"Enhancing visible-light photocatalytic hydrogen evolution with sub-5 nm Fe-doped CeO_2 nanocrystals in confined spaces"

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Significance and Relevance

This study demonstrates the effectiveness of the reverse micelle (RM) method for synthesizing sub-5 nm Fe-doped CeO_2 nanocrystals, enhancing visible-light photocatalytic hydrogen production from methanol solutions. The superior performance of RM-synthesized catalysts over conventionally prepared ones is confirmed through comprehensive characterization. Compared to literature reports on ceria-based catalysts, our Fe (2.5 mol%)-doped CeO_2 nanocrystals exhibit significantly higher normalized photocatalytic hydrogen evolution rates, despite the absence of noble metals and high-temperature calcination. Moreover, Fe-doped CeO_2 prepared by the RM method was stable for six reuse cycles.

Preferred and 2nd choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors, Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

The efficiency and feasibility of photocatalytic water splitting hinge on the properties of the photocatalyst and the use of sacrificial agents[1]. With its unique electronic structure, high oxygen storage capacity, and excellent stability, ceria has emerged as a promising photocatalyst. However, there's a pressing need to tailor semiconductor-based materials to optimize the photocatalytic process and extend its activation to visible light[2].

In this scenario, the synthesis route is crucial in influencing nanocatalyst properties and defect engineering[3]. We developed a versatile and reliable one-pot reverse micelle process to address this challenge. This approach confines reactions within reverse micelles, allowing for precise control over the nucleation and growth of nanoparticles. Unlike traditional co-precipitation, this method enables the synthesis of monodisperse, nanometer-sized particles with tailored properties.

Materials and Methods

All syntheses were performed under mild conditions without the need for specialized equipment.

In a typical synthesis, Brij C10 surfactant was dissolved in cyclohexane at room temperature under stirring. A 0.5 M aqueous solution containing cerium and iron salts was slowly added dropwise to the oil phase to form water-in-oil (w/o) micelles.

An ammonia solution was then slowly added dropwise, and the mixture was stirred for 1.5 hours at room temperature. The resulting solid was filtered, washed, dried, and calcined at 120 °C for 6 hours. The amounts of cerium and iron were calculated to obtain a nominal composition expressed as a molar

% of iron equal to 0, 1, 1.5 and 2.5 and 5 mol%. CeO_2 and Fe (2.5 mol%)-CeO_2 catalysts were also prepared by conventional precipitation

Results and Discussion

X-ray diffraction initially revealed a clear distinction between samples prepared using reverse micelles and those obtained through conventional precipitation. The displacement of diffraction peaks to higher Bragg angles, as observed for RM catalysts, is indicative of a contraction of the crystal lattice. This provides compelling evidence for the successful isomorphic doping of CeO_2 with iron ions, wherein iron ions substitute for cerium ions within the lattice structure. In addition, XRD and TEM analyses confirmed the formation of ultra-small (~4 nm) photocatalyst nanocrystals within the confined space of reverse micelles. The RM system uniquely enhanced optical properties by facilitating the incorporation of large quantities of heteroatoms, thereby tuning the band gap with iron content, extending exciton lifetimes, and modulating Ce^{3+} and Vo defect concentrations, as evidenced by Raman, UV-Vis, and photoluminescence spectroscopies. Moreover, RM synthesis yielded significantly higher surface areas compared to conventional methods.

Photocatalytic hydrogen production reached a maximum of 7566 μmol L^{-1} for RM samples with 2.5 mol% iron doping in the CeO_2 lattice, indicating this as the optimal doping level for this synthesis method, Figure 1. Fe (2.5 mol %) CeO_2 photocatalyst exhibited excellent stability, maintaining consistent photocatalytic hydrogen production over six reuse cycles. A proposed visible-light-driven photocatalytic mechanism for hydrogen evolution from methanol aqueous solution was supported by D_2O experiments and band alignment considerations. The mechanism involves the reduction of H^+ by conduction band electrons and the oxidation of methanol by valence band holes

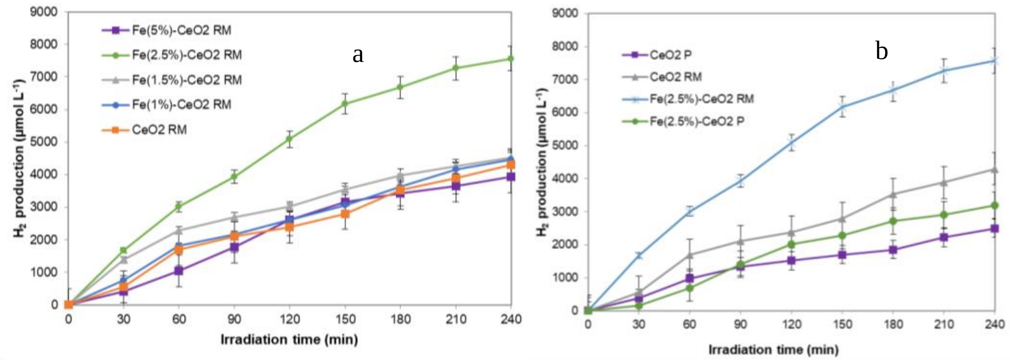

Figure 1 Hydrogen evolution under visible light for a) CeO_2 and Fe-CeO_2 photocatalysts prepared by reverse micelle (RM) and b) CeO_2 and Fe-CeO2 photocatalysts prepared by conventional precipitation (P).

References

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