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Enhancement of the photoactivity for CO_2 photoreduction by semiconductor heterojunctions

P. Reñones,[a] F. Fresno,[a] J. L. G. Fierro,[b] V. A. de la Peña O´Shea[a,*]
[a]*Photoactivated Processes Unit, IMDEA Energy, Madrid (Spain)*
[b]*Group of Sustainable Energy and Chemistry, Institute of Catalysis and Petrochemistry (ICP-CSIC), Madrid (Spain)*
** victor.delapenya@imdea.org*

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A strategy for CO_2 valorisation is represented by Artificial Photosynthesis processes, to produce fuels and value-added chemicals, using water as reducing agent. This process is mainly based on the use of semiconductor catalysts, and is particularly advantageous considering that reactions can be driven under mild conditions and using the Sun as sustainable energy source[1]. Currently, in order to improve the overall photocatalytic performance, different synthetic strategies or modifications have been developed[2,3]. Herein, we report the use of semiconductor heterojunctions with the purpose of increasing the activity in the CO_2 photoreduction.

Several semiconductor oxide heterojunction were synthetized using TiO_2 (anatase) as main photocatalyst mixed with different charges of La_2O_3 and In_2O_3. To gain a better understanding of the structure and behavior of the catalysts, they have been analysed with several structural textural, morphological and optoelectronic techniques. UV Gas-phase CO_2 photoreduction experiments were conducted in continuous-flow mode during 15h.

The activity tests of the La_2O_3/TiO_2 catalysts show that the main products of the reaction are in all cases CO and CH_4, together with H_2 from the parallel reduction of water. With La contents up to 5 wt% improved the activity respect to TiO_2. However, when higher amounts of La_2O_3 (10 and 15 %) is used, the agglomeration of the lanthanum particles occurs and in consequence the activity decrease.

The heterojunctions between In_2O_3 and TiO_2 lead to an increase in the activity respect to bare TiO_2 in the CO_2 photoreduction reaction, although the selectivity is similar with only an increase in methane production (Figure 1). The crystal size of these commercial In_2O_3 particles is 80 nm as observed by XRD. In order to decrease this crystal size, In_2O_3 was prepared in the laboratory (named as In_2O_3p) which led to a crystal size of 13 nm. Activity tests with this new heterojunctions resulted in a change in the selectivity towards CH_4, Figure 1.

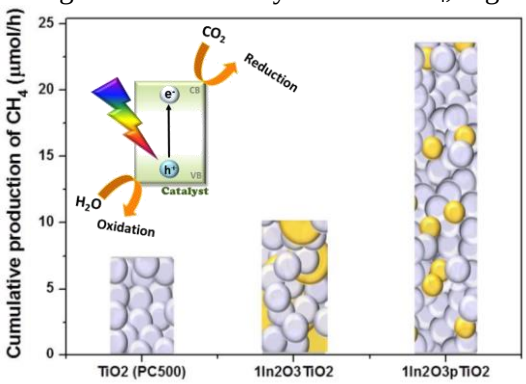

Figure 1. Cumulative production of CH_4 for TiO_2, $1In_2O_3/TiO_2$ and $1In_2O_3p/TiO_2$ catalysts.

The studies of characterization showed that the enhancement in the activity is related to a retarded electron–hole recombination and improved charge transport and transfer as observed by fluorescence spectroscopy, as well as to a better adsorption of CO_2, depending on the case.

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