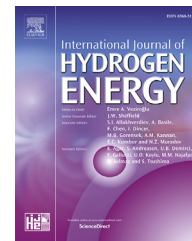




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Chloride ion: A promising hole scavenger for photocatalytic hydrogen generation

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ABSTRACT

The investigation pertains to elucidation of promising role of in-situ chloride ions generated during the photoreduction of HAuCl_4 as an internal sacrificial donor for photocatalytic hydrogen generation. The hydrogen evolution rate (HER) observed was 4.16 mmol h^{-1} using in-situ route of photocatalyst formation which is significantly higher than the conventional route of formation of recovered photocatalyst. This unreported and unprecedented enhancement is explained on the basis of role of chloride ions released from the gold precursor. Experimental data inferring the effect of chloride ions on photocatalytic hydrogen generation using Au-TiO_2 are also briefly explained. The role of anionic sacrificial donors suggests several potential possibilities for their applications in photocatalysis considering their presence in wastewater as well as their low cost and abundant availability. The work also introduces one-step photodeposition and hydrogen generation process against traditional recovered photocatalyst, wherein the catalysts were prepared first by normal route of photodeposition, recovered and then employed for hydrogen generation.

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Introduction

Since pioneering work of Honda-Fujishima, scientists around the world are greatly attracted toward semiconductor photocatalysis to generate hydrogen from the water splitting reaction [1,2]. Recent work of article [3,4] showed enhanced photoelectrochemical properties using In-situ route synthesized $\text{CdS/CdWO}_4/\text{WO}_3$ & $\text{BiVO}_4/\text{WO}_3$ heterojunction film respectively. Another articles [5] introduced Bi_2S_3 nanowire@ TiO_2 nanorod for photoelectrochemical hydrogen generation. A large number of materials have been reported for photocatalytic water splitting reaction. However, rapid electron-hole recombination restricts the performance of

TiO_2 and other potential semiconductors [6]. This limitation can be overcome by adopting various techniques [7] like addition of organic-inorganic electron donor [8], metal ion doping [9,10], noble metal loading [11,12] non-metal doping [13,14] etc. In spite of extensive work in this area for three decades, there is very less development in the overall water splitting and use of sacrificial donor still persists as an essential practice. The donors explored so far are both organic and inorganic species such as ethanol [15], methanol [16], propanol [17], lactic acid [18], formic acid [19], formaldehyde [19], carbonate salts [20], $\text{S}^{2-}/\text{SO}_3^{2-}$ [21], $\text{Ce}^{4+}/\text{Ce}^{3+}$ [22] and IO_3^-/I^- [23] shuttle redox mediator etc. All these donors are very effective and peculiarly improve hydrogen output. However, the

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addition of these donors can also contribute to the hydrogen production with their consumption in the system. Excess use of donor alters the mechanism to solvent reforming as a major reaction instead of water splitting. The recent articles reported on hydrogen [24–32] mostly focuses on hydrogen production, their kinetics and storage using metal hydride based thermal system. The other articles which approaches one step method towards hydrogen production [33,34] are also based on thermal dehydrogenation which requires very high temperature. These reports unambiguously indicate that there is a need for the simple water splitting and hydrogen generation system, which produces better hydrogen output.

The earlier work of photocatalytic water splitting mostly relies on the sacrificial donor based system and very few researchers have reported on the halogen based sacrificial donor system. Recently Lei Huang and coworkers [35] studied pure water splitting with Cl–TiO₂ prepared by hydrothermal method and proved with XPS study that, Cl[–] can be easily adsorbed on the surface of titania. Yang Shi-ying et al. [36] reported photo-degradation of organic species by chloride ion. Lee et al. [37] reported photocatalytic hydrogen generation by using cyanide ions as a sacrificial donor. Alternatively, Luo et al. [38] reported Br and Cl doped TiO₂ for enhanced photocatalytic activity. To the best of our knowledge, this is the first time we have reported the effect of chloride ion released from gold precursor during in-situ photodeposition as an internal sacrificial donor for photocatalytic hydrogen generation. In this work, photocatalyst Au–TiO₂ was used merely to understand the effect of chloride ions released from metal salt solution. One can consider metal salts such as H₂PtCl₆, CuCl₂, CoCl₂ and metal oxides Ga₂O₃, Fe₂O₃, CuO, CeO etc. This concept of chloride ion effect applies to all the metal salts for the effective reduction of metal ions to the metal on the surface of metal oxide and simultaneous hydrogen generation. Further investigation on this topic using different metal salt, including bi-metals and metal oxides is in progress in our laboratory.

With this research, we have attempted to present study on the effect of chloride ions released during the photoreduction of HAuCl₄ on the photocatalytic hydrogen generation. In photocatalytic hydrogen generation, Au nanoparticles (NPs) deposited on the surface of TiO₂, are reported to be very effective [39], and was therefore selected for this study. In this study, two Au–TiO₂ photocatalysts were synthesized through two different routes mainly to ensure the presence and absence of chloride ions for subsequent photocatalytic hydrogen generation reaction - i) in-situ photodeposition without recovery of catalyst and ii) photodeposition with the recovery of catalyst. Both the catalysts are re-designated as AuTiO₂-IS and AuTiO₂-RC respectively. The photocatalytic activities of these photocatalysts were evaluated in terms of hydrogen generation to especially study the effect of available chloride ions as a sacrificial donor.

Experimental section

Photocatalyst preparation

Chemically pure Titania (TiO₂/P-25) was purchased from Aeroxide, chloroauric acid (HAuCl₄.3H₂O) and ethanol used

were from Merck. All chemicals were used as received and solutions were prepared in deionized H₂O. The photocatalyst AuTiO₂-RC was synthesized by the simple photodeposition method. In both the experiments, chloroauric acid was used as a gold precursor. In AuTiO₂-IS experiment, chloroauric acid was dispersed in water and used directly with Titania (TiO₂/P-25).

The details of the two synthesis procedures are given below.

Synthesis of recovered photocatalyst

A known amount of chloroauric acid (metal salt) containing 50% assay was dissolved in the 100 ml of deionized water and used as a gold precursor. This Au precursor (1% w/w) with 150 mg of titania (metal oxide support) was added in a triple jacketed photoreactor containing water and ethanol in the ratio of 10:0.5. This reaction mixture was flushed with inert gas for half an hour, then illuminated using UV–Vis light of 450 W medium pressure mercury lamp (ML) as a radiation source. This radiation source has wavelength maxima at 265, 297, 313, 365, 404, 453 & 546 nm. The colour shades of the reaction mixture were observed to change from yellow to purple during the process. The subsequent mixture was centrifuged and washed with alcohol. Finally, recovered catalyst dried at 60 °C under reduced pressure.

This prepared AuTiO₂-RC catalyst was then employed for hydrogen evolution experiment separately.

Synthesis of in-situ photocatalyst

The in-situ photodeposition of the photocatalyst was implemented by using similar setup and apparatus described above in Section 2.1.1. However, in this case, a mixture of TiO₂ (150 mg), water, ethanol and 1% gold precursor irradiated directly with ML light for simultaneous photodeposition as well as hydrogen evolution experiment instead of recovering the photocatalyst separately as in recovered method. The photocatalyst was recovered only after completion of evaluation process with a subsequent centrifuge and drying to carry out the analysis of the in-situ sample (spent material). The spent liquid collected after centrifugation was used for the confirmation of chloride ions using analytical titration method.

Characterization & analysis

The characterizations of two samples AuTiO₂-RC (without chloride) and IS (with chloride) were performed to examine the role of chloride ions (released during the photoreduction of HAuCl₄) on the photocatalyst. The optical absorption study of the materials was performed using Agilent Cary 5000 UV-VIS-NIR spectrophotometer with a dedicated DRS facility. The scanning range used was between 200 nm and 800 nm and standard PTFE was used as a reference. The XRD patterns of both samples recovered and in-situ were collected by using Rigaku Miniflex-II X-ray diffractometer equipped with Cu K α radiation ($\lambda = 0.15406$ nm), in a 2θ range of 10–90°. The scanning type maintained was continuous with step width 0.02 and scan speed of 1 °C/min. The standard database diffraction patterns were used as a reference to compare spectra obtained. Transmission Electron Microscopy (FEI TECNAI G2 F20,

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