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A review on the recent advances in the design and structure–activity relationship of TiO_2-based photocatalysts for solar hydrogen production

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The major issues that determine the efficiency of photocatalyst composite materials for solar hydrogen production, with or without a sacrificial agent, are efficient visible light harvesting properties, efficient separation of charge carriers and their utilization of redox sites, and stability. Thus, significant efforts have been devoted in the past few decades to modify the above characteristics by integrating constituent components of composites using different approaches. In the present review, we aim to summarize the recent advances, predominantly, in the area of TiO_2-based photocatalyst composites for solar hydrogen production. Firstly, we present the recent progress in material integration aspects by discussing the integration of TiO_2 with different categories of materials, including noble/3d metals, metal oxides/sulphides/selenides, other low bandgap semiconductors, C-based materials, and dye sensitizers. Furthermore, we discuss how material integration helps in tailoring the electronic and optical properties for activity tuning in solar H_2 production. Subsequently, critical changes in the physico-chemical and electronic properties of composites with respect to their preparation methods, morphology, crystallographic facets, particle size, dopant, calcination temperature, and structure–activity relationship to solar hydrogen production are addressed in detail. Moreover, we discuss the importance of fabricating a photocatalyst in a thin film form and performing solar hydrogen production in different reactor set-ups for enhancing its photocatalytic performance, while addressing device scalability. Despite the significant advancements made in this field, solar-to-hydrogen conversion efficiency still needs to be improved to realise the practical application of solar hydrogen production. In this case, the direct conversion of water to hydrogen *via* overall water splitting and renewable H_2 production from wastewater or biomass components by employing suitable photocatalysts are some possible ways to improve the energy efficiency, and continuous research in the above directions is highly desirable.

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1. Introduction

The steadily increasing demand for energy due to population growth and industrialisation poses a serious concern owing to the depletion of fossil fuels (oil, gas and coal), which account for >85% of energy production and currently the major source of energy.[1,2] Besides the general consensus on limited fossil fuel reserves, the combustion of fossil fuels leads to the emission of CO_2 and other harmful gases, which is a major issue resulting in an almost irreversible change in the atmosphere and thus drastic climate changes. In this case, carbon-free hydrogen production *via* water splitting, with and without a sacrificial agent, in the presence of a semiconductor utilizing solar energy is a renewable process and is considered a promising alternative for an economically and socially sustainable future to meet the increasing energy demand.[3] Given that the overall water splitting reaction for H_2 production is an uphill reaction with a positive Gibbs free energy of 238 kJ mol^{-1}, a photocatalyst that can efficiently harvest solar radiation is essential to make the reaction process energetically and economically feasible.[2] Accordingly, different semiconductor materials, such as TiO_2, Cu_2O, Co_3O_4, CdS, and $ZnIn_2S_4$, have been examined to evaluate their potential as photocatalytic materials in the water splitting reaction to produce hydrogen.[4] Recently, poly(heptazine imide) ionic carbon nitrides are another emerging class of photocatalytic materials applied for hydrogen evolution.[5] Among the various photocatalytic materials, TiO_2 has been an extensively studied semiconductor material due to its several advantages, such as availability, low cost, interesting physico-chemical properties, non-toxicity, environmentally friendly nature, feasible synthesis at low temperatures, amenability to integration with different materials, and high chemical and photostability.[6]

Since the potential of TiO_2 for the photolysis of water was revealed by Fujishima and Honda for the first time in 1972,[6] its performance has been widely explored for a variety of applications, such as photocatalytic degradation of pollutants,[7] supercapacitors,[8] solar cells,[9] carbon dioxide reduction,[10] lithium-ion batteries,[11] biomedical devices,[12] self-cleaning,[13] and water splitting.[14] However, the wide bandgap (3.2 eV) of TiO_2 restricts its light-harvesting ability to mainly the UV region (which is ~5% of sunlight), and the fast recombination of photo-generated electron–hole pairs in bare TiO_2 limits its photocatalytic functionality.[6] Thus, to overcome the above-mentioned inherent drawbacks of TiO_2 and enhance its photocatalytic performance for solar H_2 production, significant efforts have been devoted to designing catalysts, such as doping with metals and non-metals,[15,16] dye sensitization,[17] use of noble metals (Pt, Pd, Au and Ag) as a co-catalyst,[18] engineering the band structure to match particular energy levels,[19] and fabrication of semiconductor heterojunction and/or Schottky junctions.[20]

In the past few years, several excellent review articles have been published on photocatalytic water splitting for hydrogen production, which are based on different catalyst systems including semiconductor-based catalyst systems,[21,22] metal-free photocatalysts,[23] spinel materials,[24] ionic carbon nitride,[25–28] carbon-based materials,[29] transition metal complexes,[30] and TiO_2-based semiconductor materials.[31–36] Also, although there are few reviews available on TiO_2-based photocatalysts for solar hydrogen production,[31–36] they emphasized the general aspects of photocatalytic H_2 production. Thus,

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