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A Study of Nanocomposite for Photocatalytic Degradation of Organic Contaminants under visible light

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Abstract - The escalating concerns regarding environmental pollution have spurred significant interest in developing efficient photocatalytic materials for the degradation of organic contaminants. This study investigates nanocomposites for visible-light photocatalytic destruction of organic pollutants, considering the limitations of UV-only photocatalysts. Given that a significant fraction of the solar spectrum is visible light, the capacity to utilize this light for catalytic reactions is critically important. The nanocomposite consists of a semiconductor material doped with noble metal nanoparticles, designed to enhance light absorption and charge separation efficiency. Through a series of synthesis techniques and characterization methods including X-ray diffraction, scanning electron microscopy, and UV-Vis spectroscopy, the structural and optical properties of the nanocomposite are thoroughly investigated.

Keywords - Nanocomposite, Photocatalytic, Visible-Light, Catalysis

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INTRODUCTION

In recent years, the escalating concerns over environmental pollution and the depletion of natural resources have spurred extensive research into innovative materials and technologies for sustainable remediation strategies. In the realm of photocatalysis for the degradation of organic contaminants, nanocomposites have particularly emerged as a promising category of materials. Nanocomposites are all the rage in the world of photocatalysis due to their large surface area, improved charge carrier separation efficiency, and greater light absorption. To overcome the shortcomings of conventional photocatalysts, which mainly react to ultraviolet (UV) light, this study zeroes in on nanocomposites engineered for visible light photocatalytic degradation of organic pollutants. Given that a significant fraction of the solar spectrum is visible light, the capacity to utilize this light for catalytic reactions is critically important. Consequently, the development of nanocomposites that can efficiently absorb and utilize visible light broadens the scope of photocatalysis, making it more energy-efficient and applicable in diverse environmental settings.

NANOCOMPOSITES

Mixtures of two or more materials are called composites. Due to their increased properties and the fact that they are generated from a variety of functional group materials, they have multiple uses [C. H. Yanga 2016]. Solid structures called nanocomposites are created by mixing a matrix of regular material with nanosized particles ranging from half a milligramme to five percent by weight. By which the qualities of the material can be increased. Material attributes including "strength, toughness, stability of dimension, modulus, conductivity of electricity, reduced gas, the permeability of water and hydrocarbon, flames retardancy, thermal stability, chemical resistance, surface appearance, optical clarity, catalysis, separation, sorption, and fuel cells" are listed in the 2009 study by Camargo et al. [P. H. C. Camargo 2009]. Various combinations of nanocomposites, such as metal-metal oxide, mixed metal oxide, polymer-metal oxide, & carbon nanotube-metal oxide, can be used as active materials in gas sensors (R.A.M. Said, 2020). The high surface-to-volume ratio of nanocomposites allows them to be modified with various compositions. Computer chip thin-film capacitors, fuel cells, and food packaging are just a few examples of the many applications for nanocomposites, which are one thousand times stronger than the bulk component materials. Consequently, nanocomposites find use in a wide variety of significant technical contexts. The magnetic, optical, electrical, mechanical, & physical properties of nanocomposites are well-documented. Modifying the internal structures of any traditional material allows for their production. This includes polymers, metals/alloys, and ceramics. Various methods from the field of fundamental science can be used to synthesise nanocomposites, including solid state processing and liquid metallurgy. According to S. Sivasankaran (2019), nanotechnology allows for the synthesis of eco-friendly materials. According to their characteristics, nanocomposites are classified as structural & functional materials.

CATALYSIS

The field of catalysis, which encompasses both science and technology, has enormous practical importance. Figure 1.1 depicts the four main economic sectors that rely on catalytic processes: the petroleum & energy production sector, the chemicals and polymer production sector, the food business, and pollution control. Sunlight is a natural & abundant energy source, and semiconductor-based photocatalysis, also known as heterogeneous photocatalysis, has attracted a lot of interest because of its possible uses in treating wastewater & making hydrogen fuel (Anjum 2017). The phrase "reaction assisted by photons in the presence of semiconductor photocatalyst" describes it. The word "photocatalysis" was initially coined in various labs. Although it was reported concurrently by Stone and Hauffe for CO adsorption/desorption on ZnO surfaces & CO oxidation on ZnO surfaces, respectively, as J.M. Herrmann pointed out. Simultaneously, Juillet and Teichner investigated sunlight-induced TiO2 photoresponse and alkane oxidations. Water splitting into H2 & O2 utilizing semiconductor photocatalysts (TiO2) has gained momentum in the realm of science & technology when Fujishima and Honda [4] revealed it. The use of semiconductor photocatalysts for water splitting & purification under solar light has been the subject of extensive research.

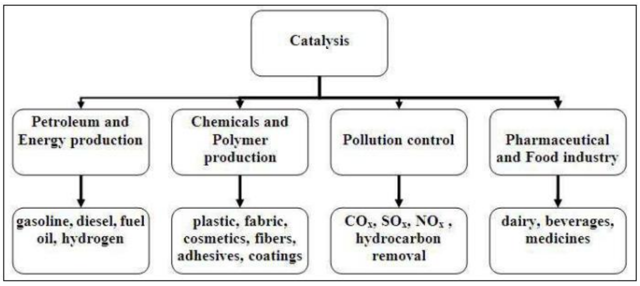

Figure 1: Catalytic process is involved in four different areas

CATALYSIS HISTORIOGRAPHY

There is a rich history of applications for catalyst technology. Enzyme catalysts were used to make cheese, wines, & soaps, while inorganic catalysts were used to make soaps. In 1875, the first industrial catalysts were produced when sulfuric acid was mass-produced using a platinum catalyst. In subsequent years, several significant catalytic processes were refined. By oxidizing ammonia on Pt gauge, Ostwald developed a process for nitric acid production in 1903. Haber, Bosch, & Mittasch also achieved a great deal in the years 1908–1914 with their ammonia synthesis using increased iron.

Hydrogenating carbon monoxide to convert synthesis gas into liquid hydrocarbons was one of the most groundbreaking energy industry developments of the 1920s and 1930s. In the years 1935–1940, the catalytic cracking method came into play, completely changing the energy scene in the petroleum industry. This process made history by using a solid catalyst in the petroleum industry. Hydro treating petroleum feedstock to remove sulfur, nitrogen, and metals (1960) & catalytic naphtha reforming (1950) were two other catalytic hydrocarbon processes that were developed in the decades that followed. After the Ziegler-Natta catalyst was found in 1955, the polymer industry grew at a phenomenal rate. One of the earliest industrial homogeneous catalytic processes was the Walker process, which, in 1960, converted ethylene into acetaldehyde. Products that were exclusively shape selective came into being in 1964 as a result of the development of form selective catalysts for cracking, such as zeolites or molecular sieves. The years 1970–1980 witnessed yet another major development in catalysis, this time with an eye toward lowering environmental pollution levels. The development of catalysts composed of noble metals allowed for the mitigation of hydrocarbon, carbon monoxide, and nitrogen oxide emissions from vehicles. A catalyst based on vanadia-titania & zeolite was developed to selectively decrease NOx. The constant development of catalysis as a discipline, defined by the identification and use of new catalysts, has led to substantial progress in the chemical industry.

CATALYTIC REACTIONS

In a chemical reaction that can be supported by thermodynamics, a catalytic reaction takes place when a tiny quantity of a chemical substance accelerates the process of attaining equilibrium without actually changing the material. Substances that speed up a reaction are called catalysts. Catalysts provide a different way that use a lower-energy transition stage to achieve their purpose. The activation energy of the catalytic process is reduced compared to the uncatalyzed reaction, as shown in Figure 1.2.

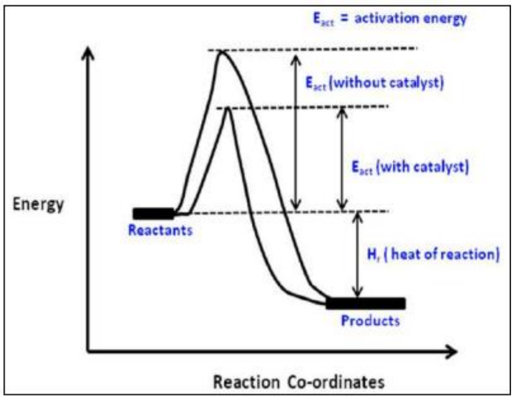

Figure 2: Catalytic & non-catalytic systems' activation energies that are exothermic

PHOTOCATALYSIS

Photocatalysis is the process or activity that occurs when a light source interacts with the surface of a substance, such as semiconductor materials. An oxidation reaction utilizing photogenerated holes & reduction reaction utilizing photogenerated electrons must both be carried out concurrently for this activity to occur. The two processes indicated above must be perfectly coordinated to ensure that the photocatalyst species stays unaltered during the procedure. In 1972, Fujishima and Honda achieved the first-ever electrochemical photocatalysis of water at a semiconductor electrode. The discovery that TiO2 (titanium dioxide, more often known as titania) helps break down cyanide in water piqued interest in the material's possible environmental applications (Heegde MS 2004). Titanium dioxide (TiO2) is a useful material for photocatalysis because of its many advantageous characteristics, such as its low cost, high chemical stability, and widespread & quick availability. Implementing photocatalysis in a practical & efficient manner in the real world has the potential to decompose a range of pollutants and enhance air quality. As a result, photocatalysis has potential applications in the building industry for improving the air quality within buildings.

The area of semiconductor photo-catalysis frequently uses it to create, analyze, and apply doped or undoped nano-structural materials for photocatalytic applications, paying special attention to particle sizes & shapes. Porous metallic oxides, metallic nanoparticles, porous carbons, and synthetic mixtures of these materials have a wide range of potential applications, including gas storage, energy conversion/storage devices, and photocatalysis & electro-catalysis.

The term "photocatalysis" describes the catalytic reaction that occurs when light rays contact with one another. Common belief holds that a conductive nanomaterial should be able to absorb light directly, increasing its energy state, and then transmit that energy to a reactive substance, inducing a chemical reaction. This would make it an ideal photo catalyst material.

PHOTOCATALYSIS TYPES

When it comes to photocatalysis, the two main categories:

A. Homogeneous Photocatalysis

When both the reactants and the photocatalysts are present in the same phase—for example, as gases—this process is called homogeneous photocatalysis. The ozone & photo-Fenton systems (Fe+ and Fe+/H2O2) are widespread examples of homogeneous photocatalysts. Here, the hydroxyl radical (•OH) is to play the role of the reactive species, serving a variety of functions. Here are two possible ways that ozone can produce hydroxyl radicals (•OH).

$$O_3 + h\nu \rightarrow O_2 + O(1D)$$

$$O(1D) + H_2O \rightarrow \bullet OH + \bullet OH$$

$$O(1D) + H_2O \rightarrow H_2O_2$$

$$H_2O_2 + h\nu \rightarrow \bullet OH + \bullet OH$$

Similarly, the Fenton system (Fe+) can generate hydroxyl radicals (•OH) through the process illustrated in the following.

$$Fe^{2+} + H_2O_2 \rightarrow HO\bullet + Fe^{3+} + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO\bullet 2 + H^+$$

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^-$$

Additional OH radical sources are taken into account in photo-Fenton systems (Fe+ and Fe+/H2O2) type processes, specifically by photolysis of H2O2 or reduction of Fe3+ ions under UV light, in the following ways:

$$H_2O_2 + h\nu \rightarrow HO\bullet + HO\bullet$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO\bullet + H^+$$

Hydroxide (H2O2) concentration, pH, and UV light intensity are a few of the operational parameters & variables that affect the efficiency and efficacy of Fenton type operations. The innovative part of this technology is that it can use sunshine with a light sensitivity of up to 450 nm, which gets rid of the requirement for pricey UV lamps and electricity. The major disadvantages of homogeneous photocatalysis are the requirement for low pH values (iron (Fe) precipitates at higher pH values) & elimination of iron (Fe) after treatment, despite the fact that these reactions are more practical & cost-effective than other types of photocatalysis.

B. Heterogeneous Photocatalysis

From the definition, it is clear that catalysts & reactants in "heterogeneous catalysis" are in various phases. Mild or total oxidation reactions, dehydrogenation, hydrogen transfer, 18O2–16O2 and deuterium–alkane isotope exchange, metal deposition, water detoxification, gaseous pollutant removal, and many more reactions are all part of heterogeneous photocatalysis.

Transition metal oxides & semiconductors, two types of heterogeneous photocatalysts, each exhibit distinctive properties and find widespread application. While metals have a continuous range of electronic states, semiconductors often have inefficient energy zones where the levels of energy needed to create the rejoining of an electron & hole created by photo-activation are not present. The band gap is the empty space between the filled valence band's upper edge & empty conduction band's lower edge.

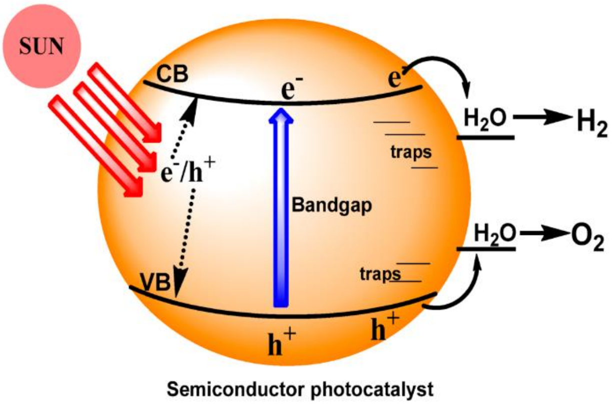

Figure 3: Semiconductor photocatalyst

The method involves absorbing a photon with an energy level higher than the band gap of the material by means of the semiconductor. Then, an electron is excited to move from the valence band to the conduction band, creating a positive (+ve) hole in the valence band. The exciton is a phenomenon characterized by a photogenerated electron-hole pair. The energy obtained when the electron was excited can be released as heat when the excited electron & hole recombine or reunite. Exciton and recombination are undesirable processes that lead to an inefficient photocatalyst at increasing concentrations. Many researchers working on practical photocatalysts aim to increase electron-hole separation or prolong the exciton duration. This is achieved through various methods that rely on structural features like phase hetero-junctions (including anatase-rutile interfaces), noble-metal nanoparticles, silicon nanowires, and substitutional cation doping, among others. Encouraging and facilitating reactions between excited electrons and oxidants to produce reduced products is the primary goal of photocatalyst design. Furthermore, for the purpose of generating oxidized products through reactions involving the reductants & holes that are formed along with them. This is why redox reactions take place on semiconductor surfaces: to create positive (+ve) holes & electrons.

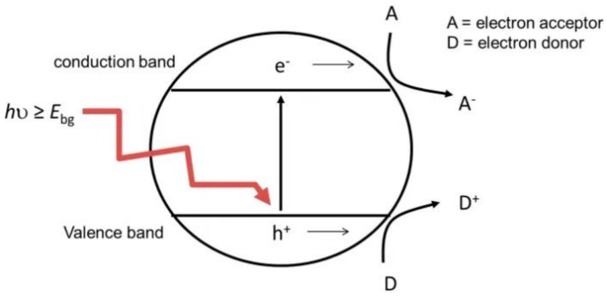

Figure 4: mechanism of the oxidative reaction

As you can see in the oxidative reaction mechanism illustrated below, a hydroxyl radical (•OH) is produced when the positive holes in the substance (metal oxide) react with the moisture on its surface. In the first step of this reaction, which is abbreviated as MO, photo-induced exciton production takes place on the surface of a metal oxide:

$$MO + h\nu \rightarrow MO\,(h^+ + e^-)$$

The following oxidative reactions can occur as a result of the photocatalytic effect:

$$h^+ + H_2O \rightarrow H^+ + \bullet OH$$

$$2\,h^+ + 2\,H_2O \rightarrow 2\,H^+ + H_2O_2$$

$$H_2O_2 \rightarrow 2\,\bullet OH$$

Below are the reductive processes that occur as a result of the photocatalytic effect:

$$e^- + O_2 \rightarrow \bullet O_2^-$$

$$O_2^- + H_2O + H^+ \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \rightarrow 2\,\bullet OH$$

subsequently in both of those processes, hydroxyl radicals (•OH) are generated. These hydroxyl radicals (•OH) have a redox potential of (E0 = +3.06 V) and are highly oxidative & non-selective.

MECHANISM OF PHOTOCATALYSIS

We have used fresh & varied tactics as time has passed. Surface or interface modification, particle size and shape management, composite or coupling materials, transition metal doping, nonmetal doping, co-doping applications (such as metal-metal, metal-nonmetal, nonmetal-nonmetal), noble metal deposition, organic dye sensitization of surfaces, and boosts to photocatalytic properties are all examples of such methods.

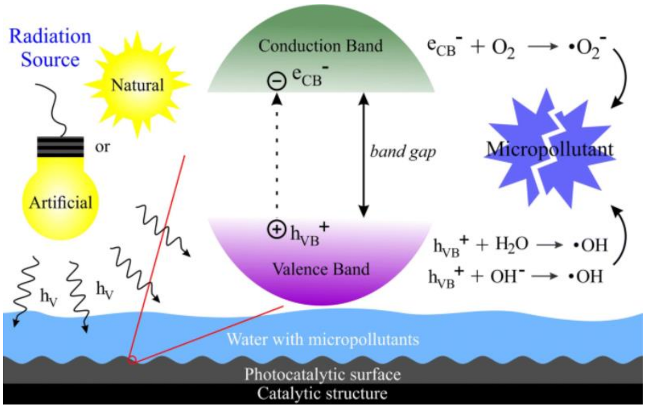

Figure 5: Mechanism of Photocatalysis

a) Doping

Doping is the process of introducing contaminants into a formerly clean substance. One kind of doping is cationic doping, while the other is anionic doping.

When metals like aluminum, copper, vanadium, iron, nickel, cobalt, manganese, etc. are doped into semiconductors, this process is called cationic doping. Alternatively, nonmetals like N, S, F, C, etc. are used in anionic doping. Every dopant has its own distinct effect on the photocatalyst's crystal structure. Metal & nonmetal ion doping brings photocatalysts into the visible light spectrum by lowering their band gap and creating new energy levels (impurity states) among the valence & conduction bands. Light excites electrons, which move them out of the impurity state and into the conduction band (CB).

Siriwong et al. (2012) studied the photocatalytic activity of many nanoparticles, including Fe-doped TiO2, WO3/ZnO, & Fe-doped CeO2. In contrast to Chen et al. (2012), who created a metal-doped Strontium titanate (SrTiO3) photocatalyst for water splitting, Zhang et al. (2013) investigated or clarified the impact of nonmetal dopants such as B, C, N, F, P, and S as anions on the electronic structures of SrTiO3. Anandan et al. (2012) investigated the effects of rare-earth metal La doping on the photocatalytic activity of zinc oxide (ZnO) & titania (TiO2). However, Maeda and Yamada (2007) demonstrated that TiO2 semiconductors could be doped with Cu, Al, and Fe. Doping photocatalysts with both metals & nonmetals increases their photocatalytic activity. Several studies have shown the co-doping of Cr + N in ZnO and/or Cu + Al in ZnO, as well as Ga + N in TiO2 & W + C in TiO2 nanowires, among other topics.

b) Composites/Coupling

Coupling semiconductors or composites is another practical way to improve the uv-light efficacy of photocatalysts for a range of uses. When semiconductors with different band gaps are connected, the result is a lower level of conduction band (CB). The implication is that electrons from the conduction band (CB) can be introduced into the large band gap semiconductor from the narrow band gap semiconductor. Although the transfer of electrons across various semiconductors is the key distinction, this process is otherwise very comparable to dye sensitization. It has been studied how to synthesize hydrogen utilizing reduced graphene oxide and linked SnO2, CdS, CdS/ Pt-TiO2, & NiS/ZnxCd1-xS.

c) Metallization

The photocatalytic activity of semiconductors has been enhanced by the incorporation of several noble metals, such as Pt, Au, Ag, Ni, Cu, Rh, Pd, etc. This process enhances photocatalytic reaction rates by decreasing the likelihood of electron-hole recombination or rejoining, which in turn leads to effective charge separation. Since noble metals can make electron transit easier, they are more effective photocatalysts.

d) Dye Sensitization

An advantageous method for developing & modifying photocatalyst surfaces for the purpose of utilizing uv-light for energy conversion is dye sensitization. Solar cells and photocatalytic devices can benefit from dyes because of their oxidation-reduction properties or visible light sensitivity. The visible light enables the dyes to inject electrons into the semiconductors' Conduction band (CB), which in turn initiates a catalytic process. In solar cells or during hydrogen synthesis, the best conditions for efficiently converting absorbed light into electrical energy include a rapid forward reaction and a moderate backward injection of electrons.

CONCLUSION

The investigation into the nanocomposite for photocatalytic degradation of organic contaminants under visible light has yielded promising results. The incorporation of noble metal nanoparticles into the semiconductor matrix has notably improved light absorption and charge separation, leading to enhanced photocatalytic performance. The experimental evaluation of the nanocomposite's photocatalytic activity against organic contaminants commonly found in wastewater has demonstrated its superior efficiency under visible light irradiation. Additionally, long-term stability studies and assessment of potential environmental impacts are imperative to ensure the viability and safety of these materials for real-world applications.

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