TiO_2 on Gold Nanostars Enhances Photocatalytic Water Reduction in the Near Infrared Regime

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Significance and Relevance

The synthesis of gold nanostars coated with a conformal layer of crystalline titanium dioxide (AuNS@TiO_2) through a simple hydrothermal route has enabled the photocatalytic evolution of hydrogen from water under solar illumination. The innovative combination of the photocatalyst's nanostar morphology, which generates a higher flux of hot electrons easily transferred through the thin TiO_2 tips, and the reversal of the coupling order of the two materials, with gold on the inside and the semiconductor on the outside, allowed solar radiation to be used up to the infrared portion of the spectrum to produce green hydrogen.[1]

***Preferred and 2nd choice for the topic*:** Photocatalysis and photoelectrocatalytic approaches, solar energy utilization; H_2 storage and transportation, green H_2 production, hydrogen vectors

***Preferred presentation*:** Oral preferred or Short Oral

Introduction and Motivations

Hydrogen, as an energy carrier, has emerged as one of the possible solutions to climate change, being an energy-rich substance that facilitates translocation and/or storage (in the form of gaseous, liquid, or solid H_2 or through chemicals) for the purpose of using it in a temporal and/or spatial context distinct from the original production site. Hence, there is the to find production routes that come from sustainable sources and at the same time are viable and industrially competitive.
In this scenario, heterogeneous photocatalysis enabled by nanoparticles in suspension emerges as one of the most promising processes. It does not require intermediate systems that generate energy, such as photovoltaic panels or wind turbines, and the surface area available for light absorption for the water splitting reaction is greater by not being fixed on a substrate.
TiO_2, while being the desirable semiconductor for these applications, due to its stability under reaction conditions, low cost, and proper alignment of valence and conduction bands, unfortunately has a wide band gap that limits its applicability mainly to UV irradiation conditions. However, by exploiting star-shaped plasmonic nanoparticles as promising additives to TiO_2, it is possible to extend the photocatalytic efficiency of the semiconductor into the visible and near-infrared (NIR) for hydrogen generation.

Materials and Methods

TiO_2 growth on gold nanostars was performed from titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$ as the precursor in a non-aqueous environment (isopropanol). Acetic acid was added to the growth solution to control TiO_2 growth. Next, crystallization occurred by heat treatment of AuNS@TiO_2 particles in isopropanol at a temperature of 70°C for two days. The solution was washed with 1:1 MilliQ water and ethanol mixture and then dried to produce a powder. Photocatalytic activity of the samples was tested via batch-phase water reduction with methanol as a sacrificial agent. The as-produced AuNS@TiO_2 catalyst was dispersed in 10 mL of reaction solution via sonication. The reactor was illuminated by a 150-W xenon ozone-free arc lamp (Newport). Magnetic stirring was employed to ensure that the AuNS@TiO_2 remained suspended in the reaction medium. The hydrogen production rate was monitored of the reactor headspace gas into the thermal conductivity detector of a GC (Agilent 7890B).

Results and Discussion

By epitaxially growing a conformal shell of crystalline TiO_2 on the nanostructures via a low-temperature hydrothermal protocol, a defect- and strain-free interface between gold nanoparticles and TiO_2 is generated. This unencumbered morphology allows plasmonically generated hot electrons to be more easily transferred across the Schottky barrier between the Fermi level of the metal (Au) and the conduction band of the semiconductor (TiO_2). Furthermore, the intimate contact between metal and semiconductor allows for more efficient light absorption and subsequent hydrogen production than conventional approaches that deposit metal clusters on TiO_2. *(Figure 1)*

The high potential of this new nanomaterial led to the birth of the StarLIGH_2T technology. A project based on the patented catalyst just described can make the most of the solar spectrum, absorbing more than 90 percent of the radiation, far exceeding the limitations of conventional photocatalysts, which are only able to utilize a small fraction of the entire solar radiation.

StarligH$_2$t revolutionizes the state of the art in photocatalysis with this innovative photocatalyst capable of producing seven times more hydrogen than the commercial P25 TiO_2 photocatalyst. This figure highlights a major breakthrough over existing technologies, representing a concrete and highly competitive alternative for photocatalysis aimed at hydrogen production.

Figure 1

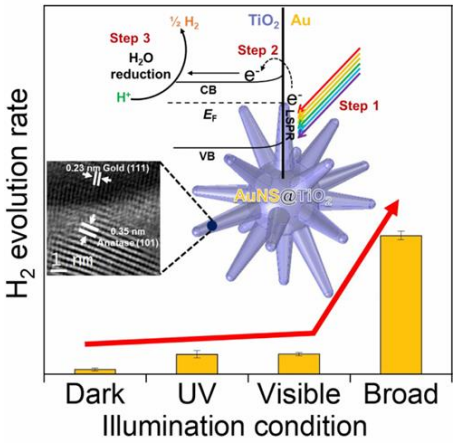

Figure 1 *Broad-spectrum light illuminates the TiO_2 coated gold nanostar (step 1). While shorter wavelengths interact with the TiO_2 band gap and the gold transverse LSPR band, longer wavelengths (800 nm) excite the longitudinal LSPR band of gold nanostars. The hot electrons at the nanostar tips overcome the Schottky barrier at the clean interface between the two materials and transfer into the conduction band of the TiO_2 semiconductor (step 2). Conduction band electrons then reduce protons and evolve hydrogen (step 3).*

References

1. Atta, S.; Pennington, A. M.; Celik, F. E.; Fabris, L. TiO_2 on Gold Nanostars Enhances Photocatalytic Water Reduction in the Near-Infrared Regime. *Chem.* **2018**, *4*, 2140– 2153, DOI: 10.1016/j.chempr.2018.06.004

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