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TiO_2-reduced graphene oxide-Pt nanocomposites for the photogeneration of hydrogen from ethanol liquid and gas phases

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ABSTRACT

The production of hydrogen by photocatalysis presents attractive features but also stringent requirements of materials properties. A series of TiO_2-based photocatalysts containing reduced graphene oxide (rGO) and platinum, TiO_2-rGO(x)-Pt(y) (x=0−5 wt%; y=1.5, 2.5, 3.8 wt%), were synthesized by a simple two-step procedure. The ternary composites exhibited promising performance for hydrogen generation, in both liquid and gas phase photocatalysis, using ethanol as hole scavenger, under UV light. The effect of the concentration of ethanol, graphene oxide, and Pt, as well as photocatalyst loading and solution pH were assessed. The photocatalyst TiO_2-rGO3%-Pt3.8%, in the liquid phase, produced gases containing over 95% hydrogen at very high initial production rates, ~560 $mmol h^{-1} g_{cat}^{-1}$. The gas production *vs* irradiation time (6 h) showed linear dependence in a two-slope graph, with a drastic decrease of the rate due to Pt poisoning. Solution pH reached values of 3.5, regardless of the initial value. In the liquid phase, partial oxidation of ethanol took place with the dehydrogenation of ethanol to acetaldehyde. In the gas phase photocatalysis, TiO_2-rGO3%-Pt3.8% showed capability for photo-reforming as indicated by produced gases with a molar ratio H_2/CO_2 of 3. rGO reinforces the effect of Pt as a suppressor of charge recombination.

1. Introduction

The energy demand is expected to increase significantly worldwide by 2030 due to the accelerated population growth. Thus, there is an urgent need to develop clean energy systems to meet the increasing world energy consumption and simultaneously reduce the fossil fuels dependence and the negative environmental impact of their use [1,2]. Renewable hydrogen as an energy vector has been regarded as a sound alternative to the use of fossil fuel due to its environmental friendliness and high energy content [3]. Nowadays, H_2 is mainly produced by steam reforming of natural gas, coal or crude oil. Other technologies for producing hydrogen include electrolysis, reforming of biofuels and photocatalysis. Among them, photocatalytic hydrogen production from water, using solar radiation as energy source, is one of the most promising technologies.

A large number of photocatalytic materials have been studied for water splitting since the seminal work of Fujishima and Honda [4], showing great potential for solar energy conversion, including the production of hydrogen. The irradiation of a suspension of a semiconductor oxide presents attracting features but also stringent requirements regarding materials properties, which include tailoring of the electronic structure: band gap - essential for the absorption of solar energy, and flat band potential - higher than the redox potential of the couple H^+/H_2. 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 at the semiconductor surface [1,2,5]. It is emphasized that the mentioned reaction steps have very different time scales: femtoseconds for the generation of an electron-hole couple, while their recombination occurs in 10–100 ns. In a comparative time scale are the oxidation reactions which also take about 100 ns. The reduction reactions need times of the order of ms [6]. One of the used strategies is the trapping of generated electrons by depositing an adequate work function metal on the semiconductor. In this way, the created Schottky barrier [7] at the metal/semiconductor interface can operate as an efficient electron trap and so increase the efficiency of the process. Another strategy includes making holes react

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