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Photocatalytic Hydrogen Production using Noble and Transition Metals Surface Modified Titania

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INTRODUCTION

A large number of photocatalytic materials have been studied for water splitting since the seminal work of Fujishima and Honda¹, showing great potential for solar energy conversion, including H₂ production. The irradiation of a suspension of semiconductor oxides, as is the case of TiO₂, presents attracting features but also stringent requirements regarding materials properties, including the tailoring of the electronic structure. Furthermore, efficient charge transport is necessary, as well as effective charge separation and prevention of electron-hole pair recombination, before the redox reactions can proceed^{2,3}. In this work, the catalytic activity under UV excitation of TiO₂-Au photocatalyst for H₂ production was undertaken using glycerol and ethanol as sacrificial agents. Furthermore, substitution of Au by transition metal Cu was attempted with good results. Comparison is made with results obtained using TiO₂-rGO-Pt catalyst under analogous loading conditions.

EXPERIMENTAL

The rGO-TiO₂ composites were synthesized by a hydrothermal method using GO and Degussa P25 TiO₂ as starting materials in an ethanol/water mixture at 125 °C for 4 h. For the Au and Cu photocatalysts synthesis, a photodeposition method was followed using Degussa P25 TiO₂ and the previously prepared rGO-TiO₂, Au and Cu salt precursors, in a 10 % methanol aqueous solution (v/v) at room temperature under UV irradiation. The photocatalysts were characterized by SEM, TEM, UV diffuse reflectance and XRD. The photocatalytic hydrogen production experiments were performed using water/sacrificial agent mixtures, containing ethanol or glycerol, in a 0.3 L sealed reactor under UV light. The generated gas obtained during 6 h irradiation was analyzed in an Agilent Micro GC 3000 gas chromatograph.

RESULTS AND DISCUSSION

Recent studies conducted by the authors using TiO₂-Pt and TiO₂-rGO-Pt photocatalysts gave significant initial hydrogen production rates when using short chain alcohols as sacrificial agents⁴. In an attempt to substitute Pt in the photocatalysts, a series of Au and Cu-TiO₂ based photocatalysts, with and without RGO, were synthesized, characterized and evaluated for H₂ production using ethanol or glycerol in water mixtures. Figure 1a) shows selected results for the TiO₂-Au1.5% and TiO₂-rGO-Au1.5% in glycerol/water solutions indicating a pH effect and rates in the range 30-40 mmolh⁻¹g⁻¹, with no significant variations with concentration between 5 and 40 vol% glycerol. In any case, rates were higher than those reported in literature with other Au photocatalysts³.

Gas composition indicated H₂ (>85%), followed by CO and CO₂. The gas production rate for ethanol is constant for the TiO₂-Au photocatalyst but shows the same average value as for TiO₂-Pt catalyst with same metal loading of 1.5 wt%. The main product in the gas phase is H₂ (>95 %), the remaining components being CO and CH₄ and minor amounts of CO₂, C₂H₆ and C₂H₄. Substituting noble metals for a transition metal such as Cu, displays a one slope linear time dependence of the produced gases. High rates were found, comparable to those obtained with TiO₂-Pt based catalysts, see figure 1b). Gas compositions contained H₂ above 93%, with similar components in the mixture as found for TiO₂-Au photocatalysts in ethanol.

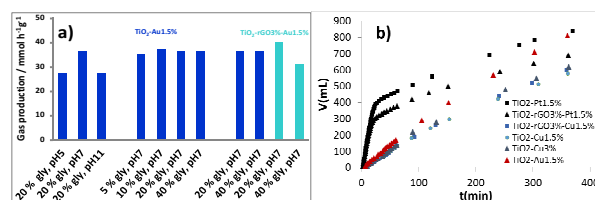


Fig.1 Gas production from aqueous solutions (a) TiO₂-Au1.5% and TiO₂-rGO3%-Au1.5% in 5-40% glycerol/H₂O mixtures, (b) Pt, Au, Cu TiO₂ based photocatalysts in 5M ethanol. Operational conditions: T= 40 °C, UV irradiation (6h), 0.5 g_{cat}L⁻¹.

CONCLUSION

New synthesized Au photocatalysts exhibited high rates of H₂ production, under 6 h UV irradiation, when using short chain alcohols as sacrificial agents. Rates for ethanol were equivalent to those found for TiO₂-Pt based catalyst but with a constant average rate, indicating no effect due to adsorbed intermediaries. Equivalent features were observed for glycerol but at slower rates.

Low cost alternative materials substituting Pt or Au by 3 d transition metal Cu gave excellent results, with equivalent high average rates to TiO₂-Pt based catalyst.

Further work is under way to understand kinetics and mechanisms and allow a more effective light utilization.

REFERENCES

1. A. Fujishima and K. Honda, *Nature* 238, 37-38 (1972).
2. K. C. Christoforidis, P. Fornasiero, *ChemCatChem*. 9, 1523-1544 (2017).
3. M. Z. Rahman M. Batmunkh, M. Bat-Erdene, J.G. Shapter, C.B. Mullins, *J. Mat. Chem. A.*, 6, 1305-1322 (2018).
4. P. Ribao, M.A. Esteves, V.R. Fernandes, M. Rivero, C.M. Rangel, I. Ortiz, *Int. J. Hydrogen Energy*, 44, 101-109 (2018).

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