

Photoassisted CO₂ conversion

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The current energy sources, in which more than 80 % of the energy needs are covered by fossil fuels, is not sustainable. In addition, the combustion of enormous amounts of hydrocarbons has originated important environmental problems derived from the increase in the atmospheric concentration of greenhouse gases. A change in the energy sources is currently taking place shifting to renewable energies, the direct use of solar light being one of the primary sources.

Moving toward this revolutionary change, there will be a transitory period in which windmills and photovoltaics will contribute in increasing percentage together fossil fuels combustion to cover the energy needs. In this transition from conventional power stations to the exclusive use of renewable electricity, there will be a large incentive for using CO₂ as feedstock for the production of fuels. Our group has been studying various possibilities including the direct CO₂ splitting using deep UV light,[1] the photoassisted methanation of CO₂ [2] and the photocatalytic reduction of CO₂ by H₂O [3]. The presentation will comment the advantages and disadvantages of these three types of processes and probable scenarios in which they could be of interest and doable. The emphasis in the presentation will be the description of the materials (“*photocatalysts*”) that exhibit activity for these transformations, the efficiency of the processes, particularly in the photocatalytic CO₂ reduction by H₂O and the understanding of the photocatalytic mechanism.

For these processes a series of different materials that are able to produce CO₂ conversion will be commented. Among them, one of the most efficient is TiO₂ modified by Au-Cu alloy nanoparticles. It will be discussed that the presence of Au NPs introduce visible light photoresponse upon excitation in the plasmon band (λ_{\max} 560 nm) that serves to overcome one of the major limitations of TiO₂ as photocatalyst that is its lack of photoresponse under visible light excitation. The available data suggest that the role of Cu is to drive the selectivity of the process from H₂O reduction to CO₂ reduction and transient absorption spectroscopy shows direct evidence of the quenching of charge separation by CO₂ when Cu is present in the TiO₂ photocatalyst. In this way, CH₄ production rates under concentrated simulated solar light as high as 2000 $\mu\text{mol}\times\text{h}^{-1}\times\text{g}^{-1}$ have been achieved using thin Au-Cu/TiO₂ beds as photocatalyst. Other materials that will be commented include metal nanoparticles supported on graphenes and metal organic frameworks (Figure 1).

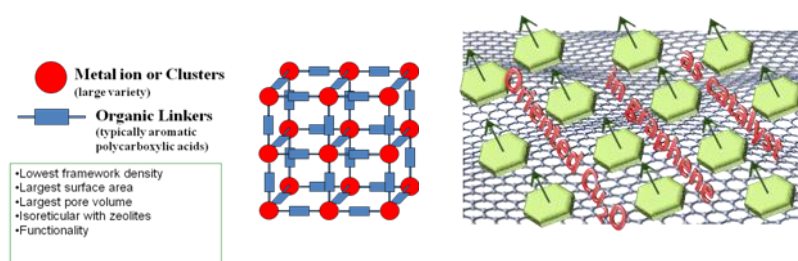


Figure 1. Pictorial illustration of the structure of metal organic frameworks (left) and Cu₂O nanoparticles on graphene (right). These two materials have shown photocatalytic activity for CO₂ reduction,

Besides artificial photosynthesis, photoassisted methanation of CO₂ by H₂ is a process at moderate temperatures below 250 °C is a process that can occur at high reaction rates using Cu and Ni based catalysts. The photoassisted methanation can occur with unusually high apparent quantum efficiencies of about 11 % and give an opportunity to develop continuous

flow reactions in where light exposure times are shorter than seconds. Kinetic data and the use of quenchers support that the reaction mechanism can involve charge separation and that the direct single-electron reduction of CO₂ by electrons can occur. In fact, the CO₂ reduction rate in the methanation in the presence of various photocatalysts follows a linear relationship with the oxidation potential of sacrificial electron donors.

Acknowledgements

Financial support by Spanish Ministry of Economy and Competitiveness (Severo Ochoa) and Generalitat Valenciana (Prometeo 2013-014) is gratefully acknowledged.

References.

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