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138	HE09	Carmen M. Rangel	Hydrogen Energy	Photocatalytic Hydrogen Production using Noble and Transition Metals Surface Modified Titania

Photocatalytic Hydrogen Production using Noble and Transition Metals Surface Modified Titania

Anabela Capelo[1], Maria A. Esteves[1], Vítor R. Fernandes[1] and C. M. Rangel[1]

[1]Laboratório Nacional de Energia e Geologia, LNEG I.P. Estrada do Paço do Lumiar 22, 1649-038 Lisboa Portugal.
carmen.rangel@lneg.pt

INTRODUCTION

A large number of photocatalytic materials have been studied for water splitting since the seminal work of Fujishima and Honda[1], showing great potential for solar energy conversion, including H_2 production. The irradiation of a suspension of semiconductor oxides, as is the case of TiO_2, 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 TiO_2-Au photocatalyst for H_2 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 TiO_2-rGO-Pt catalyst under analogous loading conditions.

EXPERIMENTAL

The rGO-TiO_2 composites were synthesized by a hydrothermal method using GO and Degussa P25 TiO_2 as starting materials in an ethanol/water mixture at 125 ºC for 4 h. For the Au and Cu photocatalysts synthesis, a photodeposition method was followed using Degussa P25 TiO_2 and the previously prepared rGO-TiO_2, Au and Cu salt precursors, in a 10 % methanol aqueous solution (v/v) at room temperature under UV irradiation. The photo-catalysts 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 TiO_2-Pt and TiO_2-rGO-Pt photocatalysts gave significant initial hydrogen production rates when using short chain alcohols as sacrificial agents[4]. In an attempt to substitute Pt in the photocatalysts, a series of Au and Cu-TiO_2 based photocatalysts, with and without RGO, were synthesized, characterized and evaluated for H_2 production using ethanol or glycerol in water mixtures. Figure 1a) shows selected results for the TiO_2-Au1.5% and TiO_2-rGO-Au1.5% in glycerol/water solutions indicating a pH effect and rates in the range 30-40 $mmolh^{-1}g^{-1}$, 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 photocatalysts[3]. Gas composition indicated H_2 (>85%), followed by CO and CO_2. The gas production rate for ethanol is constant for the TiO_2-Au photocatalyst but shows the same average value as for TiO_2–Pt catalyst with same metal loading of 1.5 wt%. The main product in the gas phase is H_2 (>95 %), the remaining components being CO and CH_4 and minor amounts of CO_2, C_2H_6 and C_2H_4. 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 TiO_2-Pt based catalysts, see figure 1b). Gas compositions contained H_2 above 93%, with similar components in the mixture as found for TiO_2-Au photocatalysts in ethanol.

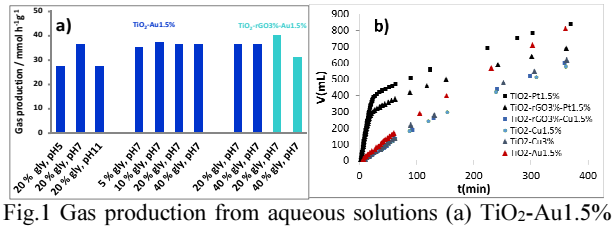

Fig.1 Gas production from aqueous solutions (a) TiO_2-Au1.5% and TiO_2-rGO3%-Au1.5% in 5-40% glycerol/H_2O mixtures, (b) Pt, Au, Cu TiO_2 based photocatalysts in 5M ethanol. Operational conditions: T= 40 ºC, UV irradiation (6h), 0.5 $g_{cat}L^{-1}$.

CONCLUSION

New synthesized Au photocatalysts exhibited high rates of H_2 production, under 6 h UV irradiation, when using short chain alcohols as sacrificial agents. Rates for ethanol were equivalent to those found for TiO_2-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 TiO_2-Pt based catalyst.

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

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