Artificial Photosynthesis: The Role of Photocatalysis in the Energy Transition

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Abstract

Artificial photo-synthetic approaches are gaining spreading interest in order to exploit solar light for the production of fuels. Different applications are proposed, among which the most explored are the production of H_2 and the reduction of CO_2 and, much more recently, attention is also paid to the photosynthesis of ammonia. Despite the enormous progresses in the field of materials development and characterization, which allowed to understand the main phenomena driving photo-catalysed up-hill reactions, the productivities achieved still do not justify the scale up of the processes to relevant scales and efficiencies are still very low, calculated over natural irradiance, in most cases much lower than 1%.

In this work we focus on a multiscale approach to improve the conversion and productivities, with special reference to the photoreduction of CO_2, developing a coupled approach to optimize materials, condizions and irradiance. On the materials scale, TiO_2 has been extensively used as photocatalyst, being an inexpensive and non-toxic semiconductor, with manufacturing at industrial scale and recyclability options, but it is absorbing UV radiation, only, ca. 5% of sunlight. Furthermore, photogenerated electrons and holes must survive enough to migrate to the photocatalyst surface and react with the adsorbed species, but unfortunately the charge recombination rate in titania is quite fast. The metal-free polymeric catalyst, graphitic carbon nitride (g-C_3N_4) is a relatively novel material, characterized by wider absorbance in the visible region. Its junction with a second semiconductor or with metals can also improve the lifetime of the photogenerated charges.

From the process conditions side, we developed and innovative photoreactor operating at high pressure, up to 20 bar, which is unprecedented in photocatalytic applications, where transparent windows are needed. This allows to boost the solubility of CO_2 in water when operating the reactor as tri-phase liquid/gas/solid device, and improves the surface adsorption over the catalyst. The best productivity for HCOOH so far achieved with this system at 18 bar, pH = 14 and by using Na_2SO_3 as hole scavenger was ca. 1.4 g/h g_{cat}, orders of magnitude higher than literature values.

Finally, the coupling with concentrating solar devices as a follow up of this study will make available a higher irradiance, further boosting the productivity.