

Application of photo-catalyst for removal of organic air pollutants

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INTRODUCTION

Light is introduced in our life using sunlight in days and moonlight in nights. People gradually learned that, they can obtain light from heat, electricity and chemical reactions. The researchers noticed that the light can be used to improve daily life in various field of science. In this regards, chemists focused on converting of light to energy and developing the chemical process using light. One of the important areas in our life is photo-catalytic removal of chemical pollutants from air.

The atmosphere has an important role in the hydrologic cycle and it can be absorb most of the cosmic rays from outer space and protect organisms from their effects. It also absorbs most of the electromagnetic radiation from the sun, allowing transmission of significant amounts of radiation. The most significant feature of atmospheric chemistry is the occurrence of photochemical reactions resulting from the absorption by molecules of light photons ($h\nu$).

Air pollution isn't a new problem; modernization and progress over the years have resulted in the more polluted air pollutants can be emitted from various sources and can cause serious health problems.)

In order to overcome atmospheric pollution problems, a number of removal techniques are available. One of these methods is photo-catalytic oxidation (PCO).

PCO has been studied by researchers for several decades and results are shown as an effective method for air purification. semiconductors like TiO_2 and ZnO are commonly used as the photocatalyst.

The structure of TiO_2 and its electrical and optical properties have an important role in its performance. TiO_2 naturally crystallizes in three forms: rutile, anatase and brookite phase. Since the anatase phase has a band gap of 3.2 eV, it is highly transparent to visible light and absorbs below 380 nm wavelength.

In TiO_2 , the valence band (VB) is created by O_{2p} states whereas the conduction bands (CB) is formed by Ti_{3d} states. The energy band gap size is essentially established by hybridization of these 2 orbitals. The electronic band structure of Titania has a wide indirect band gap of about ~ 3.2 eV for anatase and ~ 3.0 eV for rutile.

Generation of Charge Carriers

The electromagnetic radiation spans from the near ultraviolet to near infrared ranges. In terms of energy (wavelength), this is radiation from ~ 4.1 eV (300 nm) to ~ 1 eV (1200 nm), which most of the chemical transformation occurs in these energy ranges. More interestingly, the part of the solar spectrum that reaches earth falls into these ranges and making the semiconductors important materials for solar energy transformation and environmental applications. Fig.1 shows Schematic illustration of the absorption of light in a semiconductor and the subsequent generation of an e-h pair.

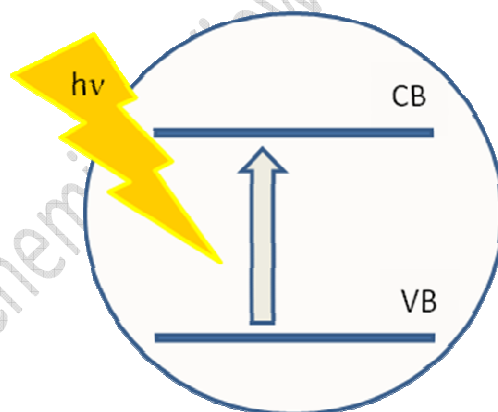


Fig.1: Schematic illustration of the absorption of light in a semiconductor

The light absorption in semiconductors promotes electrons from the VB to the CB and leaves behind positive holes in the VB or creates e-h pairs. The fate of photo-generated charge carriers could follow several pathways depending on the physical circumstances (Fig.2).

The lifetime of the charge carriers in the excited state, is on the order of nanoseconds in semiconductors in contrast to femto-seconds in metals.

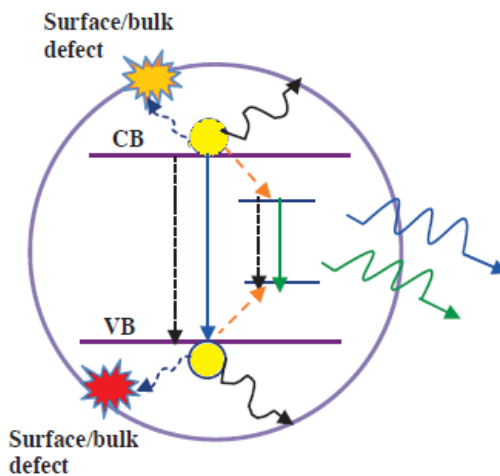


Fig. 2: the e-h pair generation and different paths for charge carriers.

Once the charge carriers arrive at the interface with the reactive medium, they may take part in redox reactions which involves transfer of the charge carriers between the surface of TiO_2 and the adsorbed chemical species. This process is called interfacial charge transfer and is a central process in the PCO (Fig3).

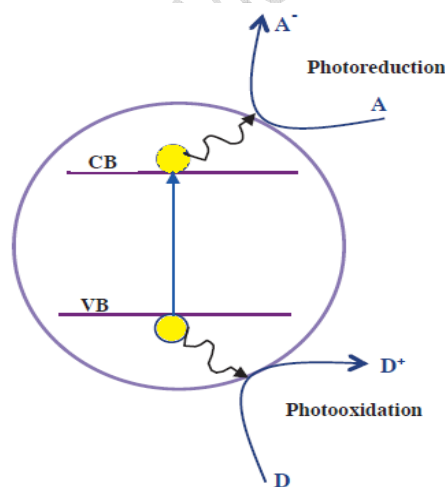


Fig. 3: Representation of photo-oxidation and photo-reduction of the surface of semiconductor

The transfer of photo-generated electrons from the CB of the photo-catalyst to the acceptor is referred to as photo-reduction whereas the transfer of electrons from the donor to the VB of the photo-catalyst is referred to as photo-oxidation. Surface reactivity is the number of surface active sites and is an important parameter for applying the semiconductors. These are operational sites at the surface where the reactants tend to adsorb and react with photo-generated charge carriers

and eventually lead to new products. In this regard, the surface structure and surface area of photo-catalysts play important roles in determining active sites. In physisorption, the adsorbed molecules are in proximate contact with the surface via weak Van der Waals interaction. No chemical bond is formed between the physisorbed adsorbates and the surface, which results in no change in the electronic structure of the involved substances. In chemisorption, a strong chemical bond is formed in a monolayer on the surface upon transfer electrons among the adsorbates and the surface. Chemisorption consequently modifies the density and position of electronic states of the surface-adsorbate complex. Chemisorption is the dominant adsorption mechanism in heterogeneous photo-catalytic systems.

Improving TiO₂ Photo-catalytic Performance

TiO₂ can be used as a good material through modifications of its surface chemistry. The fundamental approaches proposed to enhance the performance of TiO₂ are [4]:

- Optimization of the charge transport and minimizing charge carrier recombination;
- Provision of adequate quality and quantity of active surface sites;
- Band gap engineering and/or use of photo-sensitizers for broadening of the absorption wavelength range.

Photo-catalytic application for removal air pollutants

The PCO process involves the adsorption of pollutants on the surface sites, and the chemical reaction to convert pollutant into carbon dioxide and water. Titanium dioxide is used as a photo-catalyst and its activation of is achieved through the absorption of a photon ($h\nu$) with ultra-band energy from UV irradiation source. This results in the promotion of an electron (e^-) from the valence band to the conduction band, with the generation of highly reactive positive holes (h^+) in the valence band. This causes aggressive oxidation of the surface adsorbed toxic organic pollutants and converts them into CO₂ and water. The photo-catalyst for the reaction process needs to be: (a) photo-active; (b) able to utilize near-UV light; (c) biologically and chemically inert, (d) photo-stable and (e) inexpensive. TiO₂ meets these criteria and is one of the best semiconductors for photo-catalytic reactions. Photo-catalytic oxidation using UV and titanium dioxide thin film coated on several supports such as glass or metal surface has been used to eliminate hazardous indoor air pollutants, for example VOCs and NO_x in gas phase.

The process involves the pollutant gases and organic compounds to diffuse through the porous surface and stick to the titanium dioxide nano-particles of the construction materials and coatings. Absorption of UV light by the incorporated TiO₂ leads to its photo-activation and formation of OH[•], which degrades the pollutants absorbed onto the particles.

The PCO process is a good candidate for removal of air pollutants from industrial sites and urban places, because of its advantages such as high efficiency, environmental and economic consideration

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