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Insights in the CO₂ photo-activation over Titania-Based Photocatalysts for Artificial Photosynthesis

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The development of CO₂ valorisation strategies has become a crucial issue and represents a priority for the European Union, which is actively promoting international agreements to control climate change and different programmes for CO₂ conversion. Currently, less than 1% of the total anthropogenic CO₂ emissions (31.2 Gt/y) are recycled into chemicals or used in industrial applications. One of the most promising strategies is the photocatalytic reduction of CO₂ to produce fuels and chemicals by using sunlight as a sustainable energy source (Artificial Photosynthesis, AP). The main drawback arises from the fact that the CO₂ molecule is highly stable, which makes very difficult its activation[1].

This work focuses on the study of the gas phase CO₂ photoreduction with water using TiO₂-based catalysts. Coupling of TiO₂ semiconductor with plasmonic noble metal nanoparticles was studied as a pathway to retard the recombination processes and improve the photocatalytic performance in AP process.

Catalysts were fully characterized by XRD, ICP, BET, TGA, SEM, TEM, Raman. Further, in-situ synchrotron-based spectroscopy techniques were performed in ALBA NAP endstation (CIRCE) to get a better understanding of the CO₂ photoreduction mechanism. Photocatalytic activity was tested in a continuous-flow gas phase reactor under UV illumination.

Photocatalytic experiments in combination with in-situ spectroscopy studies revealed the influence of surface-adsorbed carbon species in the CO₂ reduction mechanism. These studies showed the activation of CO₂ molecules under UV illumination to obtain CH₃OH and CO. Moreover, these measurements confirmed that the photoreduction mechanism occurs via carbonate/bicarbonate intermediates. The exposure to CO₂ + H₂O leads to the formation of CO₃²⁻ and CO₂⁻ species. When the sample is irradiated with UV light, new peaks appeared in the O1s and C1s spectra, which are assigned to CH₃OH and gas-phase CO, respectively. On the other hand, the introduction of noble metal NPs significantly changed the selectivity of the process, yielding more reduced products, such as CH₄. These observations, which were confirmed by spectroscopy studies (including NAP experiments), suggested an enhancement of the charge separation processes due to the electron scavenging ability of the plasmonic metal NPs[2-3].

References

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