DEVELOPMENT OF 2D-2D HETEROSTRUCTURES OF MOF DERIVED Co_3O_4 NANOSHEETS AND g-C_3N_4 FOR CO_2 PHOTOREDUCTION

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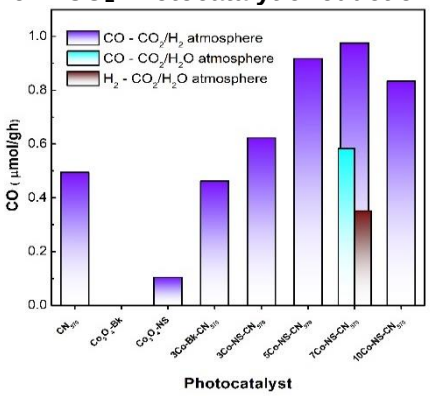
ABSTRACT:

Climate change and energy crisis are imposing the utilization of clean and renewable energy systems [1]. Solar fuels produced via photocatalytic pathways are a promising alternative to fossil fuels. In this direction, the development of appropriate, non-toxic and cost-effective materials that can be used as photocatalysts is highly important.
Herein, we present the case of carbon nitride functionalized with Co_3O_4 of different morphologies (nanosheets (NS) and bulk (Bk)). CN has been synthesized by melamine poly-condensation and was post-modified by a facile thermal treatment at different temperatures. For the development of the heterostructures, MOFs (ZIF-67 and modified-ZIF-67) are used as templates for Co_3O_4, and they are combined in different percentages with the pre-formed CN. Oxides are developed in situ on the surface of CN after calcination. The utilization of MOFs allows the control of Co_3O_4morphology.
The Individual materials and the composites are characterized for their structural, optical and electronic properties. Specifically, SEM and TEM verified that the morphology of Co_3O_4 may be controlled (Bk vs. NS) by the MOF structure used as precursor. Concerning the optical properties, CN samples exhibit an absorbance onset at ca. 450 nm, while all composites present light absorption in the whole visible region, attributed to the Co_3O_4. Surface area analysis shows that the thermal exfoliation and the presence of Co_3O_4 ameliorate the available total area. XPS characterization showed that Co_3O_4-NS possesses more abundant oxygen vacancies in comparison with Co_3O_4-Bk.According to EPR and photocurrent results, it is suggested that formation of photo-generated electrons is enhanced in the case of the 2D-2D heterostructure.
Concerning their photocatalytic performance, all composites show higher activity than their individual counterparts (Fig. 1). Noteworthy, the composites bearing Co_3O_4-Bk presented lower activity than the 2D-2D heterostructures. Supplementary experiments of CO_2 photoreduction, with H_2O as the reducing agent, were carried out for the most active photocatalyst, showing good selectivity towards CO formation over H_2.

Figure 1: CO_2 Photocatalytic reduction results



References

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