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Hydrogen Generation from Wastewater-Derived Organics via Solar Photocatalysis Using Low-Cost Cu-TiO_2 Composites

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Abstract

Recent research has focused on developing Cu-based TiO_2 photocatalysts for sustainable hydrogen production via solar photoreforming of organic compounds typically present in urban and industrial wastewater. Copper, either in solution or integrated into TiO_2, forms heterojunctions that enhance photocatalytic H_2 generation by improving visible light absorption and promoting charge carrier separation.
This study investigates hydrogen evolution from oxygenated organic compounds, such as alcohols and carboxylic acids, using Cu-modified TiO_2-P25 catalysts synthesized via a simple in situ photodeposition method. The incorporation of Cu nanoparticles significantly alters the optical properties of TiO_2, boosting its activity under solar irradiation. Experimental results demonstrate notably higher hydrogen production rates with Cu-TiO_2 compared to bare TiO_2-P25. For instance, glycerol yielded 5.5 μmol H_2/min with Cu-TiO_2, versus 2.1 μmol/min with unmodified TiO_2. However, no enhancement was observed with benzyl alcohol, 2-propanol, or acetic acid, suggesting that hydrogen evolution is substrate-specific and likely influenced by adsorption behavior and oxidation pathways. A mechanism has been proposed to explain these variations based on light absorption and charge transfer dynamics.

Keywords: Photocatalysis; Hydrogen production; Wastewater treatment; TiO_2; Copper.

1. Introduction

Hydrogen generation via solar photocatalysis represents a sustainable and environmentally friendly approach for addressing energy demands, particularly when combined with wastewater treatment [1,2]. Among the materials explored, Cu-based TiO_2 composites have gained attention due to their low cost and effectiveness in promoting hydrogen production through the photoreforming of organic compounds typically found in urban and industrial wastewater streams [3]. These compounds, including alcohols and carboxylic acids, serve as sacrificial agents, offering a dual benefit of simultaneous pollutant removal and clean energy production.

Cu-modified TiO_2 photocatalysts exhibit enhanced performance due to the formation of a heterojunction structure that extends light absorption into the visible spectrum and improves charge carrier separation. The use of copper in various forms, either in solution or supported on TiO_2, has been extensively studied for its influence on the optical and photocatalytic properties of the material. In this study, Cu-modified TiO_2-P25 photocatalysts were synthesized via a simple photodeposition method. This process led to significant changes in the optical properties of the catalysts, significantly altering the material's light absorption profile and enhancing its photocatalytic activity.

2. Results

Photocatalysts were thoroughly characterized before and after use, employing a suite of techniques including XRD, DLS, TG, EDX, FT-IR, DRUV, PL, HR-TEM, and FE-SEM. These analyses helped correlate catalyst morphology, composition, and structure with photocatalytic activity. DRUV spectra showed increased absorption in the 520–580 nm range, indicative of local surface plasmon resonance (LSPR) from copper nanoparticles. This effect enhances visible light absorption and reduces recombination, improving charge carrier lifetimes [4].
Experimental data confirmed that upon photodeposition of Cu species, a rapid increase in H_2 production was observed. The photoreforming of glycerol yielded 5.5 μmol H_2/min with Cu-TiO_2, versus 2.1 μmol/min with unmodified TiO_2 (Figure 1). The activity plateaued over time, with no additional overshoot upon restarting the light source, suggesting a stable, light-driven catalyst transformation early in reaction. The system's optical behavior also shifted, with solution color changing from white to purple, signaling ongoing Cu deposition [5]. The presence of metallic Cu nanoparticles (~5 nm), confirmed via EPR, Raman, and XRD, contributed to enhanced activity by forming Schottky barriers at the Cu/TiO_2 interface. These barriers facilitate electron transfer to the metal, enabling proton reduction while suppressing electron-hole recombination.
The role of TiO_2 crystallographic phases was assessed using various commercial photocatalysts. P25-TiO_2,

composed of anatase (80%) and rutile (20%), outperformed pure anatase or rutile due to synergistic effects at the anatase-rutile interface. This homojunction improves charge separation, as supported by photoluminescence analysis.

Photocatalytic tests using methanol, glycerol, ethanol, formic acid, and other oxygenated organics demonstrated that H_2 production is highly dependent on the substrate's molecular structure. Small, multifunctional molecules like glycerol and glucose showed higher hydrogen yields due to stronger adsorption on the photocatalyst surface, enhanced by multiple hydroxyl groups. In contrast, bulky or single-OH compounds like isopropanol and benzyl alcohol exhibited weaker interactions and lower H_2 generation rates.

Reaction mechanisms were proposed based on adsorption strength. Strongly adsorbed species (i.e., glycerol, glucose, methanol, formic acid) interact directly with surface-bound positive holes, while weakly adsorbed species (i.e., benzyl alcohol, 2-propanol, or acetic acid) primarily undergo oxidation via hydroxyl radicals in solution. These radicals, however, can also participate in recombination reactions, lowering efficiency.

Temperature also played a role in performance. Higher temperatures, such as those occurring naturally in solar reactors, improved hydrogen generation. This enhancement may relate to the activation energy required for photoreactions, although further investigation is needed.

The presence of chloride ions, particularly when using formic acid as a sacrificial agent, was found to influence the system's efficiency, potentially through competitive adsorption or catalyst surface modification.

A detailed mathematical model was developed to simulate H_2 production under various conditions using methanol or glycerol as substrates. The models help optimize operating parameters and predict performance trends [5].

Overall, this work highlights the promising potential of Cu-TiO_2 photocatalysts for sustainable hydrogen generation via wastewater photoreforming. The integration of material design, reaction engineering, and detailed mechanistic understanding paves the way for scalable, cost-effective solar hydrogen production technologies.

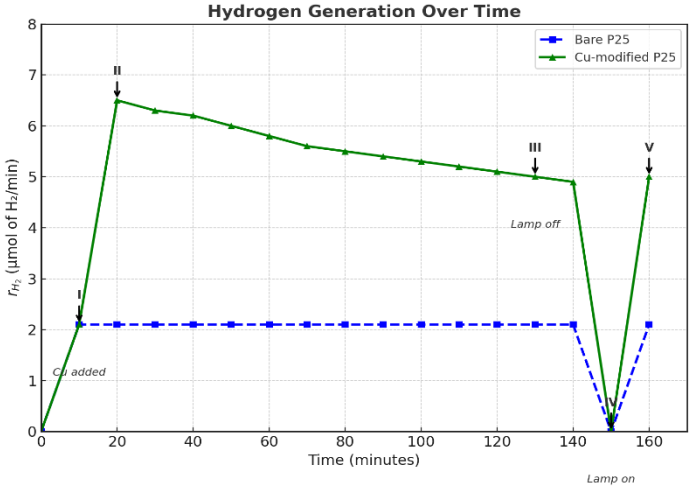

Figure 1. H_2 produciton rates over bare P25 TiO_2 and Cu-modified P25 TiO_2 photocatalysts.

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