PhD Proposal 2025

School - Location: CentraleSupélec, Gif-sur-Yvette (10 miles from Paris)	
Laboratory: SPMS	Web site: https://spms.centralesupelec.fr/
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Title: Possible degradation pathways in per- and polyfluoroalkyl substances (PFAS) using the piezo-photocatalysis process : a theoretical study supported by experimental inputs

Scientific field (one among the list- remove other choices):
Engineering & Technology: Chemical engineering

Free Key words: : *ab initio* calculations, dissipative molecular dynamics, potential energy surface, polycarbonate, PFSA, classical molecular dynamics, ring polymer molecular dynamics, path integral molecular dynamics, piezo-photocatalysis
Remarks: Possible joint PhD (cotutelle) with the University of Texas at San Antonio, UTSA
Period: from now (for 3 years)

Details for the subject:

General context:

Per- and polyfluoroalkyl substances (PFAS) are around 5,000 synthetic chemical molecules with carbon chains of varying lengths and fluorine atoms with the most known PFOA ($C_8F_{15}O_2H$), PFOS ($C_8F_{17}SO_3H$) or PFBS ($C_3F_9SO_3H$). These molecules are used in a wide range of industries, including automotive, textiles, food packaging, non-stick pans, cosmetics and electronics [1]. PFAS are today omnipresent in the environment, where they are released throughout their life cycle, from production to the destruction of products containing them [2]. Resistant to many forms of degradation, PFAS are highly persistent in the environment (from a few decades to several centuries), hence their nickname of "eternal pollutants" [3]. Recently, in SPMS laboratory at CentraleSupélec, University of Paris-Saclay, we developed a new and advanced oxidation process that is piezo-photocatalysis using laboratory-designed oxide nanoparticles [4,5] which are capable to efficiently degrade many antibiotics or endocrine disruptors including PFAS molecules. This piezo-photocatalysis technique exploits mechanical and light energy to activate the piezo-photocatalysts, yielding to the oxidation and hydrolysis of pollutant molecules like PFAS. For instance, light irradiation induces electrons in the valence band to move to the conduction band, generating photo-induced electron and hole pairs. These electron-hole pairs react then with available oxygen, water, and hydroxyl groups, leading to the formation of reactive oxygen species, namely ROS, such as hydroxyl radicals ($\dot{\mathrm{O}}\mathrm{H}$) and superoxide radical anions ($\dot{\mathrm{O}}_2^-$). These reactive species attack and degrade, in their turn, pollutant molecules, tackling thus the challenge of persistent pollutants.

While our preliminary experimental results on piezo-photodegradation of PFAS using our nanoparticles are promising, still computational modeling are crucial in understanding the complex mechanisms that govern piezo-, photocatalysis, a prerequisite for the strategic design and engineering of effective semiconductor piezophotocatalyst systems.

Description of the work:

This project aims therefore to investigate the oxidation of PFAS pollutants under different species such as $\dot{O}H$, or $\dot{O}_2^-$ and its possible degradation pathways in order to bring a deeper understand on the mechanisms involved and to identify the intermediates to improve the piezo-photocatalysts, employed at SPMS. Theoretical studies will be conducted during this PhD work using different techniques that would provide a more realistic description of piezo-photocatalysis process of PFAS. The obtained results will be compared to experiments carried out at SPMS. To meet the challenge of simulating catalysis of pollutant molecules such as PFAS, multiscale modeling based on sophisticated computational techniques will provide a solution by combining the results at different scales. On the atomistic level, methods such as Coupled cluster (CCSD(T)) or Density Functional Theory (DFT) provide fundamental parameters, such as geometries, reaction barriers, bond dissociation energies and reaction kinetics or overpotentials, including excited states involved in the piezo-photocatalytic process. This approach combined to Molecular Dynamics (MD) methods will be then used to describe the emerging chemical environment and reconstruction of nanocatalysts while Coarse-grained approaches for mesoscale modeling provide the dynamics of reactions and allow for identifying rate-limiting reactions. See for example this review [6].

The PhD candidate will join a dynamic and world recognized team on both modelling and experiments. The PhD work will be also carried out in close collaboration with the US theoretical group of Prof. Abelardothe Ramirez-Hernandez at the University of Texas at San Antonio, UTSA. exchange and long term stay in the US institution is planned during the PhD.

References:

[1] Anses "PFAS : des substances chimiques dans le collimateur". 12 mai 2022. https://www.anses.fr/fr/content/pfas-des-substances-chimiques-dans-le-collimateur

[2]https://www.lemonde.fr/les-decodeurs/article/2023/02/23/polluants-eternels-explorez-la-carte-d-europe-de-la-contamination-par-les-pfas_6162942_4355770.html

[3] Sinclair, G.M., Long, S.M., Jones, O.A.H., 2020. What are the effects of PFAS exposure at environmentally relevant concentrations? Chemosphere 258, 127340

[4]W. Amdouni, M. Fricaudet, M. Otoničar, V. Garcia, S. Fusil, J. Kreisel, H. Maghraoui-Meherzi, B. Dkhil, $BiFeO_3$ Nanoparticles: The "Holy-Grail" of Piezo-Photocatalysts?. *Adv. Mater.* 2023, 35, 2301841

[5] W. Amdouni, M. Otoničar, D. Alamarguy, E. Erdem, P. Gemeiner, F. Mazaleyrat, H. Maghraoui-Meherzi, J. Kreisel, S. Glinsek, B. Dkhil , Enhancement of the Piezocatalytic Response of La-Doped $BiFeO_3$ Nanoparticles by Defects Synergy. *Small* 2024, 20, 2406425

[6] Bipasa, S.; et al. Chem. Soc. Rev., 2022,51, 3794-3818.