TiO_2 or Nb_2O_5 composites with graphene or graphene oxide as photocatalysts for Photoreforming of organics to obtain H_2

Alberta GENCO[1,2]*, Elisa I. García-López[3], Narimene Aoun[1], Bartolo Megna[1], Conchi O. Ania[4] , Giuseppe Marcì[1]

[1]Department of Engineering (DI), Viale delle Scienze, University of Palermo, Palermo, Italy
[2]Department of Chemistry, University of Perugia, Perugia, Italy
[3]Department of Chemistry (STEBICEF) University of Palermo, Italy
[4]POR2E Group, CEMHTI CNRS (UPR 3079), Université d'Orléans, 45071 Orléans, France

**alberta.genco@dottorandi.unipg.it*

Significance and Relevance

The conversion of solar energy into other energy vectors is a promising approach to address the challenges of global sustainability. The production of H_2 from sunlight represents an attractive alternative to the use of fossil fuels to meet current energy demands. In this study, photoreforming reaction in the presence of aqueous solutions of ethanol, glycerol or microplastics (polyethylene terephthalate or polylactic acid) aqueous dispersions and of a semiconductor irradiated under UV or natural solar light were performed to obtain H_2. The heterogeneous photocatalysts used consisted of an oxide (Nb_2O_5 or TiO_2) forming a composite with a carbon-based material such as graphene (G) or graphene oxide (GO).

Preferred presentation: Oral

Introduction and Motivations

The photoreforming of aqueous solutions containing organic compounds integrates the photocatalytic splitting of water with the oxidation of organic substances into a single process under ambient conditions. In this technology a semiconductor, excited by suitable energy, generates electron/hole pairs allowing redox reactions; i.e. protons are reduced by the electrons to obtain H_2 and an organic molecule acts as a hole scavenger resulting in the production of a partially oxidized derivatives. Previous investigations showed that Nb_2O_5 can act as an excellent catalyst with activity comparable to that of TiO_2, which is one the most used photocatalyst for H_2 production[1]. Both TiO_2 and Nb_2O_5 suffer from rapid recombination of charge carriers and low solar-energy utilization, due to their large bandgap. Various strategies to make them active under sunlight and to enhance their photocatalytic activity have been explored, including the combination of these semiconductors with carbon materials such as graphene (G) or graphene oxide (GO).

This research focuses on the development of composite photocatalysts that realize heterostructures obtained by varying the amount of carbon material (ranging from 5% to 20%) relative to the mass of the oxide semiconductor (TiO_2 or Nb_2O_5) for the photoreforming of organic compounds dissolved in water[2]. In these composites, the oxide semiconductor acts as the photocatalyst, while graphene and graphene oxide play the role of electron reservoirs and carriers, facilitating electron transfer to the reaction sites. Photoreforming tests were performed using as hole scavengers ethanol or glycerol by irradiating the solid under UV or natural sunlight. Selected experiments using microplastics as scavengers were also conducted to explore their possible degradation considering the continuous and worrying expansion of this type of residue in aquatic environments and its devastating effects on ecosystems and human health.

Materials and Methods

Nb_2O_5 was synthesized through a hydrothermal process using Ammonium Niobium Oxalate as precursor whereas TiO_2 was commercial Evonik P25. The composites with Graphene were prepared by sonication of G (commercial Graphene-XT) and the semiconductor in CH_3CN. The amount of G with respect to the oxide ranged from 5 to 20 % w/w. The samples were labelled Ti-G or Nb-G, followed by the mass of G per 10 g of semiconductor, i.e. Ti-G-10:0.5; 10:1 or 10:2. Graphene Oxide was prepared using Hummer's method[3] and the composites oxide-GO were prepared in a 10:1 mass ratio and labelled as Ti-GO-10:1 or Nb-GO -10:1.

Photoreforming tests were performed in a 50 mL cylindrical Pyrex photoreactor with 35 mL of aqueous solution of ethanol, glycerol, PET or PLA, 0.32 $g \cdot L^{-1}$ of photocatalyst. In the current investigation experiments were carried out in the absence and in the presence of Pt corresponding to 1% Pt w/w relative to the total mass of catalyst[4]. The photocatalytic activity of the materials was evaluated under UV LED or natural sunlight irradiation.

Results and Discussion

The histograms in Figure 1 show the H_2 productivity (moles of H_2 formed per gram of catalyst and per hour of irradiation) under UV LED irradiation of photocatalysts in the presence of Pt using different substrates. TiO_2-based photocatalysts were more active than those of Nb_2O_5. In general, better results were obtained with heterostructures Ti-G 10:1 and Ti-GO 10:1. The photoreforming of ethanol Fig. 1(A) gave rise to the best performance, particularly in the presence of Ti-G 10:1, which evidenced a better performance than the corresponding pristine TiO_2. The results reported in Fig 1(C) are significantly lower when compared to Figs 1(A) and 1(B), demonstrating how ethanol and glycerol, due to their simpler structure, can be easily oxidized with respect to microplastics, which have high structure complexity.

The highest performance was achieved with Ti-G 10:1 in the presence of Pt using ethanol. In these conditions, the productivity was of 311 $mmol \cdot h^{-1} \cdot g^{-1}$ with an apparent quantum efficiency (AQE) of 100% under UV light and 13 $mmol \cdot h^{-1} \cdot g^{-1}$ with AQE 18% under natural sunlight irradiation.

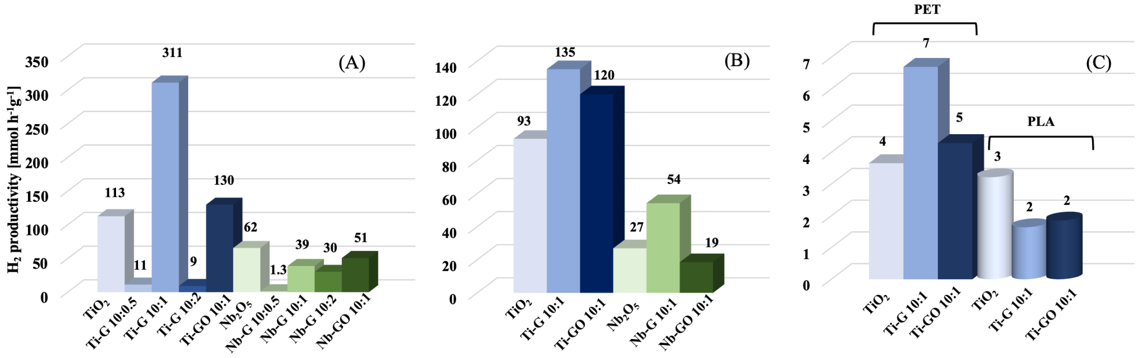

Figure 1 H_2 productivity under UV irradiation in the presence of (A) ethanol (B) glycerol and (C) PET and PLA

References

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