"Unveiling enhanced green hydrogen generation: Constructing a photocatalytic hybrid system by physical enrichment"

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## **Abstract**

*This study presents photocatalytic systems comprised of gold nanoparticles (AuNPs) immobilized by ionic liquids (IL) which demonstrates remarkable efficacy, and versatility in facilitating hydrogen evolution reactions (HER) through water-splitting (WSR) or organic photo reforming (OPR). Obtaining these highly efficient photocatalysts involves the combination of two promising approaches: magnetron sputtering and IL superficial covering, creating hybrid materials with direct metal-TiO2 interfaces. Under the investigated conditions, the AuNPs (Ømean=4-10 nm) presence profoundly enhances the photocatalytic activity of the pristine TiO2 in methanol photo reforming (MPR) producing from 0.02 up to 8.25 mmol of H2 per gram of catalyst per hour. This remarkable difference is attributed to the synergistic interaction of the tricomponent IL-metal-TiO2 surface, leading to a robust modification of the electronic and photophysical properties. Our investigation systematically explores the impact of factors such as nanoparticle size, IL composition, photophysical effect, scavenger agent, and the sequence of local deposition on the surface. This comprehensive approach sheds light on the intricate mechanisms underlying the increased efficiency of the photocatalytic system in the quest for an ideal one.*

*Keywords: enhanced HER, ionic liquids, gold nanoparticles, titanium dioxide, photocatalysis.*

## Introduction

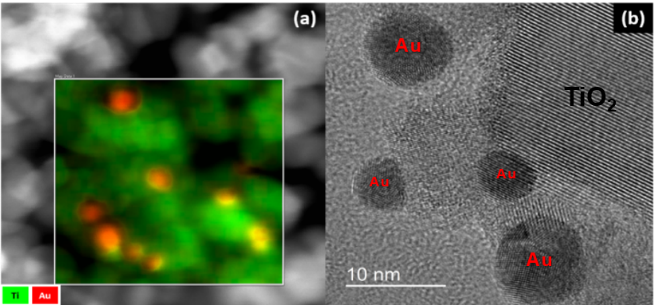
The production of green hydrogen is a current area of research that seeks sustainable solutions for generating a clean and versatile fuel.[1] Metal nanoparticles can perform numerous challenging chemical reactions with outstanding performance and specificity. In hydrogen evolution reactions, these systems favor processes like water splitting reaction. MNPs with plasmon properties are one of the most employed due to their capacity of sensitizing the semiconductor surface facilitating electron trapping and efficient charge separation.[2,3] In such devices, the visible light absorption of plasmonic allows the injection of their photoactivated electrons into the semiconductor conduction band, creating a charge separation that facilitates the Red-Ox process.[4] The magnetron sputtering offers exciting new opportunities for manufacturing supported MNPs since it usually generates highly active clean surfaces without chemical stabilizers and/or solvents.[5-7] Moreover, employing ionic liquid is an encouraging method for influencing the physicochemical characteristics of semiconductors via modulation of superficial electronic properties. [4,8] In this work, we present the preliminary results on the performance of IL@Au@TiO2 type hybrid systems as promising systems for HERs via photocatalytic WSR and OPR.

## Experimental

All manipulations were conducted at atmospheric conditions, and all reagents were used as received. The MNPs were produced by depositing Au over TiO2 using a direct current (DC) magnetron sputtering system working at different conditions and then impregnated by three different imidazolium-based ILs ([BMIm.OAc] (IL1); [BMIm.NTf2] (IL2) and [BMIm.BF4] (IL3). The characterizations and the synthesized systems’ validation were performed using different state-of-the-art techniques; meanwhile, the photocatalytic reactions were conducted using a quartz reactor and irradiated by a Xe 300W lamp as a solar simulator.

## Results and discussion

Spherical gold nanoparticles (AuNPs) were magnetron sputtered onto TiO2 to create photocatalytic systems. The AuNPs, mainly spherical and comprising 1-5 wt.% Au (Figure 1; Table 1), were then treated with selected ILs (IL1-IL3). These hybrid materials were validated in HERs, WSR and OPR. The HRTEM and EDX analysis evidenced the presence of spherical AuNPs in the 4-10 nm range uniformly scattered over the surface. These systems presented typical UV absorption (< 400 nm), related to the TiO2 intrinsic band gap absorption, ascribed to the electron promotion in the semiconductor from the valence band (VB) to the conduction band (CB), [9] and a prominent symmetric band centered at 530 nm corresponding to the Au plasmonic band. As expected, the optical band gap data in Table 1 showed a value of 3.04 eV for pure TiO2,[10] and lower energy values for this parameter in samples containing Au as the metal concentration increases. The absence of modifications in the BET area and XRD diffraction patterns suggests that Au is somehow in solid interaction with the TiO2 surface. Surprisingly, incorporating IL further decreases band gap values and increases pore volume, denoting the physical and electronic effects generated on the surface. This fact can be corroborated when the HER from methanol photo reforming (MPR) observed for pristine TiO2 is considerably low when compared with Au4@TiO2 (0.02 and 4.75 mmol per gram of catalyst per hour respectively). A calculated apparent quantum yield of 19.30 % displayed by Au4@TiO2 under UV (365 nm) is highly impressive, indicating that Au acts as a photocatalyst rather than a simple photosensitizer by an electronic influence over the system. After covering Au4@TiO2 with any of the studied IL, HER critically increases (up to 8.25 mmol. g-1.h-1 for IL2), thus confirming IL's electronic influence over the system. However, XPS and TGA measurements determined a decomposition process for IL1 and IL3 probably due to both IL’s hydrophilicity, which leads to interacting with aqueous media and TiO2 surface.



**Figure 1.** (a) Chemical mapping from Au4@TiO2 prepared nanomaterial showing the Au (red) and TiO2 (green) nanoparticles. (b) HRTEM micrograph of Au@TiO2 prepared nanomaterials.

**Table 1** Energy band gap with an indirect application of the Tauc plot and superficial parameters obtained for Au1-4@TiO2 as-prepared materials

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Catalyst** | **Egopt (eV)** | **BET surface area**  **m2g-1 (± 2)** | **Pore vol.**  **[cm3.g-1]** | **FAAS/PIXE**  **[% Au]** |
| TiO2 | 3.04 | 56 | 0.14 | - |
| IL2@TiO2 | 2.98 | 49 | 0.28 | - |
| Au1@TiO2 | 2.93 | 50 | 0.15 | 0.10 |
| Au2@TiO2 | 2.91 | 52 | 0.17 | 0.24 |
| Au3@TiO2 | 2.91 | 52 | 0.16 | 1.11 |
| Au4@TiO2 | 2.95 | 53 | 0.15 | 5.00 |
| IL2@Au4@TiO2 | 2.82 | 57 | 0.30 | 5.00 |

## Conclusions

Using the magnetron sputtering deposition and subsequent IL embedding fabrication methods, we have synthesized and fully characterized hybrids photo-dispositive type AuTi1-4 and IL@AuTi1-4. They has shown excellent catalytic performance for HER from MPR and chemical stability due to both direct IL-Metal-surface interaction. Comparative XPS, DRUV, and MS studies were leading to determine that the addition of ILs to the Au@TiO2 system can interact with both the surface of TiO2 and Au, shifting Bandgap and stablishing a modification of the Fermi level of the Au nanoparticle. This fact becomes more evident when adding a hydrophobic IL because of stability and resistance to leaching.

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