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Recent advance on engineering titanium dioxide nanotubes for photochemical and photoelectrochemical water splitting

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ABSTRACT

Photochemical and photoelectrochemical water splitting is both an attainable and sustainable strategy for generating environmentally friendly energy sources. One-dimensional (1-D) TiO_2 nanotubes is a promising photochemical/photoelectrochemical material due to the general availability, low-cost, chemical stability, large surface-volume ratio and straight electron transfer pathway. In this paper, we present recent progress on hydrogen evolution through water splitting by using 1-D titanium dioxide nanotubes (TNTs) as photoelectrode materials. The basic principles behind the technology of photochemical water splitting are discussed, such as light absorption, suppressing charge recombination, modifying redox potential as well as increasing stability, followed by engineering consideration and design of the 1-D TiO_2 nanotube photo-anodes. The links between photochemical properties of nanostructured TiO_2 and H_2 conversion are discussed. Meanwhile, rationally orienting the nanostructured TiO_2 in chemical reactors for hydrogen conversion and engineering prospects are highlighted for potential development.

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1. Introduction

Nowadays, hydrogen has become commonly acknowledged to be a pollution-free energy source which is storable with high energy density. 95% of the hydrogen for commercial use is derived from water electrolysis [1], where a large amount of electric energy is required. As a result, searching for a cost-effective and sustainable strategy to produce hydrogen is urgent. At this point, taking advantage of the abundance in solar energy for hydrogen production has attracted significant attention.

Photochemical (PC) water splitting for hydrogen production using semiconductor materials dates back to 1972 [2]. Based on the photochemical mechanism, overall water splitting requires that the photocatalysts must have a band gap of at least 1.23 eV (thermodynamic potential for water splitting) and band edge potentials straddling hydrogen and oxygen redox potentials. However, overpotential due to slow reactions and resistances in the system increases the energy required to drive the reaction to 1.6–2.4 eV [3]. Fig. 1 lists the band edge distribution of common semiconductors and work function of ITO (Indium Tin Oxide)/ FTO (Fluorine-doped tin oxide) glass and noble metals compared to hydrogen and oxygen redox potentials [4–7]. Semiconductors in the blue group readily show their applicability and have therefore been intensively studied for water splitting [8–12]. Those shown in the green region have to be chemically modified before utilized in a water splitting system due to their unsuitable band edges. In addition to these basic requirements, several key criteria must be fulfilled for PC water splitting process [13]: (1) sufficient light absorption: bulk band gap of the semiconductor material must absorb a significant portion of the solar spectrum; (2) quick charge separation: photogenerated electron/hole pairs (e^-/h^+) are separated and transmitted to their respective reaction sites; (3) low redox potential: charge transfer from the surface of semiconductor to the solution must be facile to minimize energy losses due to kinetic overpotential and selective for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER); (4) good stability: the system must exhibit long-term stability against corrosion in aqueous electrolytes. To date, research groups from different discipline around the world are exploring new material systems to meet all these criteria..

Photoelectrochemical (PEC) water splitting is in principle the same as PC water splitting [14]. To be more general on the concept, PEC cell can be considered as one of the configurations for PC water splitting. These two systems are in accordance with each other regarding to the mechanism of splitting water. The difference is that both HER and OER half-reactions happen in the suspending photocatalyst particles in the suspension system, resulting in evolution of a mixture of oxygen and hydrogen. On the contrast, water redox reaction in the PEC system are performed on two different surfaces (photoanode and photocathode) respectively, which in large extend simplifies the subsequent gas separation process and promotes engineering production of hydrogen or oxygen. In addition, it is possible to include a low potential bias in a PEC cell configuration so that the reaction can happen more efficiently under the combined action of photons and electrons.

Among the semiconductor materials, titanium dioxide (TiO_2) is one of the earliest and most extensively studied candidates for water splitting. Actually, the semiconductive oxide has widely used for solar cells [15,16], gas sensor [17,18], water splitting [2] and biological applications [19,20] due to its strong chemical stability against photo-corrosion and abundant reserves on the earth. The working principles of TiO_2 based PC water splitting are associated with generation, transportation and recombination of photo-induced electron-hole (e^-/h^+) from semiconducting TiO_2 under direct light illumination. However, large band gap and low photoconductivity limits the photochemical activities of TiO_2 material. Thus intrinsic semiconductive properties of the material have to be improved for increasing photoactivities under solar illumination [1,21–23].

Conventional TiO_2 nanoparticle (NP) is unfavorable for photocatalysis applications because the possibility of recombination of photo-induced e^-/h^+ pairs is very high [24–26]. The discovery of 1D nanostructures in the 1990s has helped to solve the problem. TiO_2 nanotubes (TNTs) were first time synthesized by Hoyer [27] using a template-assistant method. This ground breaking work was followed by Kasuga [28] and Zwilling [29,30] who prepared nanotubular structures by hydrothermal treatment and electrochemical anodization methods, respectively. The resulting unique hollow 1D nanostructures exhibit high electron mobility and quantum confinement effects, large specific surface area, and even high mechanical strength [31,32]. Most importantly, by using electrochemical anodized TNTs, straight forward pathways were provided for fast electron transportation through self-assembled nanotube walls. The as-prepared anodized TNTs are ready to be used as a photoelectrode in PEC cell water splitting system due to its one-piece (free standing membrane or attached to Ti foil) appearance. TNTs fabricated by hydrothermal treatment, on the other hand, appears to be geometrically randomly distributed and is ideal for forming an aqueous suspension system. To date, neither of the aforementioned synthesis process is clear, but there have been several advanced theorems which we can refer to [32–35].

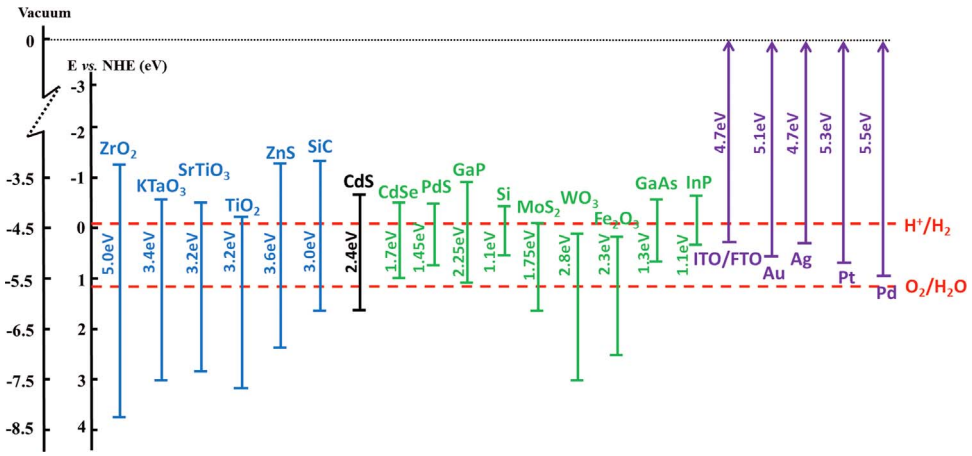

Fig. 1. Diagram of energy levels. Energy levels of commonly used semiconductors (blue, black and green), noble metals (purple) and redox potential of splitting water into H_2 and O_2 (red). [4–7].

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