

TiO₂-based photocatalysts for hydrogen production from lactic acid: a supercritical antisolvent approach

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The constantly rising energy demand and the depletion of non-renewable fossil fuels have highlighted the need for more sustainable energy alternatives. Hydrogen is widely considered a promising clean energy carrier, as its combustion does not produce greenhouse gas emissions. In recent years, hydrogen production technologies have significantly advanced, with photocatalytic water splitting emerging as a sustainable method for efficient hydrogen generation.

Due to the thermodynamic uphill nature of water splitting and the rapid reverse reaction, sacrificial agents are often introduced to increase electron availability for H⁺ reduction to H₂. Organic acids, which decompose into CO₂ during oxidation, can inhibit electron-hole recombination, thereby promoting H₂ production. This enables the use of renewable sources and the valorization of waste-derived materials. Among these, lactic acid is a particularly promising sacrificial agent due to its ease of oxidation - attributable to the hydroxyl group on the α -carbon next to the carbonyl - and its wide use in pharmaceutical, cosmetic, and food industries. Nevertheless, photocatalytic hydrogen production using lactic acid remains relatively underexplored.

Supercritical antisolvent (SAS) precipitation is a promising technique for photocatalyst synthesis, offering control over particle morphology and size, as well as complete removal of residual solvents that might interfere with photocatalytic activity.

This research focuses on photocatalytic hydrogen generation from an aqueous solution of lactic acid. The SAS process was used to micronize titanium oxide (IV) acetylacetonate, a precursor for TiO₂, reducing particle size. After calcination, the resulting photocatalyst was tested for hydrogen production. To enhance H₂ evolution, the TiO₂ was also doped with copper (2Cu-TiO₂ SAS).

Photocatalytic tests were carried out in a batch Pyrex cylindrical reactor irradiated by four lamps for up to 240 minutes. The system included a nitrogen distribution (N₂ flow rate= 0.250 NL min⁻¹), and gas-phase data were collected using an ABB analyzer connected to LabVIEW software for real-time H₂ and CO₂ monitoring. Various photocatalyst dosages were tested, and the role of water in hydrogen production was assessed. Photocatalyst reusability tests were also performed.

The performance of the SAS-produced photocatalyst was compared with that of a non-micronized counterpart, revealing that the first one enabled higher hydrogen production (4040 μ mol/L) compared to the non-micronized catalyst (3500 μ mol/L).

Keywords: *hydrogen production, photocatalysis, supercritical micronization.*