



MW-assisted Pt@C₃N₄/TiO₂ composites for glycerol photoreforming for H₂ production

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Significance and Relevance

Nowadays, hydrogen is considered as one of the most promising energy carriers and studies for green production are increasing in scientific literature. Glycerol photoreforming represents one of the greenest methods to produce hydrogen due to the use of both, a photocatalytic method, and glycerol as biomass-derived material. As known, TiO₂ is the most widely used photocatalyst, and to improve its use under visible light C₃N₄/TiO₂ composites are studied by using a MW-assisted procedure. The effectiveness of the MW is evident not only for its low-energy impact methodology but also for its effect on the morphology of the synthesized materials.

Preferred and 2nd choice for the topic: 1) H₂ storage and transportation, green H₂ production, hydrogen vectors, 2) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization

Preferred presentation: Poster /Short Oral

Introduction and Motivations

Hydrogen and its generation through renewable raw materials are at the heart of the energy transition. Nowadays, hydrogen is often produced by using fossil fuels as starting materials. For this reason, the development of sustainable processes is an increasingly priority goal. In this context, glycerol photoreforming for hydrogen production represents one of the greenest methods.¹ In fact, glycerol is, a biomass-derived material and photocatalysis is considered one of the most attractive ways to convert solar energy into usable chemicals. TiO₂ is, nowadays, the most used photocatalyst due to its efficiency, safety and affordability. Its principal drawbacks are its limited absorption to UV radiation and fast electron-hole pair recombination. C₃N₄ is a semiconductor that presents a narrower bandgap (2.7-2.8 eV) than TiO₂ (3.2 eV) so the corresponding C₃N₄/TiO₂ composites are able to extend the absorption to the visible light range. In a previous paper, the composites were produced in two different steps forming C₃N₄ on commercial TiO₂ P25. Here, with the aim to optimize and to make the process more sustainable, one-pot MW-assisted procedure is studied. C₃N₄/TiO₂ composites were thus prepared in only one step from melamine and Ti(iOPr)₄ precursor. The effectiveness of the MW is evident not only for its low-energy impact methodology but also for its effect in the morphology of the synthesized materials. Finally, Pt was deposited and tested as Pt@C₃N₄/TiO₂ composites for hydrogen photoproduction through glycerol photoreforming.

Materials and Methods

Here, an example of the synthesis of MW-assisted Pt@C₃N₄/TiO₂ materials is reported.

To obtain the heterojunction between titania and carbon nitride, melamine was dissolved in distilled water prior to adding titanium (IV) isopropoxide dropwise. The amounts were chosen to have a melamine: titania (w/w) ratio of 5. According to the MW-assisted procedure the solution was introduced in a microwave at 180 W for 20 cycles (on for 15 s and off for 20 s). Finally, the solid was filtered, washed with distilled water and dried. The solid was calcined at 550 °C for 1 h in a semi-closed system and denoted as MW_TiO₂CN. Pt@C₃N₄/TiO₂ was prepared by wetness impregnation. Briefly,



the appropriate amount of PtCl_2 so as to incorporate 1 wt.% of platinum was added to 0.5 g of each catalyst and the solid was calcined at 350 °C for 3 h.

Results and Discussion

Different titania-based photocatalysts were prepared by conventional or MW-assisted methodology²⁻³ and compared as catalysts for hydrogen production through glycerol photoreforming. Carbon nitride was added, already prepared or in a one-pot procedure to improve the use of these systems under visible light. According to the design of this study, it is possible to compare the synthetic procedure (conventional/MW), if it has been carried out as a one-pot procedure or in two steps, and the influence of C_3N_4 in the systems. In all cases, Pt was impregnated onto the solids. All materials were well characterized by means of XRD, ICP-MS, N_2 adsorption-desorption, TGA/DSC, XPS, IR, and UV-Vis spectroscopy. From preliminary tests, microwave-synthesized solids show a lower bandgap value than conventional ones, which could improve their photocatalytic efficiency under visible light. Moreover, the influence of the microwave-assisted procedure seems evident also in hydrogen production and the results can be ascribed to the different crystallinity and surface area of MW materials.

References

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