Development of Photon Up-conversion Materials Incorporated Photocatalysts for Hydrogen Generation using Visible light

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The rising worldwide energy demand, alongside the exhaustion of fossil fuels and the adverse environmental effects of their combustion, has necessitated an urgent quest for sustainable and renewable energy sources. Solar energy is a substantial, untapped resource. Nonetheless, the effective transformation of solar energy into useable fuels, such as hydrogen, still presents a difficulty due to the restricted sunlight absorption by traditional photocatalysts. Many semiconductors are available for photocatalysis, but their activity has been restrained significantly due to their high band gap ≥ 3.0 eV, high charge recombination process, site selectivity, etc. Herein, particularly to address this issue, we aim to develop efficient photocatalyst material by utilizing an up-conversion strategy. Upconversion materials possess the capability to absorb low-energy photons from the IR, NIR or visible spectrum and transform them into higher-energy visible or ultraviolet photons. Upconversion-incorporated photocatalyst enhances solar spectrum utilization and facilitates visible light-driven processes, providing a means for more efficient and sustainable hydrogen production.

Chapter 1: A brief review of visible light-assisted photocatalysis for the generation of hydrogen using semiconductor materials and the related difficulties has been provided in this chapter. The definition of upconversion materials, their production process, and all the steps involved in upconversion have all been covered. The working principles of the UC-integrated photocatalyst systems for visible light-based hydrogen generation, together with the thorough research procedures and results, have been briefly described.

Chapter 2: This chapter describes the in-situ production of a TiO_2 nanosystem incorporating an upconversion material ($CeF_3:Ho^{3+}$) using the polyol reduction process. The potential application for the production of photocatalytic hydrogen has been displayed. There has been evidence of photocatalytic activity in media that contain aqueous methanol as a sacrificial agent. When exposed to visible light, the $CeF_3:Ho^{3+}$ integrated TiO_2 nanosystem (CHT) exhibits enhanced photocatalytic activity, as evidenced by its peak hydrogen evolution rate (79.85 μmol h^{-1}). At peak rate, its apparent quantum efficiency (4.00%) and computed solar to hydrogen conversion efficiency (1.37%) demonstrated its promise as a potent photocatalyst. According to the results of wavelength-dependent photocatalytic studies, the process continues by absorbing energy at a broad range of visible light wavelengths, made possible only by the incorporation of UC material that converts visible light into ultraviolet light. XRD, UV-Vis, XPS, TEM, BET, and SEM studies confirmed the effective formation of the TiO_2-integrated up-conversion particle.

Chapter 3: The optimisation of synthesis parameters (usually precursors concentration) of the above-developed up-conversion semiconductor nanosystem (CHT) to maximise the efficiency of solar-to-hydrogen conversion is the focus of this chapter. The photoluminescence, conductivity, and dielectric have been evaluated in order to characterise their impact on up-conversion. A greater dielectric constant improves efficiency by reducing electron-hole recombination, which makes charge separation easier. On the other hand, low dielectric loss promotes effective charge transfer with reduced energy dissipation, improving electron transport to reaction sites. The optimisation procedure has produced particles with spherical and nanotubular shapes. It is concluded that the optimum concentration of fluoride results into desirable microstructure and effective photocatalysis.

Chapter 4: This chapter presents the synthesis of nitrogen-doped graphene oxide nanospheres (N-GONs) and their possible use in photocatalytic water splitting. Traditionally, this component has been derived via a "bottom-up" method. The N-GONs comprised nearly 14% nitrogen and 39% oxygen. The evaluated band gap of N-GONs is about 2.61 eV. N-GONs' valence and conduction band alignments, as established by UPS and XPS analyses, demonstrate their applicability for photocatalytic water splitting. N-GONs exhibit n-type semiconductor behaviour and a significant charge carrier density (1.12×10^{22} cm^{-3}) revealed by Mott–Schottky analysis. Usually, 1 g of N-GONs produced about 1.5 mmoles of oxygen in an hour. Notably, N-GONs found ineffective as semiconductor for hydrogen generation. The intrinsic mechanistic process has been demonstrated to validate and formulate the site selectivity of N-GONs using the RRDE technique.

Chapter 5: This chapter describes the synthesis of the $YAlO_3$ holmium (Ho^{3+}) and erbium (Er^{3+}) integrated SiC nanosystem (β-SiC@UC-50) and its possible use in the production of hydrogen under visible light. PL studies have provided a detailed explanation of the UC-50's up-conversion mechanism. Polydopamine-induced post-surface functionalisation of β-SiC@UC-50 (β-SiC@UC-50 _PDA) has been demonstrated. Measurements have been made in 0.1M Na_2S and 0.1M Na_2SO_3 electrolytic solutions for photocatalysis and photo electrocatalysis. The photocatalyst β-SiC@UC-50 exhibits approximately 3.94 times more hydrogen than β-SiC. Further, β-SiC@UC-50_PDA produced around 4.6 times more hydrogen than β-SiC when exposed to visible light, confirming the synergistic impact of polydopamine coating and UC integration. Furthermore, at 1.7 V vs RHE, β-SiC@UC-50_PDA exhibits the strongest transient photocurrent response, almost 2.9 times greater than that of β-SiC. Assessments have been made of the incident photon to current conversion efficiency (IPCE), Sun to hydrogen conversion efficiency (STH), and apparent quantum efficiency (AQE). This work offers a novel and promising method for using the wide fraction of solar for photocatalytic hydrogen production.

Chapter 6: The conclusions drawn from current research round up this chapter. Future prospects for the work have also been discussed, along with several significant recommendations.

Publication from the present work:

1. **A. K. Verma,** P. Tripathi, A. Dubey, N. K. Vishwakarma, A. S. K. Sinha*, S. Singh*, **"***Visible Light-Promoted Enhanced Photocatalytic Hydrogen Generation by the* $CeF_3:Ho^{3+}$ *Incorporated* TiO_2 *Nanosystem",* ACS Appl. Energy Mater. **2023**, 6, 5739─5752. (Featured on Front Cover Page)

2. **A. K. Verma,** P. Tripathi, Z. Alam, S. K. Mishra, B. Ray, A. S. K. Sinha*, S. Singh*, "*Photocatalytic Production of Oxygen by Nitrogen Doped Graphene Oxide Nanospheres: Synthesized via Bottom-Up Approach Using Dibenzopyrrole",* Willey ChemistrySelect **2022**, 7, e202202813.

3. **A. K. Verma,** P. Tripathi, A. S. K. Sinha*, S. Singh*, "*Upconversion Nanomaterial,* $YALO_3:Ho^{3+}/Er^{3+}$ *Integrated and Polydopamine functionalized* β-*SiC for Efficient Hydrogen Production utilizing Visible Light."* (**2024)** (under publication)

4. **A. K. Verma,** P. Tripathi, A. S. K. Sinha*, S. Singh*, "*Optimization of Synthesis Parameters of Up-Conversion-Semiconductor Nanosystem (*$CeF_3:Ho^{3+}/TiO_2$*) to Achieve Maximum Solar to Hydrogen Efficiency."* (**2024)** (under publication)

5. **A. K. Verma,** P. Tripathi, A. S. K. Sinha*, S. Singh*, *Sustaining Sub-bandgap Photons via Upconversion for Solar Splitting Cells*, Intechopen Publishing, (ISBN: 978-0-85466-880-9), **2024**, 227 – 246. (Book Chapter)