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Review

Heterostructures construction on TiO_2 nanobelts: A powerful tool for building high-performance photocatalysts

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ABSTRACT

Semiconductor photocatalysis is a promising approach to combat both environmental pollution and the global energy shortage. Advanced TiO_2-based photocatalysts with novel photoelectronic properties are benchmark materials that have been pursued for their high solar energy conversion efficiency. Among the different morphological TiO_2 nanostructures, TiO_2 nanobelts (NBs) attract more attention due to their unique physical properties and ideal 1D ribbon-like morphology that is favorable for constructing heterostructures by assembling second-phase nanoparticles on the surface of the NBs. A large number of studies have proven that well-designed TiO_2 NB heterostructures can not only broaden the photocatalytically active light band of TiO_2 but also enhance the light absorption performance and the photo-induced carrier separation ability. The TiO_2 NB heterostructure has become a versatile and powerful tool for building high-performance TiO_2-based photocatalysts, which has stimulated intense research activities focused on the growth, properties, and applications of the 1D TiO_2 NB and its heterostructures. This review attempts to cover all these aspects, including the underlying principles and key functional features of TiO_2 NBs and TiO_2 NB heterostructures in a comprehensive way and also discuss the prospects of this type of novel hybrid photocatalyst.

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1. Introduction

The world is facing two major challenges at the moment: environmental pollution and energy shortage. Semiconductor photocatalysis is a promising approach to combat both of these challenges. Potential applications of photocatalysis include photodegradation of hazardous substances [1,2], photocatalytic water splitting [3,4], artificial photosynthesis for fuel production [5–7], photo-induced super-hydrophilicity [8], and photoelectrochemical conversion [9,10]. Semiconductor materials are the key factors in photocatalysis reactions. Among these semiconductors, TiO_2 is the earliest and best-studied photocatalyst with a very high ultraviolet (UV) light activity, and P25 (a TiO_2 nanoparticle with approximately 80 wt% anatase and 20 wt% rutile) [11,12] is the most popular commercial photocatalyst product. Unfortunately, TiO_2 does not possess photocatalytic properties under visible light, which limits its application when using solar light, which has an energy distribution of less than 5% for UV light, approximately 40% for visible light, and more than 50% for infrared (IR) light [11]. Because the ultimate objective of photocatalysis is the efficient utilization and conversion of solar light, many visible-light photocatalysts, such as CdS [13,14], CdSe [15], InP [16], GaZnON [17], WO_3 [18], Ag_2O [19], Ag_2S [20], Cu_2O [21], Bi_2MoO_6 [22] and Bi_2WO_6 [23], have been developed. However, all of the existing photocatalysts have some common shortcomings: 1) a narrow light spectrum for photocatalytic activity limited to a typical light spectrum range, causing low efficiency in the utilization of sunlight; and 2) the photo-induced charge carriers in single-crystalline nanostructured materials recombine easily, causing a low production of effective charge carriers and then a decrease in the photocatalytic efficiency. Overcoming these disadvantages is a huge challenge that researchers must face.

It is well accepted that an excellent photocatalyst should have the following characteristics: 1) more active photocatalytic facets; 2) a broad absorption spectrum; and 3) a means of facilitating the separation of photo-induced charge carriers [11]. As mentioned above, TiO_2 is the first photocatalyst with an excellent UV-light photocatalytic property [24]. So far, many researchers have made significant progress by using TiO_2-based photocatalysts to achieve a high photocatalytic property [25–28]. In terms of increasing the active facets, by controlling the growth process of TiO_2 nanocrystals to enable the exposure of more highly active facets, researchers can increase the proportion of the active surface and improve the photocatalytic efficiency [29–31]. To broaden the optical absorption spectrum, cationic or anionic dopants [32], and metal nanoparticles created by a primitive plasma resonance absorption process [33,34] are used to extend the absorption spectra of TiO_2 to the visible and even the infrared region. To improve the separation of the photo-induced carriers, energy band matching of the two crystalline TiO_2 phases (anatase and rutile) can be used to realize a directional movement of photo-generated carriers and enable their separation, which can enhance the photocatalytic efficiency [35].

However, the above approaches are associated with certain difficulties or limitations in obtaining TiO_2 nanoparticles with high photocatalytic performance. For example, although the exposed facets of the semiconductor nano/microcrystals can be controlled to achieve a high proportion of the active surface area, the well-crystallized nano/microcrystals are generally larger in size than granular nanoparticles, and the amount of the active surface per unit mass is not impressive. In addition, the complexity and high cost of controlling the growth of the crystal faces restricts these methods to the theoretical side of research. Anion- and cation-doped TiO_2 nanoparticles can obtain visible light catalytic properties through the defects in their energy levels [36], but two shortcomings exist. One is that the defects reduce the intrinsic excellent UV catalytic activity of the TiO_2 nanoparticles themselves [37]; the other is that the visible light photocatalytic properties of the TiO_2 nanoparticles will decrease during the photocatalysis process due to the recovering of the defects, which limits both their performance and practical application. Band structure matching of the two TiO_2 phases to achieve the efficient separation of photo-induced carriers is a very valuable means of improving the performance of TiO_2 nanoparticles, and it has been successfully applied in the famous commercial photocatalyst P25. It is consistently found that the valence band maximum of rutile is 0.7 ± 0.1 eV above that of anatase [38]. Therefore, electrons (e^-) easily transfer from rutile to anatase, and holes (h^+) move to the rutile phase in the process of photocatalysis, thus resulting in highly efficient photocatalysis. Unfortunately, P25 nanoparticles are too small to be removed/collected from the reaction system after degradation of the organic pollutant. The cost of operation of a high-speed centrifuge to recycle P25 after the photocatalytic process is even higher than the cost of purchasing the P25 [11]. In addition, TiO_2 nanoparticles can be integrated with other semiconductor nanoparticles to form heterostructures; this can improve the photo-induced carrier based on the band-matching principles. In a similar manner, TiO_2 nanoparticles can be combined with visible light photocatalytic nanoparticles to broaden the spectrum for photocatalysis. However, the heterostructures based on TiO_2 nanoparticles tend to form core-shell structures or random aggregates of mixed particles

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