Factors affecting the efficiency of a water splitting photocatalyst: A perspective

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ABSTRACT

To design an efficient photocatalyst (PC) for semiconductor (SC)-mediated, solar-driven water dissociation to generate hydrogen, a host of strategies has been adopted, including the fabrication of semiconductor composites, substitution of impurities for achieving extended absorbance, and coating with a metal to promote charge transfer. Despite these efforts, a photocatalyst exhibiting requisite efficiency has not been developed. This article reviews the factors governing the water splitting photoactivity of an SC material, and provides an account of our recent research on this subject. As per our investigations, the mode of adsorption of the water molecules on the semiconductor surface and their subsequent interaction with the charge carriers play a crucial role in the overall performance of a water splitting photocatalyst, rather than the much-discussed SC→SC or SC→metal charge transfer effects alone. The water–to-SC binding is controlled by a combination of several physicochemical properties of a composite PC, such as the preparation-dependent grain morphology, doping-affected grain nucleation, pore structure-dependent water adsorption/desorption kinetics, exposure of specific facets, and SC/SC or SC/metal interfacial characteristics. Our studies revealed strong particle size dependence and the facet-based sensitivity of modified metal sulfide and metal oxide photocatalysts. Additionally, the effect of lattice impurity on quantum efficiency of wide gap metal oxides, such as TiO_2, In_2TiO_5, $InVO_4$, $FeNbO_4$, $GaNbO_4$, $GaFeO_3$, and $LaInO_3$, is related to the lattice-defect-induced intra-bandgap energy levels rather than the doping-induced extension of visible region absorbance. Furthermore, the dispersed gold nanoparticles served as distinct reaction sites over the surface of a TiO_2 photocatalyst besides their contribution to the plasmonic effect. Our study revealed that under certain spectral overlap conditions, the inter-semiconductor charge transfer might cause quenching of the water splitting photoactivity of a composite photocatalyst. We surmise that considering the aforementioned factors should assist in designing an efficient water splitting PC, eventually triggering technological advancements in this field.

1. Introduction

The depletion of fossil fuel reserves has driven extensive research efforts toward the use of H_2 as a sustainable energy carrier for the post fossil fuel regime. Semiconductor-mediated and solar-driven photo-catalytic dissociation of water, which was discovered in 1972, is a unique approach for producing H_2 by utilizing abundant natural resources [1]. The enormous number of review articles/perspectives published over the past decade reflects the significance of this area. A large range of photocatalytic materials such as metal oxides, metal sulfides, metal (oxy) sulfides, metal/non-metal nitrides, and metal (oxy) nitrides containing a cation with d^0 or d^{10} configuration have been investigated for this application and reviewed for their efficiency

[2–6]. Titanium dioxide (TiO_2) and its morphological variants are the most investigated photocatalysts for photosplitting of water and for environmental remediation by photooxidation of organic contaminants [7–12]. Besides TiO_2, a large number of metal oxide systems, such as ferrites [13], perovskites [14,15], vanadates [16], niobates [17], Fe_2O_3[18,19], Ag_3PO_4[20], and the oxides of Bi, Ta, La, Co, Ni etc. [21–24], have been investigated for their water splitting photocatalytic activity. Among the non-oxide photocatalysts, metal sulfides [25–28], metal nitrides [29], oxy-nitrides [30,31], and several carbon-containing materials [32–35] constitute a group of prominent materials for this application. The preparation strategies and the design principles for the fabrication of water splitting catalysts have been reported [36,37]. The prerequisites for a material to serve as an efficient photocatalyst, e.g.

effects of the particle size [38–40], surface properties [41–43], microstructure [44,45] of the catalysts as well as the charge transfer dynamics of the water photodissociation process [40,46], were reviewed. However, an ideal water splitting photocatalyst having the requisite band characteristics, viable quantum efficiency, and long-term photo-corrosion resistance is yet to be developed. Hence, a detailed investigation was carried out in our laboratory to delineate some of the hitherto overlooked physicochemical, photophysical, and microstructural properties of a photocatalyst that might limit its overall water splitting activity. Our studies on highly dispersed CdS and CdS-ZnS nanocomposites revealed that similar to the well-reported heterogeneous catalytic reactions occurring over the single crystal or nanostructured metal surfaces, photocatalytic splitting of water is a structure-sensitive process, wherein the critical particle size and certain microstructural defects at the semiconductor/substrate interfaces play an important role [47–50]. Thermally stimulated luminescence, photoluminescence, and Raman spectroscopy were employed to demonstrate the effect of particle texture, sample porosity, and presence of certain impurity-induced closely spaced intra-bandgap energy levels on the photocatalytic water splitting activity of conventional TiO_2[51] as well as several mixed metal oxides [52–57]. Thermal desorption spectroscopic investigations revealed that besides the plasmonic resonance effect, the presence of nanosized gold particles may provide certain low-energy surface sites, thus assisting the adsorption of the reactant molecules and their subsequent interaction with photo-generated charge carriers [58–61]. Rietveld refinement of XRD data provided unequivocal evidence to support the crucial role played by the doping-affected particle nucleation and hexagonal/cubic phase ratio in the photoactivity of CdS photocatalysts [62,63]. Our findings thus indicate the need for a detailed examination of the water splitting process, in order to achieve the synthesis of an efficient photocatalyst. This article presents an account of our research, highlighting the materials aspects such as microstructure, crystal structure, morphology, and the surface characteristics of semiconductor nanoparticles. Initially, the fundamental aspects of relevance are briefly described.

2. Basic aspects

The dissociation of pure water to form H_2 and O_2 is an endothermic reaction, which involves a high positive Gibbs free energy change (ΔH^0=286 kJ mol^{-1}). Accordingly, H_2 and O_2 can be produced in high yields from the thermal dissociation of water at temperatures exceeding ~2070 K [64]. This reaction can be carried out under ambient conditions by employing a photocatalytic process, i.e., over the surface of a semiconductor under irradiation-facilitated bandgap excitation.

Photocatalysis is a heterogeneous catalytic reaction initiated by excited electrons and holes that are generated by the absorption of photons in a semiconducting material serving as a photocatalyst (PC). These photogenerated charge carriers in turn interact with the reactant molecules adsorbed over the PC surface to form certain ionic or free radical transient species, eventually leading to the formation of products. Thus, a photocatalytic process involves the reaction between the excited electrons or holes with the surface-adsorbed reactant molecules, leading to a reduction or oxidation reaction, respectively. The photosplitting of water involves two half-reactions: the oxidation of water to form O_2 and the reduction of protons to form H_2[6,65].
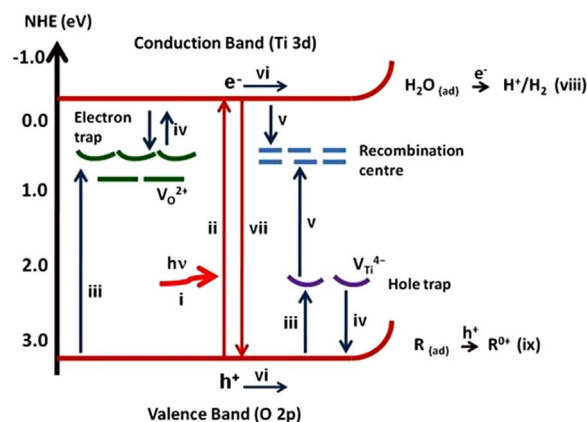
Photooxidation

$$H_2O + h^+_{vb} \rightarrow 2H^+ + ½\ O_2 \qquad (1)$$

Photoreduction

$$2\ H^+ + 2e^-_{cb} \rightarrow H_2 \qquad (2)$$

Overall water dissociation reaction:

$$H_2O \xrightarrow{TiO_2/hv} H_2 + ½\ O_2 \qquad (3)$$

Fig. 1. A schematic representation of the possible energy transfer processes occurring with the photoexcitation of a wide-bandgap material TiO_2 (bandgap ~3.2 eV). (step i) Exposure to incident radiation; (step ii) photo-absorption leading to e⁻/h⁺ pair generation; (step iii) trapping of e⁻/h⁺ at defect/impurity induced intra-bandgap energy levels; (step iv) detrapping of charges on thermal- or photo-stimulation; (step v) recombination of e⁻/h⁺ pair accompanied by photo- or thermo-luminescence emission; (step vi) transport of charges to adsorbed target molecule, a composited SC or a dispersed metal site; (step vii) excitonic recombination. Steps viii and ix represent the electron-induced photoreduction of water and photooxidation of an organic electron donor molecule (R), respectively. V_O^{2+} and V_{Ti}^{4-} correspond to the energy levels associated with the vacancies at oxygen ion and titanium sites of TiO_2 lattice, respectively.

However, radiative and non-radiative recombination of excited charge carriers might occur at a significantly shorter time scale of femto- to microseconds, thereby limiting the quantum efficiency. Moreover, the photogenerated carriers could interact with the lattice and surface defects as well as with an impurity substituting the lattice sites of a semiconductor photocatalyst. Fig. 1 presents a schematic diagram illustrating different photoprocesses that may occur with the bandgap excitation of a wide bandgap semiconducting material such as TiO_2 or $FeNbO_4$[52].

Sections 2.1–2.4 in the following text give a brief introduction of the steps mentioned in Fig. 1, and their role in determining the performance of a photocatalyst in the overall water photosplitting process. Our discussion is restricted to particulate photocatalytic systems, where the photocatalyst exists in the form of water-suspended powder particles rather than being coated over an electrode surface in a photo-electrochemical cell configuration.

2.1. Interaction of photons with a semiconducting material (step i): role of surface texture and particle morphology

With electromagnetic radiation interactions, an SC material might exhibit reflection, absorption, and transmission, depending on its band structure [66]. These optical processes are schematically illustrated in Fig. 2. The reflection of the incident radiation occurs when it is scattered at the interface between two media. Reflectivity, R, which is the measure of the fraction of incident photons reflected at the interface, is given by

$$R = I_r / I_0$$

where I_0 and I_r denote the intensity of the incident and reflected beams, respectively. The value of R depends on the index of refraction of the material under irradiation and the angle of incidence (θ).

The absorption of radiation is related to the material thickness (x) as per *Bouguer's law*, i.e.

$$I = I_0.\exp(-\alpha.x)$$

where I_0 and I denote the intensity of the incident and transmitted radiation, respectively, and α is the linear absorption coefficient of a particular material.

The intensity of the absorbed photons can be expressed as