in soil, uptake and bioaccumulation in tomato fruits and human health risk assessment, *Water Res.*, 109 (2017) 24–34.

[4] M. Zhou, M. A. Oturan, and I. Sirés, *Electro-Fenton Process: New Trends and Scale-Up*, Springer Nature Singapore, 2018.

[5] M. -H. Zhang, H. Dong, L. Zhao, D. -X. Wang, and D. Meng, A review on Fenton process for organic wastewater treatment based on optimization perspective, *Sci. Total Environ.* 670 (2019) 110–121.

[6] Z. Ye, D. R. V. Guelfi, G. Álvarez, F. Alcaide, E. Brillas, and I. Sirés, Enhanced electrocatalytic production of H_2O_2 at Co-based air-diffusion cathodes for the photoelectro-Fenton treatment of bronopol, *Appl. Catal. B-Environ.* 247 (2019) 191–199.

[7] R. Salazar, M. S. Ureta-Zañartu, C. González-Vargas, C. do N. Brito, and C. A. Martinez-Huitle, Electrochemical degradation of industrial textile dye disperse yellow 3: Role of electrocatalytic material and experimental conditions on the catalytic production of oxidants and oxidation pathway, *Chemosphere*, 198 (2018) 21–29.

[8] P. Su, M. Zhou, G. Ren, X. Lu, X. Du, and G. Song, A carbon nanotube-confined iron modified cathode with prominent stability and activity for heterogeneous electro-Fenton reactions, *J. Mater. Chem. A*, 7 (2019) 24408–24419.

[9] D. Fernández, I. Robles, F. J. Rodríguez-Valadez, and L. A. Godínez, Novel arrangement for an electro-Fenton reactor that does not require addition of iron, acid and a final neutralization stage. Towards the development of a cost-effective technology for the treatment of wastewater., *Chemosphere*, 199 (2018) 251–255.

[10] S. O. Ganiyu, M. Zhou, and C. A. Martínez-Huitle, Heterogeneous electro-Fenton and photoelectro-Fenton processes: A critical review of fundamental principles and application for water/wastewater treatment, *Appl. Catal. B-Environ.* 235 (2018) 103–129.

[11] A. J. dos Santos, I. Sirés, A. P. M. Alves, C. A. Martínez-Huitle, and E. Brillas, Vermiculite as heterogeneous catalyst in electrochemical Fenton-based processes: Application to the oxidation of Ponceau SS dye, *Chemosphere*, 240 (2020) 124838.

[12] A. H. Ltaïef, S. Sabatino, F. Proietto, S. Ammar, A. Gadri, A. Galia, O. Scialdone, Electrochemical treatment of aqueous solutions of organic pollutants by electro-Fenton with natural heterogeneous catalysts under pressure using Ti/IrO_2-Ta_2O_5 or BDD anodes, *Chemosphere*, 202 (2018) 111–118.

[13] X. Li, B. Wang, Y. Cao, S. Zhao, H. Wang, X. Feng, J. Zhou, X. Ma, Water contaminant elimination based on metal-organic frameworks and perspective on their Industrial applications, *ACS Sustain. Chem. Eng.*, 7 (2019) 4548–4563.

[14] E. M. Dias and C. Petit, Towards the use of metal-organic frameworks for water reuse: A review of the recent advances in the field of organic pollutants removal and degradation and the next steps in the field, *J. Mater. Chem. A*, 3 (2015) 22484-22506.

[15] V. K. Sharma and M. Feng, Water depollution using metal-organic frameworks-catalyzed advanced oxidation processes: A review, *J. Hazard. Mater.*, 372 (2019) 3–16.

[16] M. Cheng, C. Lai, Y. Liu, G. Zeng, D. Huang, C. Zhang, L. Qin, L. Hu, C. Zhou, W. Xiong, Metal-organic frameworks for highly efficient heterogeneous Fenton-like catalysis, *Coord. Chem. Rev.*, 368 (2018) 80–92.

[17] N. Zhang, Y. Yi, J. Lian, and Z. Fang, Effects of Ce doping on the Fenton-like reactivity of Cu-based catalyst to the fluconazole, *Chem. Eng. J.*, 395 (2020) 124897.

[18] Y. Wang, Y. Xue, and C. Zhang, Copper embedded in nitrogen-doped carbon matrix derived from metal-organic frameworks for boosting peroxide production and electro-Fenton catalysis, *Electrochim. Acta* 368 (2021) 137643.

UNIVERSITAT DE BARCELONA

Thank you for your attention

GOBIERNO DE ESPAÑA

MINISTERIO DE CIENCIA E INNOVACIÓN

AGENCIA ESTATAL DE INVESTIGACIÓN

Project PID 2019-109291RB-I00 (AEI, Spain)

国家留学基金管理委员会

CHINA SCHOLARSHIP COUNCIL