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Tungsten-based oxide semiconductors for solar hydrogen generation

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ABSTRACT

In this focused review the progress achieved in solar water splitting over tungsten based oxide photocatalysts is summarized. Beyond simple doping of WO_3, both binary and ternary oxides are discussed, presenting the various synthesis methods and resulting crystal structures. Theoretical considerations on the band structure are also given including a perspective on possible strategies for band engineering. The effectiveness of such strategies for designing tungsten-based oxide semiconductors as robust photocatalysts for stoichiometric solar water splitting, is reviewed. In addition, progress on Z-scheme based strategies using combined photocatalysts, where WO_3 is responsible for water photooxidation (O_2-evolution) while H_2 generation takes place on its counterpart, is also reviewed.

1. Introduction

Finding adequate solutions for a diversified and sustainable energy supply constitute one of the biggest challenges our society faces today. Enormous efforts are devoted to discover new materials and methods to exploit the theoretically unlimited sources of renewable energy. A solar-based hydrogen economy [1] is one such pathway although many challenges remain before widespread use of this energy carrier is feasible for residential use, and for transportation. It is worth mentioning that during the past decades many conceptually different processes for hydrogen production have been developed, including reforming, pyrolysis, electrolysis and other methods [1,2].

Although there are numerous routes for H_2 generation, from the overall energy payback perspective (to be discussed later) one of the most promising methods is solar water splitting [3]. Moreover, beyond its cost effectiveness, this process is environmentally friendly, carbon neutral, and can be implemented by utilizing renewable (solar) energy. In such a process, upon excitation of an electron from the valence band to the conduction band (by UV or visible light irradiation), the separated charge carriers are driven to the surface of the semiconductor and react with water (or other aqueous species including sacrificial reagents). The water splitting ability of the photocatalyst is dictated by the energy of the valence band (VB) and conduction band (CB) edges: the former has to be more positive than that of O_2 evolution and the latter has to be more negative than H_2 evolution [4]. Since the pioneering paper by Fujishima and Honda [5] demonstrating solar water splitting by a semiconductor photocatalyst (specifically TiO_2), this research field has grown rapidly, as seen from the exponential growth of published articles [6].

The main drawback of TiO_2 is its relatively large bandgap (3.2 eV) and consequently, only a small fraction (~5%) of the overall solar spectrum can be harnessed by this material. Motivated by this fact, tremendous efforts have been devoted both to sensitize TiO_2, and to find alternative semiconductors possessing similarly favorable properties, but having a narrower optical band gap. Moreover, it is generally accepted that several other parameters, which are directly related to the band structure of the materials, affect the efficiency of the photocatalyst, such as carrier transport, surface properties, chemical- and photo-stability. A wide range of semiconductor photocatalysts have been examined, and numerous reviews are available on this body of research [7–9]. The semiconductors can be classified into the following groups on the basis of their electronic configuration:

- d^0 metal (Ti^{4+}, Zr^{4+}, Nb^{5+}, Ta^{5+}, W^{6+} and Mo^{6+}) oxides,
- d^{10} metal (In^{3+}, Ga^{3+}, Ge^{4+}, Sn^{4+} and Sb^{5+}) oxides,
- f^0 metal (Ce^{4+}) oxides,
- non-oxide semiconductor photocatalysts.

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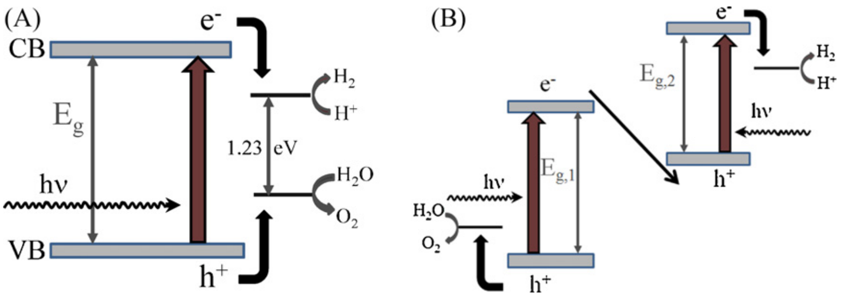

Fig. 1. Illustration of the one photon (A), and the two photon (Z-scheme) water splitting (B), on a single and a dual semiconductor photocatalyst, respectively.

Since it is rather challenging to synthesize a single semiconductor oxide which fulfills the multiple requirements mentioned above and is active for both H_2 and O_2 generation, a concept mimicking natural photosynthesis, namely the so-called Z-scheme has been introduced [10]. This scheme involves a complex system consisting of a H_2-evolving catalyst, an O_2 evolving catalyst and often, an electron mediator. The main advantage of such an assembly lies in the availability of a large variety of possible combination of narrow bandgap photocatalysts which are active either for O_2-evolution or H_2-evolution. One more important difference between the two approaches is the photon to H_2/O_2 conversion ratio, since while on a single particle photocatalyst the absorption of one photon results in an e^-–h^+ pair, in the Z-scheme, 2 photons generate a pair of excitons which are involved in the two photocatalytic reactions as depicted in Fig. 1.

In this review we focus on one particular segment of this broad field within the d^0 metal oxide group (see above), namely tungsten-based oxide semiconductors and their composites. Tungsten trioxide (WO_3) is an excellent photocatalyst for water oxidation (oxygen evolution), as was already demonstrated by Butler et al. in 1976 [11]. Furthermore, tungsten oxide shares many of the same attributes with TiO_2 in terms of chemical inertness and exceptional photo- and chemical stability in acidic to semi-acidic aqueous media over a relatively wide pH range (pH < 8). Moreover, as pointed out very early in the history of study of this material the lower E_g value of WO_3 (2.7 eV vs. 3.2 eV for TiO_2) results in more substantial utilization of the solar spectrum. Since the first report, numerous studies investigated the photocatalytic properties of WO_3, however, no spontaneous hydrogen formation was observed (neither under visible light nor ultraviolet (UV) light irradiation) because of its lower CB location with respect to the H^+/H_2 redox level [12].

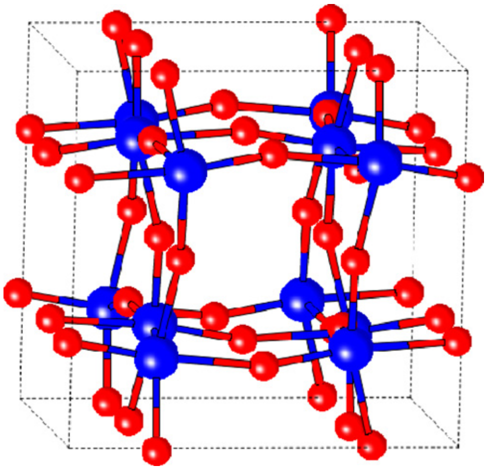

Fig. 2. Monoclinic structure of WO_3 unit cell, where W and O atoms are represented by blue and red balls, respectively.

Therefore, as reviewed below, much effort has been made to perform photocatalytic hydrogen evolution via tuning of the electronic structure of WO_3, while retaining the excellent performance of this material in photocatalytic oxygen generation. These achievements are reviewed from the materials perspective, addressing both W-containing single oxide semiconductor photocatalysts and combined systems (Fig. 1). In contrast, it is important to emphasize that we omit studies where WO_3 or other tungstates were only applied for water photooxidation with no concomitant H_2 generation. Further, *photoelectrochemical* (PEC) H_2 generation, i.e. when an external bias is applied, is not emphasized in what follows. It is worth noting that many publications use the terminology: "stoichiometric water splitting" when a photocatalyst is able to evolve both O_2 and H_2 in 1:2 ratio from an aqueous solution. Close examination however reveals, in most of these cases, sacrificial agents are utilized, containing an electron or hole scavenger such as Ag^+ or methanol, respectively.

2. Theoretical considerations

Motivated by the above mentioned advantageous properties of WO_3, various derivative oxide compounds have been synthesized with the purpose of having a CB shifted more negative than H^+/H_2, in order to achieve spontaneous photocatalytic hydrogen evolution. In addition, rational band engineering can also increase the visible light sensitivity of such tungsten based oxides [13]. Before discussing different approaches successfully utilized to modify the electronic structure of WO_3, it is important to give an overview on the bare oxide material itself, both from the crystal- and electronic-structural viewpoint.

The monoclinic WO_3 can be considered as a deformed perovskite structure, such as ABO_3 where the A ions are missing and B is replaced by W. The smallest monoclinic unit cell of WO_3 consists of 8 W atoms and 24 O atoms, where the W atoms are sixfold coordinated. The WO_3 structure can also be considered as consisting of W—O—W-like chains, where the chains are connected across the W atoms, as shown in Fig. 2. This pseudo low-dimensional structure of WO_3 has given rise to many interesting properties, including superconductivity. The inter-chain O—O interactions are rather weak.

From the band structure in Fig. 3, calculated by local density approximation of density functional theory (LDA-DFT), two nearly degenerate states are seen at the conduction-band minima (CBM). For details of the computational methodology, see Ref. [13]. The valence-band maxima (VBM) states at Γ point also split due to the distorted arrangement of the W—O octahedrons. Also, at $B \rightarrow \Gamma$, the top of the valence band is flat. This dispersionless band indicates very high effective masses for the holes along the W—O—W chain in the x-direction, which constitutes tightly bound core-like electronic behavior along that direction on the zone boundary. Similar high effective masses were found for electrons in the $\Gamma \rightarrow Z$ direction. This has some interesting consequences for the electronic