Effect of CeO_2 Morphology (cubs, rods and polyhedra) on the Photocatalytic Performance of Pd-TiO2 for Hydrogen Production

ORAL
Ph.D. Student: N
Journal: CEJ

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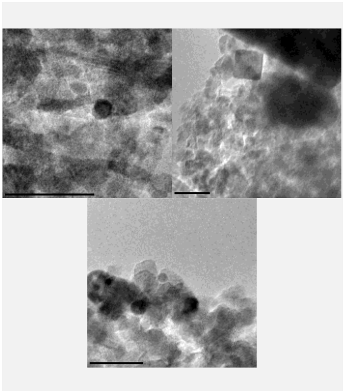

In this research study, the impact of adding cerium oxide nanoforms to titanium oxide-supported palladium systems on photocatalytic hydrogen production was analyzed. Tests under UV and sunlight-type illumination conditions showed an important promoting effect of Ceria irrespective of both morphology and illumination source nature. The measurement of the quantum efficiency was used to quantitatively assess the performance of the catalysts. Outstanding results were obtained, particularly under sunlight illumination. A complete characterization study of the materials was carried out allowing to establishing a structure-activity link correlating the capture of charge after light excitation with CeO_2 nanoforms (cubs, rods and polyhedra) incorporation.

Introduction

Photocatalysis can play a central role in the development of future energy and environmental chemical processes. Among several novel photocatalytic processes, the generation of hydrogen using renewable energy as well as utilizing bio-derived alcohols in a water medium appears as an optimum choice to generate a new energy vector such as hydrogen and, thus, to contribute to the setting-up of a new circular economy with zero net carbon emissions and respectful with the environment [1, 2].

A central problem in photocatalysis is the need for more efficiency of the processes. A way to circumscribe or minimize such issues is to design modern photoactive materials. Among them, composite materials using several components with specific optical and/or chemical functionalities are frequently used [3]. In this work, the combination of different CeO_2 morphologies (nanocubes, nanorods and nanopolyhedra) with TiO_2, having titania as one component, is shown to boost the hydrogen production from methanol:water mixtures under both UV and visible illumination conditions.

Material and Methods

n$XCeO_2$-TiO_2 photocatalysts were obtained in three stages. First, pristine CeO_2 (nanocubes, nanopolyhedra and nanorods) were synthesized via the hydrothermal method at 180, 180 and 100 °C respectively for 10 h. Then, pure TiO_2 powders were obtained by the inverse microemulsion method [4]. Finally, CeO_2-TiO_2 nanocomposites (2.5 wt% of CeO_2) were obtained using a wet impregnation methodology. Pd cocatalyst (1 wt%) addition was carried out using a chemical deposition method. The photocatalyst activity was evaluated in H_2 production reaction [4, 5].

Results and Discussion

Images obtained by transmission electron microscopy confirmed the synthesis of the different CeO2 nanoforms: nanocubes (graphical abstract), nanorods and nanopolyhedrons. In addition, these images corroborated the formation of the different palladium/ceria-titania nanocomposites (Pd/cCeTi, Pd/pCeTi and Pd/rCeTi). XRD pattern of the Pd/xCeTi materials (result not shown) reveals the presences of (101), (004), (200) planes characteristics of anatase phase of titanium dioxide in all samples (JCPDS 01-084-1286). In addition, XRD results displayed of the characteristic peaks of the (111), (200), (200), and (311) diffraction planes of the fluorite phase of CeO_2 (JCPDS 34-0394), in the materials that content the different morphologies (cubes, rods and polyhedra) of CeO_2. UV–visible spectra (resukts not shown) show a decay below 400 nm, mainly ascribed to the semiconducting nature of the dominant anatase phase. Considering an indirect gap semiconductor, as anatase is reported to be, the calculation of the band gap energy by Tauc analyses yield values from 2.92 to

2.26 eV for all samples, with limited variation with the ceria mophology.

The results of photocatalytic activity of the Pd/xCeTi and Pd/Ti materials under UV and visible irradiation in the H_2 production are shown in Figure 1.

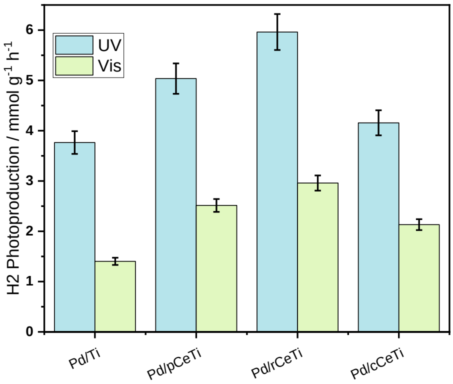

Figure 1. Hydrogen photoproduction reaction rate for the Pd/xCeTi samples and references material under UV and visible illumination conditions.

In general, all the samples present activity in H_2 production under both lighting sources used. Furthermore, it is observed that the presence of Ceria nanoforms (rods, cubs and polyhedra) significantly increases the activity concerning the reference material. A maximum of activity (optimal) is observed, with the sample containing ceria nanorods, since the materials to which the same amount of nanocubs or nanopolyhedra was added showed a decrease in activity with respect to said material. As a measure of the improvement in activity concerning the Pd/Ti system and taking as an example the results obtained from the production of H_2, it can be mentioned that CeO_2 nanorods improve the photoactivity in the order of 1.6/2.0 times under illumination with UV/visible light.

To rationalize the photocatalytic behaviour, Figure 2 shows the photoluminescence spectra obtained from the Pd/xCeTi materials and the reference sample under UV excitation (365 nm).

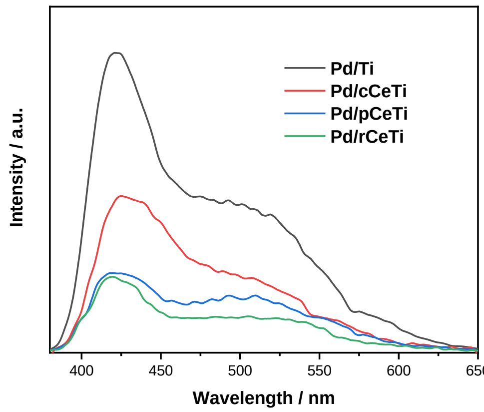

Figure 2. Photoluminescence spectra for the Pd/xCeTi samples and reference material, using 35 nm as exitation light..

It is known that the greater the photoluminescence signal, the greater the recombination process of the charge carriers (e^-/h^+). The intensity of photoluminescence emitted by the materials follows this trend: Pd/Ti > Pd/cCeTi > Pd/pCeTi > Pd/rCeTi. Correlating these results with those of H_2 production, it is corroborated that the increase in photocatalytic activity (H_2 production) is directly related to decreasing charge recombination.

Conclusions

The maximum activity was achieved with the sample containing CeO2 nanorods. This material presents hidrogen production values under visble light of 2.0 times higher than referance material. This value indicates the suitability of incorporating Ceria nanorods to generate highly active titanium dioxide-based materials for solar photocatalysis.

Acknowledgments

This study was funded by the PAPIIT DGAPA-UNAM projects: IN116424, IV100124 and IN112922. Authors want to thank the expert technical assistance of D.A. Dominguez and P. Casillas..

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