High Entropy Perovskite Oxides and graphitic carbon nitride hybrid heterojunction for Solar Fuel Production

Clarissa Coccia[a]
Costanza Tedesco[a], Luca Betti[a], Lorenzo Malavasi[a]
[a]*University of Pavia, Via Taramelli 12, Pavia, Italy*
clarissa.coccia01@universitadipavia.it

The search for new environmentally friendly catalyst for green solar fuels production is becoming a priority. Significant efforts have been addressed to modelling novel and advanced nanocomposite materials for solar fuels production. In this respect, photoactive heterojunctions based on graphitic carbon nitride (g-C_3N_4), a versatile organic polymeric semiconductor, are promising system for the photocatalytic hydrogen and ammonia evolution, two of the most important solar fuels. g-C_3N_4 presents competitive photocatalytic properties but despite its potential, operational limitations such as fast charge carrier recombination, low surface area, and poor absorption coefficient limited its extensive application.[1] A thermal oxidation in air of the g-C_3N_4 bulk phase allows to strongly increase the surface area through an exfoliation of the graphitic sheets and a suitable cocatalyst is required for the optimization of the charge carrier dynamics.[2] In the past years, there has been significant progress in the realization of hybrid heterojunction based on metal-oxides catalyst, thanks to their extremely high carrier density (modified-TiO_2, MoS, CdS) and photoactive organic semiconductor (i.e. g-C_3N_4).[3] This study focuses on the preparation and characterization of heterojunctions based on g-C_3N_4 nanosheets and nanosized High Entropy Perovskite Oxides (HEPOs). This system is suitable for running both photocatalytic reactions, namely hydrogen evolution reaction (HER) from water splitting and ammonia evolution reaction through nitrogen photo-fixation. HEPOs are a novel class of compounds with general formula ABO_3 highly tuneable in their physical-chemical properties by chemical engineering on the A- and B-sites. In this work we investigated a series of $LaFeO_3$ catalysts-based by varying elements in A-site (Ca^{2+}, Sr^{2+}, Mg^{2+}) and B-site (Mn^{3+}, Fe^{3+}, Co^{3+},Zn^{3+}). The selection of the best candidates for the target reactions has been provided by a chemometric approach, starting with the compositions that showed the highest oxygen non-stoichiometry, since these types of defects are potential active sites for redox reaction.[4] Some of the main preliminary results suggest that O-vacancy presents in HEPOs plays a key role as well as the high carrier density influences the charge carrier dynamics of the photocatalyst system for the solar fuels evolution reactions

References

[1] S. J. Mun and S. J. Park, *Catalysts*, vol. 9, no. 10. MDPI, Oct. 01, 2019. doi: 10.3390/catal9100805.
[2] A. Pisanu *et al.*, *Dalton Transactions*, vol. 47, no. 19, pp. 6772–6778, 2018, doi: 10.1039/c8dt00276b
[3] K. Afroz, M. Moniruddin, N. Bakranov, S. Kudaibergenov, and N. Nuraje, *Journal of Materials Chemistry A*, vol. 6, no. 44. Royal Society of Chemistry, pp. 21696–21718, 2018. doi: 10.1039/c8ta04165b.
[4] L. Angelo Betti, L. Rita Magnaghi, A. Bosetti, R. Biesuz, L. Malavasi, and E. SpA, J. Mater. Chem. C 12, 7695–7706 (2024).