

# Photoreforming of Glycerol for H<sub>2</sub> Production Using Au-Ni Catalysts Supported on CeO<sub>2</sub>

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### Significance and Relevance

The photoreforming of glycerol for hydrogen production offers a sustainable and environmental friendly alternative to the conventional hydrogen generation methods. This process converts glycerol, a renewable by-product of biodiesel production, and water in clean hydrogen fuel <sup>1,2</sup> using solar energy and suitable photocatalysts.

The approach aligns with global energy demands and environmental goals, providing an efficient use of renewable resources.

In this work, the use of Au-Ni photocatalysts supported on  $CeO_2$  enhances the efficiency of hydrogen production addressing also the critical need for cost-effective, stable, and high-performance photocatalysts in renewable energy applications.<sup>3–5</sup>

Preferred and  $2^{nd}$  choice for the topic: (1)  $H_2$  storage and transportation, green  $H_2$  production, hydrogen vectors; (2) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization

Preferred presentation: Oral preferred or Short Oral

## **Introduction and Motivations**

The transition toward renewable energy sources has driven extensive research into alternative methods for hydrogen production, with photocatalytic reforming emerging as a promising technology.<sup>6,7</sup> Glycerol, abundantly produced as a by-product in the biodiesel industry, can be used as potential feedstock for this process. The key to maximize hydrogen yields lies in the development of efficient photocatalysts. In this study we explore bimetallic Au-Ni catalysts supported on cerium oxide due to their unique properties: CeO<sub>2</sub> provides high oxygen storage capacity and stability, while the Au-Ni alloy exhibits enhanced catalytic properties. Nickel facilitates the oxidation of glycerol, while gold improves electron transfer, resulting in higher hydrogen yields and improved catalyst stability. This work aims to advance the understanding and the application of Au-Ni/CeO<sub>2</sub> catalysts in the solar photoreforming, promoting their use as a sustainable solution for hydrogen generation.

### **Materials and Methods**

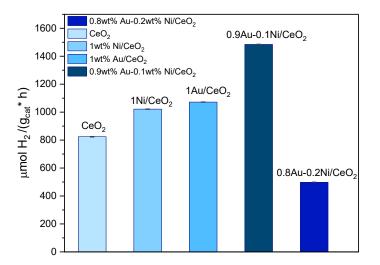
CeO<sub>2</sub> was prepared by precipitation in basic conditions starting from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, the resulting precipitate was hydrothermally aged at 120 °C and calcined at 600 °C. Ni was deposited on ceria by wetness impregnation method, using Ni(NO<sub>3</sub>)<sub>6</sub>·H<sub>2</sub>O, whereas gold was supported on ceria via deposition-precipitation method, by using a solution of HAuCl<sub>4</sub>. For the bimetallic Au-Ni catalysts, Au was deposited as first, then, Ni was added. All the prepared catalysts were calcined at 250 °C. The metal composition was 0.9wt% Au-0.1wt% Ni/CeO<sub>2</sub> and 0.8wt% Au-0.2wt% Ni/CeO<sub>2</sub> for the bimetallic catalysts, 1wt% of Au or Ni for the monometallic ones.

The photocatalytic hydrogen production was conducted under solar irradiation, with a suspension of 1 mg mL<sup>-1</sup> of catalyst in 10% (v/v) solution of glycerol in MilliQ water. The solar irradiation was performed with a special lamp specifically designed for the sunlight simulation. After 5 h of irradiation, 1 mL of reaction gases was collected with a gastight syringe and analysed by gas chromatography with a thermal conductivity detector (GC-TCD).



#### **Results and Discussion**

The catalytic activity of Au, Ni and Au-Ni catalysts supported on CeO<sub>2</sub> provided valuable insights into their efficacy in the H<sub>2</sub> production. Bare ceria and all the supported catalysts demonstrated significant H<sub>2</sub> photoreforming activity (Fig.1), with 0.9wt% Au-0.1wt% Ni/CeO<sub>2</sub> that showed heightened efficiency, suggesting an important synergistic effect between Au and Ni. In comparison with ceria alone, the addition of Ni improves the hydrogen production activity, likely enhancing the cleavage of C–C and C–H bonds of glycerol thanks to the high work function of such metal promoting efficient electron transfer and glycerol photoreforming activity.<sup>5</sup> Gold plasmonic resonance amplifies light absorption and enables greater visible light utilization, moreover, it is expected to prevent Ni agglomeration.<sup>8</sup> The interaction between Au and Ni metals appears particularly pronounced in the catalyst with composition 0.9wt%Au-0.1wt%Ni/CeO<sub>2</sub>, whereas the activity is depleted in the 0.8wt%Au-0.2wt%Ni/CeO<sub>2</sub>. Characterizations of the structural, morphological, electronic and reduction properties were carried out in order to explain the reasons that promote a such effective synergy between the two metals, in correspondence of this specific Au-Ni composition, optimizing their performance in the photocatalytic applications.



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