# A Conceptual Overview on Nanomaterials in Photocatalysis

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**Abstract**
The significant role of nanomaterials in photocatalysis is an attractive field among researchers in today's scientific community. The properties of nanomaterials are discussed in brief in order to understand its applications in photocatalysis. The synthetic ways under different conditions are also explained along with the mechanism. Commonly used photocatalysts like Ag based, Ti based and ZnO based materials are reported. Recently, graphene based materials are also used for the degradation of dyes and various pollutants. The diverse applications in energy and environment are also reported.

**Keywords**
Nanomaterials, Photocatalysis, degradation of dyes, Synthesis, Applications.

**Introduction**
The nanostructured materials are designed for various applications including energy and environmental. These constituteinteresting semiconductor materials for photocatalytic reactions due to its unique crystalline structure and extraordinary properties, which has been used extensively to tackle current challenges in the environment. Nanostructured photocatalytic materials are mainly attributed to their outstanding and superior physical and chemical properties compared with their bulk counterpart because of different chemical composition, arrangement of atoms, distinctive particle morphology, particle size, high UV absorption, wide energy band gap and high surface area (Aghighi & Haghighat, 2015). Moreover, nanostructured photocatalytic materials (NPMs) are defined as those materials composed of structural elements, majority arecrystalline in nature with a characteristic size of a few nanometers (1-100 nm). They are categorized as0D (clusters of any aspect ratio from 1 to ∞),1D (multilayers), 2D (ultrafine-grained over-layers or buried layers), and 3D (nanophase materials depend on their dimensional grain growth)materials, which generatesnew interesting properties andexhibitsremarkably enhanced functionsfor fabrication of systems in various fieldssuch as, energy, medical,biological, opto-electronics, optics, magnetic, electronic and manyothers (Fig.1). Particularly, metal and metal oxide nanostructures have beeninvestigated widely due to their high specific surface to

volume ratio(extrinsic contribution),quantum confinement effects (intrinsic contribution) and their optical and magnetic properties.In addition, their properties can be enhanced byaltering theirshape, size, chemical composition, high interfacial reactivity and type of grains present at the interfaces (Siegel, 1993). In this regard, few porous structured metal oxide photocatalysts such as, ZnO, $TiO_2$, $SnO_2$ and $CeO_2$ have been prepared and used to enhance photocatalytic performance.

The different dimensions in size make these materials exhibit different electronic changes in terms ofenergy and number of levels (Hu, Li, & Yu 2010). The photocatalytic performance of these materials strongly depends on the morphology of materials. Hence, understanding the relationship between the physicochemical properties of photocatalytic materials and their performances as well as the fundamentals in catalytic processes is important to design and synthesize photocatalytic materials. The conventional methods of preparation such as, self-assembly and template growth enables to produce the porous structures, but with primarily nonporous shells. Therefore, the design and fabrication of porous metal oxides with high photocatalyticperformance are still very challenging (Zhu et. al. 2017).

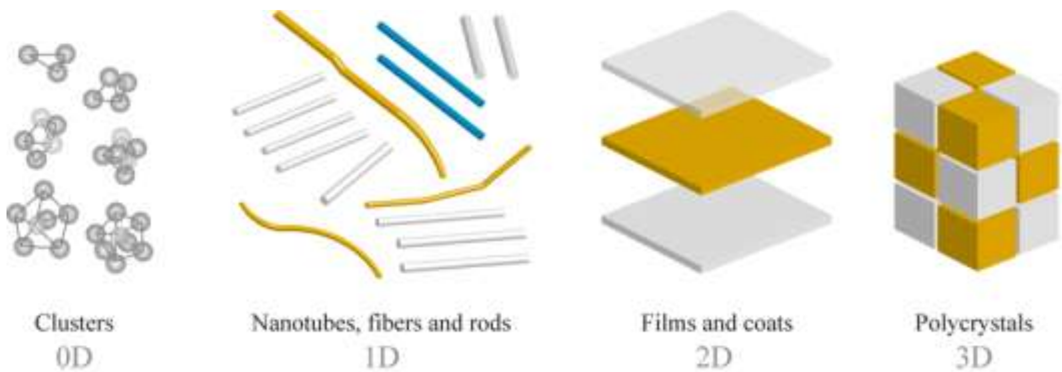


**Fig. 1. Nanostructured Photocatalytic Materials**

The photocatalysis offers possibility of extending the spectrum of applications to a variety of processes, including oxidations and oxidative cleavages, reductions, isomerizations, substitutions, condensations and polymerizations. Hence, applying the concept of nanotechnology to heterogeneous catalysis helps to understand more accurately the transformations occurring on the catalyst´s surface at a molecular level (Somorjai & Borodko, 2001). Heterogeneous photocatalysis is a method, which includes a large variety of reactions: organic synthesis, water splitting, photoreduction, hydrogen transfer, metal deposition, disinfection and anti-cancer therapy, water detoxification, removal of gaseous pollutants, etc.(Carp et. al. 2004; Herrmann, 1999).The synthesis of materials with nanometric dimensions will facilitate a better understanding of reaction mechanisms as well as to design novel useful catalytic systems. Though there are several advances in designing new methods to obtain reproducible materials,there are numerous difficulties, which have to be solved. Self-assembly of semiconductor nanocrystals into hierarchical structures has been recognized as an alternative way to improve photocatalysis efficiency in view of improved light absorption capability. sub-micrometer sized $CdS_xSe_{1-x}$(x= 0-1) spheres from monodisperse $CdS_xSe_{1-x}$ quantum dots (QDs) through the three-dimensional self-assembly and oriented attachment strategy (Wang et. al. 2017).Nanostructured photocatalytic materials are extensively investigated for numerous environmental and energy related applications. Independent from their photocatalytic properties, many nanostructured photocatalytic materialsare widely applied as additives for industrial materials such as, paintings, coatings, foods, textiles and cosmeticsand leads to an increase in production. Furthermore, researchers are constantly developing new materials in order to optimize the photocatalytic efficiency and optical properties (Friehs et. al. 2016).

**Properties of Nanostructured Photocatalytic Materials**

The nanostructured photocatalytic materials imparts novel properties such as, enhanced light absorption, quantum confinement, high specific surface area and tunable surface-to-volume ratio, hierarchical porous structure, optical and magnetic effects, etc. Thus,creating tremendous opportunities in extending their applications in various fields, including water and air purification, photocatalytic disinfection, photocatalytic hydrogen generation, and dye-sensitized solar cells (Yu et. al. 2012).

**Optical Property of NPMs and Quantum Confinement Effect**

The semiconducting photocatalyst materials have been widely studied for their photocatalytic activities under UV/Visible light. However, their industrial use is remarkably enhanced due to good visible light absorption capability, reclaiming, and high quantum yield due to fast recombination of charge carriers generated by visible light irradiation. In general, to utilize the visible part of the electromagnetic spectrum ($\lambda$>400 nm), the bandgap of a photocatalyst material must be narrow (up to 3.0 eV), and the preferred range of ionic character is between 20-30percent. Hence, searching for new types of potential photocatalytic materials that can be exploited by solar irradiation particularly under visible light ($\lambda$>400nm) along with providing better stability by separating the electron-hole pairs more effectivelyhas become an imperative issue in current photocatalysis and environmental research areas. In this regard, better photocatalytic activity is found for few semiconductor composites combining $ZrFe_2O_5$ with secondary semiconductor such as, $TiO_2$ under visible light irradiation for the degradation of toluidine blue O dye.The photo catalytic measurements showed that $ZrFe_2O_5$ nanoparticles under visible light could be efficiently used for the photocatalytic degradation of toluidine blue O dye. In order to investigate the photocatalytic action, it is imperative to appraise the optical absorption of $ZrFe_2O_5$ nanoparticles for the motive that UV Vis absorption edge is associated with energy band of the semiconductor catalyst. The optical bandgap ($E_g$) of $ZrFe_2O_5$ nanoparticles estimated from Tauc plot is 2.4 eV. From electronic structure point of view, the band potentials of $ZrFe_2O_5$ accomplish a straddling gap, which may make possible the transfer of charge carriers and retard $e^- h^+$ recombination. Photodegradation efficiency in the absence of $ZrFe_2O_5$nanoparticles showed no significant change in absorption maximum of toluidine blue O. Although, bulk $ZrFe_2O_5$exhibits the photo-catalytic ability to decompose TBO dye under visible light irradiation, degradation with $ZrFe_2O_5$ nanoparticles is tremendously more efficient than that of bulk$ZrFe_2O_5$ (Shahid et. al. 2013).

The quantum mechanical effects, such as an increased bandgap of semiconductors with reduction of size are viewed as having strong potential for future applications. The narrow sized ZnO nanoparticle was synthesized by controlling the temperatures, wherein good crystallinity and peak broadening with decrease in particle sizeare observed.It is to be noted that increasing the temperature from 60 to 65°C caused a subsequent increase in particle size from 4 to 12nm. This deciphers that an associated increase in bandgap with decrease in particle size was also noticed which is a strong indication of the quantum confinement effect(Manzoor et. al. 2016).CuO–$TiO_2$ composite photocatalysts were prepared, wherein CuO clusters acts as an effective co-catalyst to enhance the photocatalytic $H_2$-production activity of $TiO_2$. The optimal CuO content in photocatalyst is 1.3 wt.%. The quantum size effect of CuO clusters is deemed to alter their energy levels of conduction and valence band edges in the CuO–$TiO_2$ semiconductor systems, which favor the electron transfer and enhance the photocatalytic activity. The work demonstrates a new way for enhancing hydrogen production activity by quantum size effect(Yu et. al. 2011).

## Surface Area Studies

As photocatalytic degradation reactions predominantly occur on the catalyst surface, a large surface area is critically important to increase the photocatalytic efficiency.It is based on this consideration, mesoporous materials with large surface areas and special porous structures will provide a highly active catalyst for photocatalytic contamination degradation. $TiO_2$ with a wormhole-like structure and narrow pore distribution was fabricated (Sang et. al. 2010). The BET surface area was 525 $m^2$/g and its average pore size was around 4.5 nm. The wormhole-like framework structure of the resulting photocatalysts improved the surface area and the light absorption properties, which led to the enhancement in photocatalytic hydrogen evolution activity for water splitting. Impact of specific surface area of the highly functional $ZrFe_2O_5$ nanoparticles has also been discussed (Shahid et. al. 2013).

One of the factors that improved the photocatalytic performance of $ZrFe_2O_5$ to a great extent is the size shrinkage of $ZrFe_2O_5$, thereby enlarging its specific surface area, due to which it could adsorb more TBO to photodegrade on its surfaceThe difficulty in obtaining a high surface area is its unstable nature. $TiO_{2,}$ with high surface area are thermally unstable, due to the occurrence of phase transformation and crystallite growth during the calcinations. This is overcome by immobilizing the $TiO_2$ nanocrystalline on inactive supporting materials such as glass, silica, ceramic and zeolite. These supporting materials has potential advantages such as increase in concentration of pollutants near $TiO_2$ particles, adsorption of intermediates formed and recyclability of adsorbents. Silica particles are found to be a superior supporting material because of the convenience of depositing $TiO_2$ to the $SiO_2$ surface (NaWei et. al. 2016).

**Magnetic Effects**

The nanostructured magnetic semiconductors have attracted considerable attention due to their potential applications in the new emerging fields of optoelectronics, spin-polarized light emitting diodes (LEDs) and photovoltaic synthesized nanocrystalline ZnO particles doped with different concentration of Fe impurity. Numerous contradictory results on the magnetic properties of the doped ZnO nanomaterials have been reported. From all the experimental investigation on the ferromagnetism of the doped ZnO, some measurements confirmed the presence of ferromagnetism while other measurements report the absence of any magnetic order in the samples prepared using different techniques.

The few measurements relate the origin of room temperature ferromagnetism in doped ZnO with magnetic cluster or secondary magnetic phases and on the otherhand some measurements support an intrinsic ferromagnetic origin. The fact is that till now, the origin of ferromagnetism in doped ZnO remains very controversial and similar contradictory results are also observed in Fe-doped ZnO nanomaterials (Kumar et. al. 2014).It has demonstrated that 1% Fe-doped ZnO samples show diamagnetic character, while ferromagnetic nature is observed for 2 percent and 3 percent Fe-doped samples, and higher doping of Fe, paramagnetic nature dominates (Sharma et. al. 2009). The room temperature ferromagnetism in Fe-doped ZnO with additional Cu doping have been reported (Zhang et.al. 2007, Liu et. al. 2011). It is confirmed the subtle enhancement in saturation magnetization with Fe doping in ZnO matrix. The room temperature ferromagnetism in magnetic semiconductors is very sensitive to preparation methods (Dhiman et. al. 2013).

**Mechanism of Photocatalysis**

A photocatalytic reaction is initiated when a photoexcited electron is promoted from the filled valence band of a semiconductor photocatalyst (SC) to the empty conduction band as absorbed photon energy, *h*υ, equals or exceeds the band gap of the semiconductor photocatalyst, leaving behind a hole in the valence band. In concert, electron and hole pair ($e^{-}– h^{+}$) is generated. The following chain reactions have been widely accepted:

| | | |
|---|---|---|
| Photoexcitation | : $TiO_2/SC + h\upsilon \rightarrow e^{-} + h^{+}$ | (1) |
| Oxygen ionosorption | : $(O_2)\ ads + e^{-} \rightarrow O_2^{\bullet -}$ | (2) |

Ionization of water : $H_2O \rightarrow OH^- + H^+$ (3)
Protonation of superoxides : $O_2^{\bullet -} + H^+ \rightarrow HOO^\bullet$ (4)

The hydroperoxyl radical formed in (4) has also scavenging properties similar to $O_2$. Thus, doubly prolonging the lifetime of photohole:

$$HOO^\bullet + e^- \rightarrow HO_2^- \quad (5)$$
$$HOO^- + H^+ \rightarrow H_2O_2 \quad (6)$$

Both oxidation and reduction can take place at the surface of photoexcited semiconductor photocatalyst. The recombination between electron and hole occurs unless oxygen is available to scavenge the electrons to form superoxides ($O_2^{\bullet -}$), its protonated form is the hydroperoxyl radical ($HO_2^\bullet$) and subsequently $H_2O_2$ (Colmenares et. al. 2009).

**Synthesis of Nanostructured Photocatalytic Materials**

The intrinsic properties of photocatalytic materials can be effectively altered by controlling their size, shape, composition, crystallinity, and structure. The growth of nanoscale materials depends on factors such as, their thermodynamic and kinetic barriers in the reaction. It is also influenced by vacancies, defects and surface reconstruction.

It has been observed that most synthetic methods for synthesizing nanomaterials use conventional heating due to the need for high-temperature-initiated nucleation followed by controlled precursor addition to the reaction. The various methods developed for synthesis of photocatalytic materials are hydrothermal, co-precipitation, sol-gel, ultrasonic impregnation, ionic liquid-assisted photochemical synthesis, electrochemical synthesis solvothermal, facile chemical impregnation, microwave assisted synthesis etc.

**Hydrothermal Method**

It is one of the known methods of synthesisto produce different chemical compounds and materials using closed-system physical and chemical processes flowing in aqueous solutions at temperatures above 100°C and pressures above 1 atm (Byrappa& Yoshimura, 2001). It includes the ability to synthesize crystals of substances, which are unstable near the melting point, as well as large crystals of high quality (Mutta et. al. 2017).

The photocatalytic materials synthesized by hydrothermal method includes titania, silver, graphene based catalyst, cadmium and nickel sulphides, mixed metal oxide, rare earth metal oxides etc. as indicated in Fig 2.


**Fig. 2 Schematic Diagram of Hydrothermal Method of Synthesis**

**Silver (Ag) Based Photocatalysts**

Most of the Ag-based semiconductors could exhibit high initial photocatalytic activity, but they suffer from poor stability because of the photochemical corrosion. Hence, designing heterojunction, increasing specific surface area, enriching porousnanostructure, regulating morphology, controlling crystal facets and producing plasmonic effects have been considered as the effective strategies to improve their photocatalytic performance. Also, combining the superior properties of carbon materials (e.g. carbon quantum dots, carbon nanotube, carbon nanofibers, graphene) with Ag-based semiconductor has produced high efficient composite photocatalyts (Li et. al. 2015). Synthesized $Ag^+$-carbon dots (CDs)-$Bi_2WO_6$ ternary composite with excellent solar-light-driven photocatalytic performance using hydrothermal-impregnation method. The as-prepared catalyst exhibited uniformity in diameter without aggregation and micropores (0.5-2μm). $Ag^+$-carbon dots (CDs)-$Bi_2WO_6$ displayed superior photocatalytic efficiency with nearly 100% removal of TC (20 mg/L) in 20 min and 64% mineralization in 90 min (Li et. al. 2016).

**Titanium Based Photocatalyst**

A semiconductor such as $TiO_2$ is very suitable for green photocatalysis, as it is very effective, cheap and stable to photo-corrosion (Yurdakal et. al. 2017).Hetero-structuredphotocatalyst of titanium was reported. The authors succeeded in preparing $Bi_{12}TiO_{20}$-$Bi_2WO_6$heterostructures by a facile hydrothermal method. The morphology comprises of regular tetrahedrons and nanoflakes. The obtained hetero junction has been identified to posses higher photocatalytic ability for the degradation of RhB under exposure to UV-visible light (Zhang et. al. 2015).

**ZnO Based Photocatalyst**

ZnO has excellent thermal and chemical stabilities, a large piezoelectric constant and an easily modified electric conductivity. The physical properties of ZnO are highly dependent on particles morphology, size, aspect ratio, orientation etc., which designs its technological applications. In addition to that, numerous nanostructured ZnOs with various morphologies have been fabricated, such as, nanowires (Huang et. al. 2001), nanosheets (Yan et. al. 2003), nanotubes (Yu et. al. 2005) and nanoflowers (Peng et. al. 2006).The synthesized ZnO is co-doped from different noble and transition metals (Ni, Mn, Fe and Ag) doped ZnO (M/ZnO) nanostructures by hydrothermal method. Results confirmed the formation of well dispersed Ni and Ag NPs and highly agglomeration Mn and Fe NPs on the surface of ZnO nanostructures. The degradation rate of tartrazine was studies and obtained a maximum rate of 98.2 percent in 60 min using Ni/ZnO (Turkyılmazet. al. 2017).

**Sol-Gel Processing**

The sol gel process involves combination of chemical reactions which turns a homogenous solution of reactants into an infinite molecular weight polymer. This polymer is a three-dimensional interconnected pores. The various other methods of sol-gel processing are sol-gel hydrothermal (Fuentes et. al. 2017), sol-gel assisted electrospinning (Xu et. al. 2015), sol-gel microwave (Shen et. al. 2016) etc.

**Aluminium Based Materials**

The overwhelming applications of aluminium based materials are superior due to their physicochemical features. For example, $Al_2O_3$ has application in diverse fields ranging from medical, military and industrial purposes. It has reported the facile synthesis of Al doped ZnO-polyaniline hybrids by combining both sol-gel and in-situ oxidative polymerization process. (Mitra et. al. 2017)

**Titanium Based Materials**

An unusual sol–gel method utilizing novel and less chemical materials in addition to simple procedure to synthesize $ZnTiO_3$ nanostructures. Initially, the precursors along with the chelating agents were dissolved in ethanol, stirred and kept in an oven at 60ºC and 70ºC, finally grounded and calcined at 700ºC, 800ºC and 900ºC for 3 h. A large number of separate, small and uniform particles were observed after calcination at 700ºC. It is found that the amorphous gel can be transformed into pure ilmenite-type $ZnTiO_3$ through calcination at 700ºC(Niasari et. al. 2016).

**Microwave Method**

The use of MW-irradiation provides increased reaction kinetics and rapid initial heating, which results in enhanced reaction rates. This also provides energy efficiency by reducing the reaction time from hours to minutes when compared with conventional heating methods, which culminates in clean reaction products and higher yields.

**Graphene-Based Materials**

Graphene has been regarded as an important component for functional materials, especially for developing a variety of photocatalysts (Niasari et. al. 2016; Maruyama et. al.2006). It has demonstrated an easy, fast and low cost MWIapproach for the preparation of CuO/Graphene (CuO/G) hybrid composite, which includes dispersion of CuO/graphene-oxide hybrid followed by MWI reduction. Photocatalytic performance of CuO/G hybrids could be studied by degradation of MB under UV irradiation, which indicated that CuO/G hybrid is an effective photocatalyts towards degradation of MB (Darvishi et. al. 2017).

**Zinc Based Materials**

The zinc oxide (ZnO) nanoparticle has been synthesized by using crude water extract of *Psidiumguajava*Linn leaves and MWI. As a general procedure, the crude extract is mixed with zinc(II) aqueous solution, which accounts for four different zinc salts i.e., $Zn(CH_3COO)_2$, $ZnSO_4$, $ZnCl_2$ and basic carbonate form of $ZnCO_3$ have been used. The synthesis was carried out using a household microwave oven operatingat 720 W for varying cycles of 3 min-on and 1 min-off. The samples chosen for the photocatalytic studies were ZnO NPs yielded from the reaction conducted for 45 cycles and treated at 900°C. Also, ZnO NPs showed excellent surface area and efficient photocatalytic activity towards the degradation of organic dyes (Somsri et. al. 2016).

**Applications of Nanostructured Photocatalysts**

The technological and economic importance of photocatalysis hasbeen considerably increased over the past decade. These improvements inperformance have been strongly correlated to advances in nanotechnology. The introduction of nanoparticulate photocatalystshas tremendously enhanced the catalytic efficiency of specificmaterials. A variety of applications ranging from anti-fogging, antimicrobial and self-cleaning surfaces through water and airpurification and solar-induced hydrogen production, which have been developedand many of these have made their way into commercial products.However, extensive research continues to further optimize thistechnology and to widen the spectrum of potential applications.Research and application include anti-stick or anti-fingerprintcoatings, soil repellency and decomposition of organic matter, such as microbes or fats. Hence, when exposed to light certain semiconducting materials such as, “photocatalysts” trigger or accelerate chemical reactions(Hashimoto et. al. 2005). Moreover, due to their large surface area, nano-sized catalyst particles show asignificantly enhanced reactivity compared to larger particles or bulkmaterials. Also, numerous materials are under examination. However, noneappear to match the efficiency of $TiO_2$. Its application requires illuminationin the UV or at e extreme blue edge of visible spectrum. Thus, the volume applications are mainly limited to outdoor area. Furthermore, it is to be noted that despite the reduced natural illumination, even indoorproducts such as sanitary ceramics are being increasingly applied.Moreover, research is underway to widen the exploitable spectral rangetoward visible light. In the recent years, applications have been directed towards environmental clean-up, drinking water treatment, industrial and health applications are carried out through the following:

i) Removing trace metals: The trace metals such as, mercury (Hg), chromium (Cr), lead (Pb) and other metals, which are considered to behighly hazardous to health. Thus, removing these toxic metals is essentiallyimportant for human health and water quality. The environmentalapplications of heterogeneous photocatalysis includes removingheavy metals such as, mercury (Hg), chromium (Cr), cadmium (Cd),lead (Pb), arsenic (As), nickel (Ni) and copper (Cu). The photoreducingability of photocatalysis has been used to recover expensive metalsfrom industrial effluent such as, gold, platinum and silver (Nakata et. al. 2012).

ii) Destruction of organics: In this, photocatalysis has been used for destruction of organic compounds such as, alcohols, carboxylic acids,phenolic derivatives or chlorinated aromatics, into harmless products. For instance, carbon dioxide, water and simple mineral acids can be treated using photocatalysis. Also, watercontaminated by oil can be treated efficiently by photocatalytic reaction. In addition to this, herbicides and pesticides such as, 2,4,5-trichlorophenoxyacetic acid, 2,4,5-trichlorophenol and s-triazineherbicides, which contaminates water can also be mineralized (Gamage & Zhang, 2010).

## Conclusion

The overall view on the significance of nanomaterials in photocartalysis has been reported, which explained its properties like optical and magnetic properties based on quantum confinement effect and surface area is discussed. The various synthetic routes like hydrothermal, sol-gel and microwave method is explained on the basis of few examples like Ag-based, $TiO_2$-based, ZnO based, Graphene based etc. The present research study has emphasized on various applications of nanomaterials. Also, it exhibited that nanomaterials are smaller in size, but their applications are quite vast, which will fulfill the scientific and technological needs of global community.

**References**

1. Aghighi, A. & Haghighat, F. (2015). Evaluation of Nano-Titanium Dioxide ($TiO_2$) Catalysts for Ultraviolet Photocatalytic Oxidation Air Cleaning Devices, Journal of Environmental Chemical Engineering, Vol. 3, pp.1622-1629.
2. Byrappa, K. & Yoshimura, M. (2012). Handbook of Hydrothermal Technology, Second Edition, Noyes Publications, New Jersey, USA, 763p.
3. Carp, O., Huisman, C. L. & Reller, A. (2004). Photo Induced Reactivity of Titanium Dioxide, Progress Solid State Chemistry, Vol. 32, pp.33-177.
4. Colmenares, J. C., Luque, R., Campelo, J. M., Colmenares, F., Karpiński, Z. & Romero, A. A. (2009). Nanostructured Photocatalysts and Their Applications in the Photocatalytic Transformation of Lignocellulosic Biomass: An Overview, Materials, Vol. 2, pp.2228-2258.
5. Darvishi, M., Asgerani, G. M. & Yazdi, J. S. (2017). Simple Microwave Irradiation Procedure for the Synthesis of CuO/Graphene Hybrid Composite with Significant Photocatalytic Enhancement, Surfaces and Interfaces, Vol. 7, pp.69-73.
6. Dhiman, P., Chand, J., Kumar, A., Kotnala, R. K., Batoo, K. M. & Singh, M. (2013). Synthesis and Characterization of Novel Fe@ZnO Nanosystem, Journal of Alloys and Compounds, Vol. 578, pp.235-241.
7. Friehs, E., Alsalka, Y., Jonczyk, R., Lavrentieva, A., Jochums, A., Walter, J. G., Stahl, F., Scheper, T. & Bahnemann. D. (2016). Toxicity, Phototoxicity and Biocidal Activity of Nanoparticles Employed in Photocatalysis, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Vol. 29, pp.1-28.
8. Fuentes, S., Muñoz, P., Llanos, J., Vega, M., Martin, I. R. & Chavez-Angel, E. (2017). Synthesis and Optical Characterization of Er-Doped Bismuth Titanate Nanoparticles Grown by Sol–Gel Hydrothermal Method, Ceramics International, Vol. 43, pp.3623-3630.
9. Gamage, J. & Zhang, Z. (2010). Applications of Photocatalytic Disinfection, International Journal of Photoenergy, Vol. 17, pp.1-11.
10. Hashimoto, K., Irie, H. & Fujishima A. (2005). $TiO_2$ Photocatalysis: A Historical Overview and Future Propsects. Japanese Journal of Applied Physics, Vol. 44, pp.8269-8285.
11. Herrmann, J. M. (1999). Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants. Catalysis Today, Vol. 53, pp.115-129.
12. Hu, X., Li, G. & Yu, J. C. (2010). Design, Fabrication and Modification of Nanostructured Semiconductor Materials for Environmental and Energy Applications, Langmuir, Vol. 26, pp. 3031-3039.

13. Huang, M. H., Mao, S., Feick, H., Yan, H., Wu, Y., Kind, H., Weber, E., Russo, R. & Yang, P. (2001). Room Temperature Ultraviolet Nanowire Nanolasers, Science, Vol. 292, pp.1897-1899.
14. Kumar, K., Chitkara, M., Sandhu, I. S., Mehta, D. & Kumar, S. (2014). Photocatalytic, Optical and Magnetic Properties of Fe-doped ZnO Nanoparticles Prepared by Chemical Route, Journal of Alloys and Compounds, Vol. 588, pp.681-689.
15. Li, J., Fang, W., Yu, C., Zhou, W., Zhu, L. & Xie, Y. (2015). Ag-based Semiconductor Photocatalysts in Environmental Purification, Applied Surface Science, Vol. 358, pp.46-56.
16. Li, Z., Zhu, L., Wu, W., Wang, S. & Qiang, L. (2016). Highly Efficient Photocatalysis toward Tetracycline under Simulated Solar-Light by $Ag^{+}$-CDs-$Bi_2WO_6$: Synergistic Effects of Silver Ions and Carbon Dots, Applied Catalysis B: Environmental, Vol. 192, pp.277-285.
17. Liu, H., Yang, J., Hua, Z., Liu, Y., Yang, L., Zhang, Y. & Cao, J. (2011). Cu-doping Effect on Structure and Magnetic Properties of Fe-doped ZnO Powders, Materials Chemistry and Physics, Vol. 125, pp.656-659.
18. Manzoor, U., Islam, M., Tabassam, L. & Rahman, S. U. (2009). Quantum Confinement Effect in ZnO Nanoparticles Synthesized by Coprecipitate Method, Physica E, Vol. 41, pp.1669-1672.
19. Maruyama, Y., Irie, H., & Hashimoto, K. (2006). Visible Light Sensitive Photocatalyst, Delafossite Structured α-$AgGaO_2$, The Journal of Physical Chemistry B, Vol. 110, pp.23274-23278.
20. Mitra, M., Ghosh, A., Mondal, A., Kargupta, K., Ganguly, S. & Banerjee, D. (2017). Facile Synthesis of Aluminium Doped Zinc Oxide-Polyaniline Hybrids for Photoluminescence and Enhanced Visible-Light Assisted Photo-Degradation of Organic Contaminants, Applied Surface Science, Vol. 402, pp.418–428.
21. Mutta, G. R., Popuri, S. R., Ruterana, P. & Buckman, J. (2017). Single Step Hydrothermal Synthesis of Mixed Valent $V_6O_{13}$ Nano-Architectures: A Case Study of the Possible Applications in Electrochemical Energy Conversion, Journal of Alloys and Compounds, Vol. 706, pp.562-567.
22. Nakata, K., Ochiai, T. Murakami, T. & Fujishima, A. (2012). Photoenergy Conversion with $TiO_2$Photocatalysis: New Materials and Recent Applications, Electrochimica Acta, Vol. 84, pp.103-111.
23. Niasari, M. S., Soofivand, F., Nasab, A. S., Arani, M. S., Faal, A. Y. & Bagheri, S. (2016). Synthesis, Characterization, and Morphological Control of $ZnTiO_3$ Nanoparticles through Sol-Gel Processes and its Photocatalyst Application, Advanced Powder Technology, Vol. 27, pp.2066-2075.
24. Peng, Y., Xu, A. W., Deng, B., Antonietti, M. & Helmut, C. (2006). Polymer-Controlled Crystallization of Zinc Oxide Hexagonal Nano Rings and Disks, The Journal of Physical Chemistry B, Vol. 110, pp.2988-2993.

25. Sang, L., Dai, H., Sun, J., Xu, L., Wang, F. & Ma, C. (2010). Fabrication of the hydrogen-evolving photocatalyst with mesoporous structure, International journal of hydrogen energy, Vol. 35, pp.7098-7103.
26. Shahid, S. A., Nafady, A., Ullah, I., Yap, Y. H. T., Shakir, I., Anwar, F. & Rashid, U. (2013). Characterization of Newly Synthesized $ZrFe_2O_5$ Nanomaterial and Investigations of Its Tremendous Photocatalytic Properties under Visible Light Irradiation, Journal of Nanomaterials, Vol. 2, pp.257-268.
27. Sharma, P. K., Dutta, R. K,. Pandey, A. C., Layek, S. & Verma, H. C. (2009). Effect of Iron Doping Concentration on Magnetic Properties of ZnO Nanoparticles, Journal of Magnetism and Magnetic Materials, Vol. 321, 2587-2591.
28. Shen, H. Xue, T. Wang, Y., Cao, G. Lu, Y. & Fang, G. (2016). Photocatalytic Property of Perovskite $LaFeO_3$ Synthesized by Sol-Gel Process and Vacuum Microwave Calcinations, Materials Research Bulletin, Vol. 84, pp.15-24.
29. Siegel, R. W., (1993). Nanostructured Materials Mind Over Matter, Nanostructure Materials, Vol. 3, pp.1-18.
30. Somorjai, G. A., &Borodko, Y. G., (2001). Research in Nanosciences-Great Opportunity for Catalysis Science, Catalysis Letters, Vol. 76, pp.1-5.
31. Somsri, S., Sonwaew, W. & Rujiwatra, A., (2016). *Psidiumguajava* Linn. Extract Mediated Microwave Synthesis and Photocatalytic Activities of ZnO Nanoparticles, Materials Letters, Vol. 177, pp.124-127.
32. Turkyılmaz, S. S., Guy, N., & Ozacar, M., (2017). Photocatalytic Efficiencies of Ni, Mn, Fe and Ag Doped ZnO Nanostructures Synthesized by Hydrothermal Method: The Synergistic/Antagonistic Effect Between ZnO and Metals, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 341, pp. 39–50.
33. Wang, L., Di, Q., Sun, M., Liu, J., Cao, C., Liu, J., Xu, M. & Zhang, J., (2017). Assembly-Promoted Photocatalysis: Three-Dimensional Assembly of $CdS_xSe_{1-x}$(x=0-1) Quantum Dots into Nanospheres With Enhanced Photocatalytic Performance, Journal of Materiomics, Vol. 3, pp.63-70.
34. Wei, X. N., Wang, H. L., Li, Z. D., Huang, Z. Q., Qi, H. P. & Jiang, W.F., (2016).Fabrication of the Novel Core-Shell MCM-41@m$TiO_2$ Composite Microspheres with Large Specific Surface Area for Enhanced Photocatalytic Degradation of Dinitro Butyl Phenol (DNBP), Applied Surface Science, Vol. 372, pp.108-115.
35. Xu, X., Li, S., Wang, X., Ma, Y., Wang, X. & Gao, K., (2015). Fabrication and Characterization of $Ca_2Fe_2O_5$ Nanofibers Photocatalyst by Sol-Gel Assisted Electrospinning at Low-Temperature, Materials Letters, Vol. 143, pp.75-79.
36. Yan, Y., Liu, P. Wen, J. G., To, B. & Al-Jassim, M. M. (2003). In-situ Formation of ZnO Nanobelts and Metallic Zn Nanobelts and Nanodisks, The Journal of Physical Chemistry B, Vol. 107, pp.9701-9704.

37. Yu, H., Zhang, Z., Han, M., Hao, X. & Zhu, F. (2005). A General Low-Temperature Route for Large Scale Fabrication of Highly Oriented ZnO Nanorod/Nanotube Arrays, Journal of the American Chemical Society, Vol. 127, pp.2378-2379.
38. Yu, J., Jaroniec, M., Yu, H. & Fan, W. (2012). Synthesis, Characterization, Properties, and Applications of Nanosized Photocatalytic Materials, Journal of Nanomaterials, Vol. 17, pp.1-3.
39. Yu, J., Hai, Y. & Jaroniec, M., (2011). Photocatalytic Hydrogen Production Over CuO-Modified Titania, Journal of Colloid and Interface Science, Vol. 357, pp.223–228.
40. Yurdakal, S., Yanar, S. O., Cetinkaya, S., Alagoz, O. Yalcın, P. & Ozcan, L. (2017). Green Photocatalytic Synthesis of Vitamin B3 by Pt Loaded $TiO_2$ Photocatalysts, Applied Catalysis B: Environmental, Vol. 202, pp.500-508.
41. Zhang, H. W., Wei, Z. R., Li, Z. Q. & Dong, G.Y. (2007). Room-Temperature Ferromagnetism in Fe-doped, Fe- and Cu-Co doped ZnO Diluted Magnetic Semiconductor, Materials Letters, Vol. 61, pp.3605-3607.
42. Zhang, X., Zhang, L., Hu, J. S., Pan, C. L., & Hou, C. M. (2015). Facile Hydrothermal Synthesis of Novel $Bi_{12}TiO_{20}$-$Bi_2WO_6$ Heterostructure Photocatalyst with Enhanced Photocatalytic Activity, Applied Surface Science, Vol. 346, pp.33-40.
43. Zhu, G., Li, X. Wang, H. & Zhang, L., (2017). Microwave assisted synthesis of reduced graphene oxide incorporated MOF derived ZnO composites for photocatalytic application. Catalysis Communications, Vol. 88, pp.5-8.