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Visible-light Active Heterogeneous Photocatalysis for Wastewater Treatment

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Abstract: *Heterogeneous photocatalysis is an upcoming field wherein a catalyst that gets activated when solar energy falls on it, photo-degrades the organics present in the effluent into harmless water and carbon dioxide. However, most of the research in this field has been carried out on TiO_2, which has a limitation of being able to utilise only the ultra-violet light of the solar radiations only. Hence, to be able to utilise a wider range of the available radiations, research is now being focussed on developing photocatalysts which work in the visible spectrum as well. This paper discusses the state-of-the-art in this area. The first part outlines the basic principles and mechanism of photocatalysis, while the second one discusses in brief the methods in which visible-light photocatalytic materials can be synthesised and utilised that are capable of yielding a higher overall efficiency of the process.*

Keywords: photocatalysis, solar light, mechanism, TiO_2, composites

I. INTRODUCTION

Water pollution is a major problem all over the world. Thousands of biotic lives are lost annually due to improper and insufficient water availability. Most of the water pollution is caused by untreated industrial effluent getting mixed with these water bodies. To combat the issue, governments of respective countries have laid down strict rules of water/effluent discharge. Hence, treatment of industrial effluent is a necessity for industries. This treatment has three major issues, viz., i) it is energy intensive, ii) it is technology intensive, and iii) usual treatment techniques are not capable of completely breaking down the pollutant, rather convert one type of pollution into another, eg., adsorption.

Solar photocatalysis is an advanced oxidation process in which is simple in operation, utilises solar energy as an energy source and completely mineralises the organic pollutant to carbon dioxide and water. It utilises a semiconductor catalyst, which, when irradiated with solar energy, makes the organics react with oxygen and degrade it into harmless water and CO_2. The basics of solar photocatalysis, its affecting parameters and suitable photoreactor have been addressed in literature [1][2].

II. HETEROGENEOUS PHOTOCATALYSIS

Heterogeneous photocatalysis utilises a semiconductor material which has a characteristic band gap between the valence state and conduction state of an electron. This is depicted in Figure 1. As shown there, when energy of value greater than or equal to the band gap of a semiconductor material falls on it, its electrons present in the valence state gain energy, get excited and reach the conduction band (CB). Deficiency of an electron in the valence band (VB) is equivalent to generation of a positively charged hole there. These holes and electrons are highly unstable in nature and are powerful oxidants and reductants. This means they react with oxygen and water to generate strong radicals like O_2^{*-} and $^{*}OH$ that bring about reduction and oxidation of the pollutant, thereby converting them into water and carbon dioxide, via formation of a number of short-span intermediates.

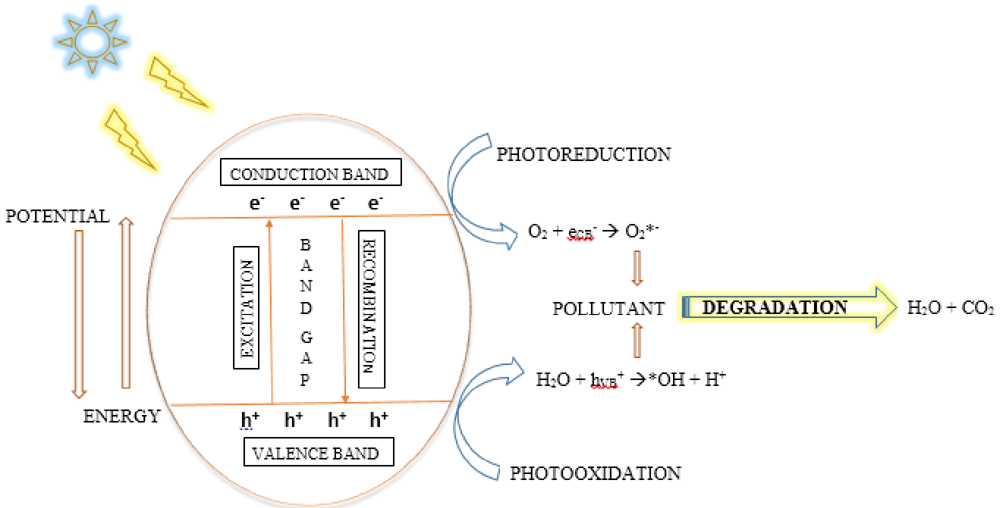

Figure 1: Basic mechanism of semiconductor photocatalysis

The reactions taking place may be summarised as follows:

Photocatalyst + hν (energy) → e_{CB}^{-} + h_{VB}^{+} (1)
e_{CB}^{-} + h_{VB}^{+} → energy (heat) (2)
O_2 + e_{CB}^{-} → O_2^{*-} (superoxide radical) (3)
H_2O + h_{VB}^{+} → *OH (hydroxyl radical) + H^+ (4)
*OH + pollutant → Intermediates → H_2O + CO_2 (5)
O_2^{*-} + pollutant → Intermediates → H_2O + CO_2 (6)

As shown in equation (1), when energy of amount hν ≥ band gap of the semiconductor photocatalyst falls on it, electrons leave the valence state and reach the conduction band (e_{CB}^{-}) leaving behind a positively charged hole in the valence band (h_{VB}^{+}).As shown in equation (2) these photogenerated e_{CB}^{-} and h_{VB}^{+} are highly unstable and thus, might recombine to release back the energy that generated them. Now the e_{CB}^{-} reacts with an available oxidant, usually oxygen, to generate strong and highly unstable superoxide radical. The h_{VB}^{+} also reacts with available water molecules to generate the hydroxyl radical. This is shown in equations (3) and (4). Both these radicals being strong and unstable, react with an organic pollutant containing C, H and O atoms and break them down, through a number of short-span intermediates, to H_2O and CO_2. Thus, the pollutant gets completely degraded.

III. COMPOSITE PHOTOCATALYSTS

As mentioned earlier, most of the research on the development of photocatalyst is based on TiO_2. TiO_2 has a band gap value of 3.2 V, hence it gets activated only by radiations as strong as and having wavelength as much as those that are characteristics of UV spectrum of the solar insolation. As the UV consists only approx. 4% of the total spectrum, hence, focus has now shifted to development of photocatalysts capable of working in the visible light region, which comprise of about 47% of the total spectrum. Some of the mechanisms of photocatalyst composites that are active in solar light are discussed herein.

3.1 P-N junction photocatalyst

The p-n junction principle is well established in semiconductor and photovoltaic principles. The same can be used in photocatalysis to separate the photogenerated electrons and holes and prevent them from recombining. The principle is depicted in **Figure 2** and may be explained as follows.

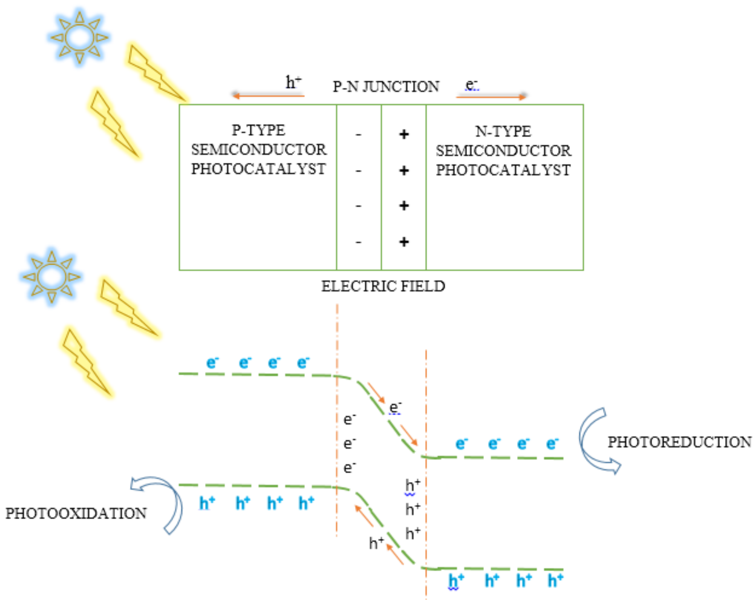

Figure 2: P-N Junction coupling photocatalysis principle

A p-type material is rich in holes and an n-type material is rich in electrons. When p- and n- type semiconductors are joined together, there is combination of the holes and electrons at the interface. This results in the creation of a depletion zone wherein an electric field is created with negative charge on the p-side and positive charge on the n-side. This depletion zone and electric field serve two purposes and help in reducing recombination. Firstly, the depletion zone is a neutral zone and hence doesn't allow more electrons to migrate and combine with holes. And secondly, the electric field set up in the process repel the like charges and thus prevent recombination. Many research papers of the same are available in literature[3][4][5][6].

3.2 Heterojunction coupling

A heterojunction coupling between two photocatalysts is characterised by composite materials with different band gaps joined together such that surface transfer of electrons and holes is made possible between them. This is depicted in **Figure 3**.

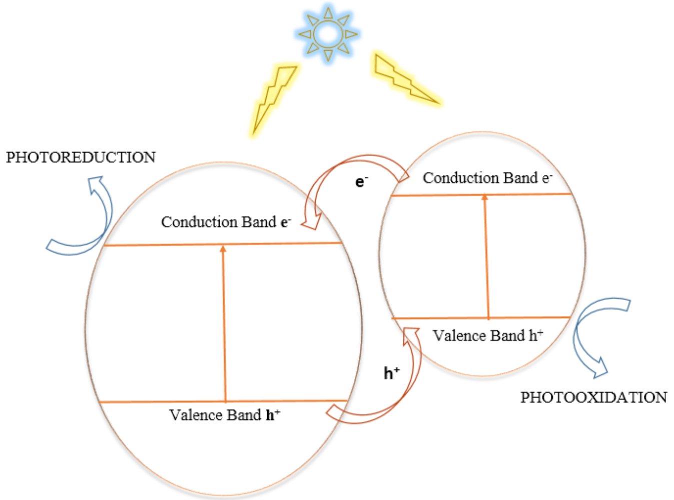

Figure 3: Transfer of electrons and holes from one surface onto the other in a heterogeneously coupled photocatalyst coupling

When two photocatalytic materials having different band gap values and band positions are irradiated, the electrons from the respective VBs get excited and reach the respective CBs, leaving behind holes in the VB. Now, if these holes and electrons are not timely captured and reacted, they are lost in recombination. In order to arrest them, these two photocatalytic materials are joined together to form a composite. Now, upon formation of a composite, the excited electrons present in the material with higher CB get transferred onto the material with a lower position of CB. Similarly, the holes with a lower VB potential get transferred onto the VB of the material with a higher VB potential level. Thus, this interfacial transfer of electrons and holes across a heterogeneous junction separates them onto different surfaces and this aids in arresting recombination. Examples of such composites are available in literature [7][8][9][10].

3.3 Surface Plasmon Resonance

Some materials have a characteristic property in which when light waves of specific wavelength strike on it, the electrons undergo localised oscillations and set up an electromagnetic field, conducive to initiate a photocatalytic reaction. This effect is known as surface plasmon resonance and is depicted inFigure 4.

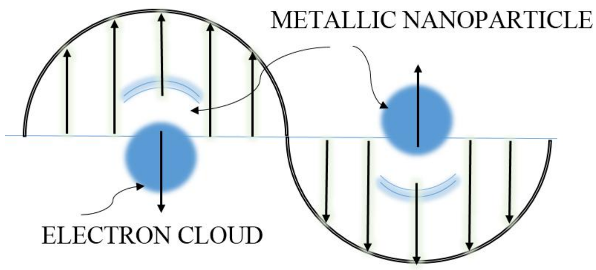

Figure 4: SPR effect exhibited by metallic nanoparticles

Most of the research on exploiting this property of surface plasmon resonance for the purpose of photocatalysis for organic pollutant degradation has been done on Silver [11][12][13][14]and Gold.

IV. CONCLUSIONS

TiO_2 is found to be active in the UV range of solar spectrum. However, to be able to utilise a wider range of the falling radiations, some composite materials need to be synthesised which have a relatively lower band gap, and yet recombination is arrested. Another method could be to use some inherent properties of materials that help in excitation of electrons and initiation of a photoreaction. There are three ways in which this can be done. Firstly, through a p-n junction composite, secondly, through composite forming a z-scheme, and thirdly, by utilising the SPR characteristic of a material. All three methods have been discussed in the former section along with examples. These methods help utilise the solar radiations for the purpose of wastewater treatment through photocatalysis to a much larger extent, as here, the visible radiations can also be utilised along with the UV spectrum. Solar photocatalysis, thus, can be concluded to be a promising technology for the effluent treatment.

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