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### Hybrid multifunctional materials for CO<sub>2</sub> photoreduction by Artificial Photosynthesis

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An interesting route for the valorization of CO<sub>2</sub> and H<sub>2</sub> production consists on its photocatalytic conversion into fuels and/or chemicals in the presence of water and suited photocatalysts [1]; this process is also known as Artificial Photosynthesis (AP). This is a quite challenging process since CO<sub>2</sub> and H<sub>2</sub>O are highly stable compound and their transformation involves a series of multi-electron reactions in combination with light management. In this sense, extensive efforts have been made to develop efficient catalytic systems capable of harvesting light absorption and reducing CO<sub>2</sub> to valuable products especially when using water as the electron donor. However, this process suffers from very low quantum yields and non-selective product distributions, due to the complexity of the involved multi-step reactions.

The design of efficient photocatalysts aims at achieving an expanded light absorption and a better charge separation to improve the overall photocatalytic performance. [1-3].

Herein, we report different strategies and modifications photocatalysts to increase process performance. Among them, an interesting approach to improve charge separation in photocatalytic systems is the use of heterojunctions.

#### Results and conclusions

In order to clarify the effect of different parallel and competitive reactions in the activity and products distribution, a series of photocatalytic experiments were performed varying the feeding flow. For the AP experiments using bare TiO<sub>2</sub>, the main products were CO and H<sub>2</sub>, with low concentrations of CH<sub>4</sub> and CH<sub>3</sub>OH. The use of different spectroscopies reveals that the CO<sub>2</sub> reduction mechanism is related to the formation of carbonate/bicarbonate species.

On the other hand, the introduction of SP NPs as co-catalyst leads to changes in the conversion and enhanced selectivity to higher demand electron products, such as CH<sub>4</sub>, while the CO and H<sub>2</sub> concentrations decrease [4].

In the case of organo-inorganic hybrid materials, Hybrid material also show a dramatically reactivity improvement in CO<sub>2</sub> photoreduction. The variation of the proportion of polymer reveals that a maximum of efficiency obtained with IEP-1@T-10. Hybrid material also has a great influence in the selectivity enhancing the relative production of methane vs. carbon monoxide, and largely promoting selectivity towards hydrogen.

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