TiO2: Next Generation Photocatalysts

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TiO2 is the most widely used photocatalyst in many energy and environmental applications. This entry describes the basic structure and properties of TiO2 as a nanomaterials. It also enlists the special properties of TiO2 which make it a best candidate for photocatalysis reaction. It also explains the drawbacks of TiO2 nanomaterials along with the strategies to overcome those.

Keywords: Photocatalysts ; Nanocomposites ; Green Chemistry ; Renewable Energy

1. Introduction

TiO_2 has received wide attention ever since 1972 when Fujishima and Honda discovered photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (UV) light [1]. Over the past decades, TiO_2 has served as a "benchmark photocatalyst" for the degradation of a wide class of organic compounds and microorganisms in the UV range [2][3][4]. TiO_2 has been the most widely studied and used in many applications because of its strong oxidizing abilities, superhydrophilicity, chemical stability, long durability, nontoxicity, biocompatibility, photocorrosion-free, low cost, and transparency to visible light [5]. In addition, it has the following advantages.

- TiO_2 can be fabricated with interesting morphologies such as spheres, nanorods, fibers, tubes and sheets. This enables them to attain unique chemical, physical, and electronic properties increasing its photocatalytic efficiency [6][7].
- TiO_2 nanomaterials can be prepared in large scale at mild temperatures and conditions. [8][9]
- TiO_2 can be supported on various substrates such as glass, fibers, stainless steel, inorganic materials, sand, and activated carbon which allows its continuous reuse [10].

Therefore, tremendous interest has been shown in studies of TiO_2 nanomaterial structures and their photocatalytic applications.

2. Structure of TiO_2

TiO_2 exists in three mineral forms, viz., anatase, rutile and brookite. These polymorphic phases of TiO_2 are shown in figure 3. In all the three forms, titanium (Ti^{4+}) atoms are coordinated to six oxygen (O^{2-}) atoms, forming TiO_6 octahedra. Anatase is made up of face (vertice) sharing arrangements of octahedra at (001) planes (Fig. 1 a) resulting in a tetragonal structure. In rutile, the octahedra share edges at (001) planes to give a tetragonal structure (Fig. 1 b), and in brookite both edges and corners are shared to give an orthorhombic structure (Fig. 1 c)[11]

Amongst the various phases, TiO_2 in the brookite phase has been scarcely used as photocatalysts. Between TiO_2 in the anatase and rutile phases, the anatase TiO_2 is more active for photocatalysis applications, even though the rutile TiO_2 possesses a smaller band gap. The reasons anatase TiO_2 is more actively used for photocatalysis are as follows [12]:

- The conduction band position of anatase TiO_2 is more negative compared to rutile TiO_2. This is responsible for the higher reducing power of anatase TiO_2 towards the adsorbed reactants and thus results in the higher photocatalytic activity of anatase TiO_2 in comparison to rutile TiO_2
- Recombination reactions adversely affect photocatalytic activity and the degree of recombination is found to be higher for rutile TiO_2 than for anatase TiO_2. The recombination reactions limit rutile TiO_2's activity.

The photocatalytic activity of TiO_2 increases with an increase in the density of physically adsorbed OH^- groups on its surface. The surface hydroxyl groups accept holes generated by UV and solar irradiation to form hydroxyl radicals and prevent electron-hole recombination thus increasing the photocatalytic activity of TiO_2. Generally, the surface of the anatase phase of TiO_2 is very hydroxylated; whereas, rutile TiO_2, being obtained at higher temperatures, has a very low density of physically adsorbed hydroxyl groups. This leads to lower photoactivity of rutile TiO_2 in comparison to anatase TiO_2

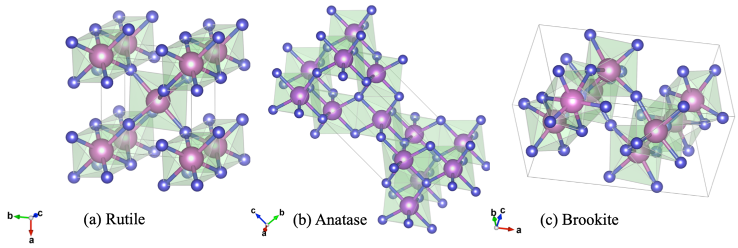

Figure 1. Polymorphic phases of TiO2

3. Drawbacks of TiO_2

Besides the aforementioned inherent advantages of TiO_2, it has following drawbacks

- The large band gap of TiO_2 (∼ 3.2 eV for anatase and brookite, ∼3.0 eV for rutile) requires an excitation wavelength that falls in the UV region. Given that less than ∼5% of the solar flux incident at the earth's surface lies in this spectral regime (solar light consists of ∼5% UV, ∼43% visible, and ∼52% harvesting infrared), only a very small portion of the solar light could be used by pure TiO_2 photocatalysts.
- Massive recombination of photogenerated charge carriers limits its overall photocatalytic efficiency

4. Strategies to modify TiO_2 nanomaterials

Various strategies have been adopted for improving the photocatalytic efficiency of TiO_2. Some of them are listed in Fig. 2.

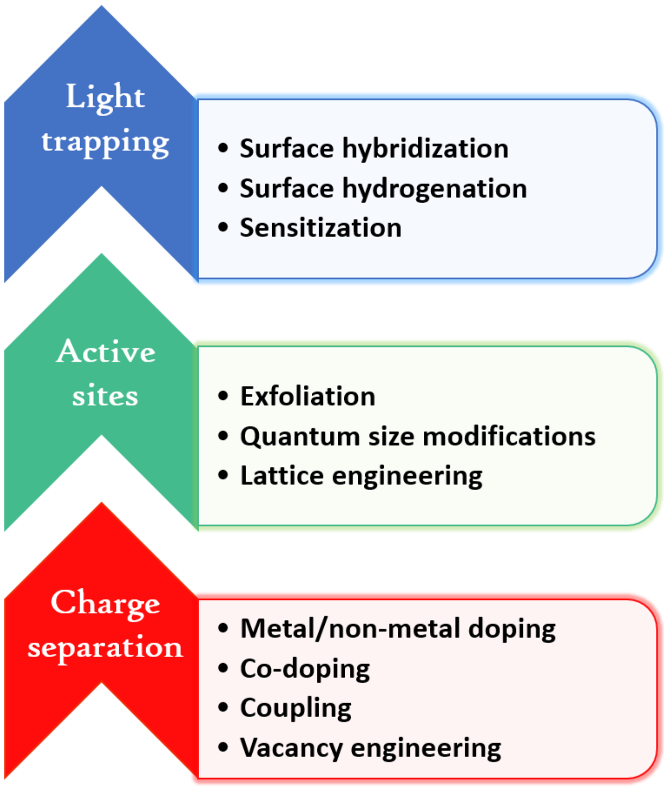

Figure 2. Strategies to modify TiO2

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