

ABSTRACT:

Engineering Nanostructured Photocatalysts for Hydrogen Production from Biomass-Derived Molecules and Waste Streams

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Photocatalytic hydrogen production from aqueous solutions containing organic compounds represents a promising strategy for coupling clean energy generation with wastewater remediation, in line with the principles of the circular economy. Recent advances in this field focus on the development of innovative photocatalysts and process intensification techniques aimed at improving efficiency, catalyst stability, and sustainability.

A first approach involves the effective immobilization of TiO₂ on lightweight, reusable polystyrene pellets. In this configuration, TiO₂ acts as the active phase, enabling hydrogen evolution under reducing conditions and promoting the degradation of organic pollutants under oxidative conditions. This dual functionality allows the same catalyst to be employed in sequential processes for both energy recovery and pollutant removal. When applied to real olive mill wastewater, the system achieved hydrogen production up to 16,954 μmol L⁻¹ while maintaining catalyst stability over at least ten reuse cycles.

A second strategy is based on the preparation of graphitic carbon nitride (g-C₃N₄) through a supercritical antisolvent (SAS) treatment of urea prior to calcination. The SAS process generated well-defined and separated elongated structures, improving the morphological and optical properties of the resulting photocatalyst. Under UV irradiation in aqueous glycerol solutions, the SAS-treated g-C₃N₄ exhibited significantly enhanced photocatalytic activity compared with the untreated material, reaching hydrogen production of 8,752 μmol L⁻¹ after 240 min, more than twice the value obtained with the non-treated catalyst. The optimal catalyst loading was identified as 1 g L⁻¹, while a glycerol concentration of 5 wt% provided the highest hydrogen evolution rate. Isotopic experiments performed in deuterated water demonstrated that water acts as the primary proton source for hydrogen generation, whereas glycerol mainly serves as a sacrificial agent and electron donor.

A third approach explores the integration of photocatalysis and non-thermal plasma technologies. Ag/TiO₂ photocatalysts were synthesized using an atmospheric-pressure plasma jet, enabling the deposition of silver nanoparticles without chemical reducing agents or high-temperature treatments. These materials were applied to photocatalytic hydrogen production from aqueous carbamazepine solutions under visible-light irradiation, while carbamazepine degradation was simultaneously enhanced

using a dielectric barrier discharge (DBD) plasma reactor. The Ag/TiO₂ catalysts exhibited improved photocatalytic performance compared with bare TiO₂, owing to enhanced charge separation and plasmonic effects. At the same time, reactive oxygen and nitrogen species generated by the plasma promoted carbamazepine degradation and mineralization, highlighting the potential of integrated photocatalysis–plasma systems for simultaneous renewable fuel production and wastewater treatment. These complementary strategies demonstrate how innovative catalyst design, supercritical-fluid processing, catalyst immobilization, and plasma-assisted technologies can significantly enhance photocatalytic hydrogen production while enabling the valorization and remediation of wastewater streams. Such approaches represent promising pathways toward sustainable and integrated chemical engineering solutions for energy and environmental applications.