Photocatalytic materials for advanced biofuels production

Supervisor: Paolo Fornasiero
Co-Supervisor: Michele Melchionna
email: pfornasiero@units.it

The increasing energy demand and the depletion of fossil-fuel reserves, threatening our energy security and the environment, have aroused intense global concern. To mitigate this, the EU aims to become climate-neutral by 2050, by targeting at the next-generation of biofuels from non-land and non-food competing crop wastes. Butanol (BuOH) and hydrogen (H_2), if produced from bio-ethanol, are among the most promising advanced biofuels due to their high energy content, long shelf-life and, in case of BuOH, compatibility with the current engines and fuel distribution infrastructure. However, their production faces challenges due to the low yields and selectivities, even when noble-metal catalysts and harsh reaction conditions are employed. In the framework of the Horizon project GlaS-A-Fuels we envision a holistic approach to transform bio-ethanol to bio-BuOH and to green-H_2 employing recyclable and cooperative single-atom catalysts from earth-abundant elements. The group has already demonstrated the criticality of the single atomic nature of transition metals in heterogeneous catalysis.[1,2] In addition, while the individual contribution of the supported metal to the overall activity of supported photocatalysts has been identified, the joint activity of mixed metal species is overlooked because of their different photoelectric properties. Therefore, we recently demonstrated that atomically dispersed Pd (Pd_1) and Pd clusters and loaded onto CdS, can serve as oxidation and reduction sites for methanol dehydrogenation. The Pd_1 substitutes Cd^{2+}, forming hole-trapping states for methanol oxidation and assisting the dispersion of photodeposited Pd clusters.[3] Moreover, engineering of the photoresponsive support (e.g. a semiconductor) is a fundamental demand, because it can affect catalytic activity and selectivity by means of appropriate band matching or affinity with the reagent, as demostrated for graphitic carbon nitride (g-CN) photocatalysts,[4,5] or tailored TiO_2 brookite active in alchol photooxidation.[6] Hence, the dual metal-atom/support cooperativity and stabilization of difficult to achieve reaction intermediates obtained via engineering the coordination sphere and the electronic structure of the catalysts will be a primary objective. [6] To realize this, the concerted effort of five EU partners will integrate key expertise in materials science for solar and thermal energy harvesting, catalysis, laser technologies for tuning light-matter interactions, intelligent process-control systems and advanced theoretical and experimental tools for catalyst function and process understanding. The PhD candidate will therefore have the opportunity to work at the very frontier of material science for catalysis, acquiring knowledge in modern synthesis of materials, advanced characterization and catalysis for sustainability.

References:

1. "Light-Induced Defect Formation and Pt Single Atoms Synergistically Boost Photocatalytic H2 Production in 2D TiO2-Bronze Nanosheet" ACS Sustainable Chem. Eng. 2022, 10, 17286-17296.
2. “Mixed-Valence Single-Atom Catalyst Derived from Functionalized Graphene” Adv. Mater. 2019, 31, 1900323.
3. "Photocatalytic methanol dehydrogenation promoted synergistically by atomically dispersed Pd and clustered Pd.", J. Am. Chem. Soc. 2024, 146, 24440-24449”
4. “Light-driven, heterogeneous organocatalysts for C-C-bond formation towards valuable perfluoroalkylated intermediates” Science Adv. 2020, 6, eabc9923
5. “Carbon vacancies steer the activity in dual Ni carbon nitride photocatalysis” Adv. Sci. 2023, 10, 2303781
6. "Defect engineering over anisotropic brookite toward substrate-specific photo-oxidation of alcohols" Chem Catal., 2022, 2, 1177-1190.