

# A Brief Review of the Recent Advances in the Field of Removal and Degradation of Organic Pollutant's Through Metal Inorganic Frameworks

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**Abstract:** *Water purification has been a big global concern over the past few decades. Many toxic organic contaminants in waste water have been degraded through photocatalysis which is considered to be one of the most promising directions for solving the worldwide environment problems. Water contamination being a serious problem is continuously threatening both the quality of human lives and aquatic lives. The present review introduces an extensive and critical analysis of the most recent studies on the use of different photocatalyst for organic adsorption and photodegradation. Overall, the discussion is organized and based on the different photocatalyst which will target different organic contaminants discharged from various industries, domestic and agriculture waste water streams.*

**Keyword:-** Metal inorganic frameworks, Photodegradation, adsorption and waste water.

**Introduction** The rapid development of industrialization and urbanization as well as huge population increase, the urgent demand for acute storage of clean water source have attracted immense attention all over the world. One of the constant concerns in waste water treatment facilities is to comply and cope with the new and changing regulations. Degradation and removal of organic contaminants required several treatments because each one has its own advantages and disadvantage.

The combination of processes such as adsorption, physiochemical oxidation, biological oxidation and membrane separation had been extensively studied for water purification but photocatalysis had been considered as one of the best options for waste water treatment. It has great potential and efficiency by using sunlight to remove the various organic contaminants and harmful bacteria. As an easily accessible, safe and renewable energy source, natural sunlight is the ideal source to supply energy for photocatalysis.

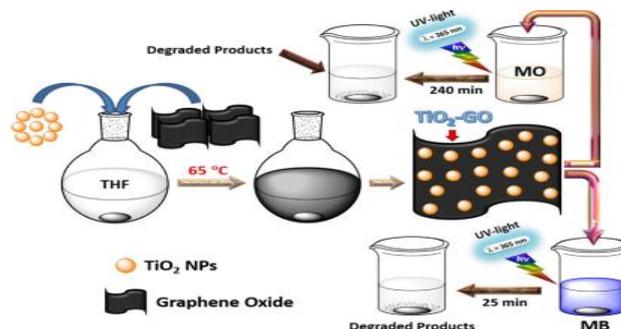
As we know that dyes are difficult to degrade, these are chemically stable, non biodegradable and exist as substance that possesses toxic and carcinogenic characteristics. For these type of degradation Advance Oxidation Processes (AOPs) is the best method which is including methods such as ozonation, photocatalysis, electrochemical oxidation, fenton and fenton like process. Almost all following methods are utilizing hydroxyl radical (.OH) as a highly oxidizing agent which is having redox potential of 2.8ev but researchers reported some other oxidizing agent like sulfate radical (So<sub>4</sub>.-), permanganate (MnO<sub>4</sub>-), hypochlorite (ClO-), chlorine dioxide (ClO<sub>2</sub>) and ozone (O<sub>3</sub>) for textile water treatment.

For photocatalytic performance TiO<sub>2</sub> is the most widely studied photocatalyst. TiO<sub>2</sub> is cost effective, nontoxic and unique photocatalytic efficiency as well as high stability but pure TiO<sub>2</sub> has some drawbacks like it has large band gap and absorb a small portion of U.V. radiation. Modify TiO<sub>2</sub> become great substance for degradation process. Researchers

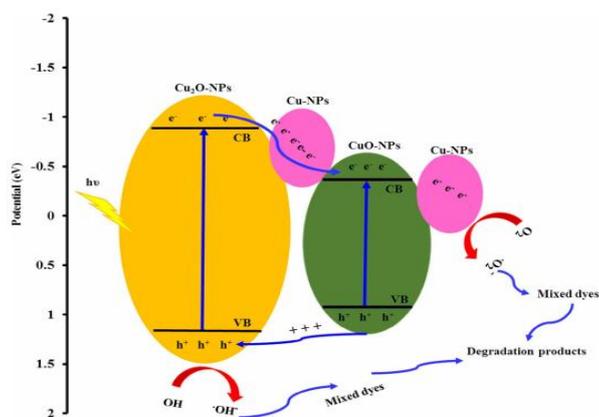
investigated lots of photocatalyst to retain the growing contamination. This review summarizes the recent progress in the design and fabrication of visible light responsive photocatalyst via various synthetic strategies, including the modification of traditional photocatalyst by doping, dye sensitization and forming a hetrostructures.

**Literature survey** Shi-Feng Yang et al. [1] reported the visible-light-sensitive Ag/AgCl/SrTiO<sub>3</sub> composites have been successfully fabricated via precipitation reaction followed by photoreduction. Compared with the pristine SrTiO<sub>3</sub> and Ag/AgCl NPs, the Ag/AgCl/SrTiO<sub>3</sub> composites possessed higher photocatalytic degradation for organic pollutants under visible light irradiation. The enhanced photocatalytic efficiency might arise from the SPR with strong visible light absorbance and efficient charge separation on the surface. The obtained photocatalysts showed good stability and recyclability in the process of photodegradation. The composition of plasmonic Ag/AgCl/SrTiO<sub>3</sub> photocatalysts in this paper could provide insights into the design and development of other excellent ideal photocatalysts in environment and energy issues.

Raji Atchudana et al. [2] studied that the potential graphene oxide grafting titanium dioxide nanocomposite (photocatalyst) was via simple solvothermal method. All the characterization techniques strongly support that the synthesized TiO<sub>2</sub>-GO nanocomposite was constructed well with stable and high pure. The resulting TiO<sub>2</sub>-GO nanocomposite used as an active photocatalyst for the (methylene blue (MB) and methyl orange (MO)) degradation in an aqueous medium under UV-light irradiation. The synthesized TiO<sub>2</sub>-GO nanocomposite displayed significantly enhanced photocatalytic activity toward MB and MO degradation in a neutral aqueous solution under UV-light irradiation than that of synthesized bare titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) (photocatalyst). The resulting TiO<sub>2</sub>-GO heterostructure achieves a maximum degradation efficiency of 100% (25 min of irradiation) and 84% (240 min of irradiation) corresponding to the MB and MO respectively. Thus, the synthesized TiO<sub>2</sub>-GO nanocomposite can be a promising candidate for the degradation of anthropogenic (MB and MO) dyes.



Schematic illustration of the synthesis of TiO<sub>2</sub>-GO nanocomposite and degradation process of MB and MO. Soleiman Mosleh et al. [3] investigated ultrasonication is a low cost green method for preparation of homogenous nanoparticles rather than conventional approaches CuO/CuO<sub>2</sub>/Cu nanoparticles were prepared by sonochemical combined thermal synthesis method and used as new photocatalyst. A novel rotating reactor for photocatalytic degradation processes based on application of blue LED as irradiation sources instead of UV lamps were described. Advantage of this reactor is the appropriate light distribution that caused the enough photocatalysts activity. Experiments were performed to photodegradation of binary mixture of safranin O (SO) and methylene blue (MB) dyes Central composite design (CCD) was used to investigate the individual and interaction effects of the parameters on the photocatalytic degradation percentage. Using of this reactor lead to the high photodegradation percentage of 98.1% and 91.91% for SO and MB, respectively. Operation parameters optimization using CCD indicate that optimum values of photocatalyst dosage, rotational speed, initial SO and MB concentration, flow rate, and time of reaction were 0.3 g/L, 900 rpm, 10 and 10 mg/L, 0.3 L/min and 90 min, respectively. Finally, results showed that synergistic effects induced by forming Cu<sub>2</sub>O/CuO heterojunction containing Cu-NPs co-cocatalyst greatly accelerate electron transfer and effectively retard the reduction of CuO by photo-generated electrons.

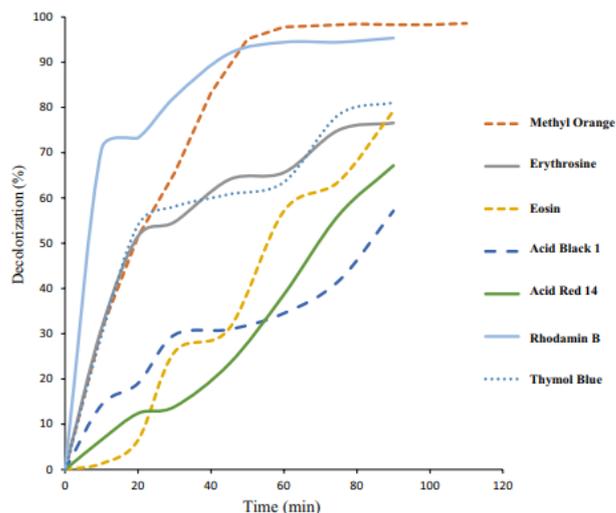


Photocatalytic dye degradation mechanism over the CuO/Cu<sub>2</sub>O/Cu photocatalyst

Li Fanga et al. [4] by using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Er(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, PVA and CO(NH<sub>2</sub>)<sub>2</sub> as main raw materials, it is successful to do the preparation of Ni<sup>2+</sup> Doped ErFeO<sub>3</sub> by microwave process. This experiment showed that Ni<sup>2+</sup> Doped ErFeO<sub>3</sub> can enhance the visible light photocatalytic activity and the best molar ratio is 0.02. The Ni<sup>2+</sup> Doped ErFeO<sub>3</sub> nanoparticles exhibited excellent visible-light photocatalytic activity for the decomposition of MO. Therefore, Ni<sup>2+</sup> Doped ErFeO<sub>3</sub> is expected to be a potential visible-light-driven photocatalyst in the sunlight-induced photocatalytic degradation of wastewater.

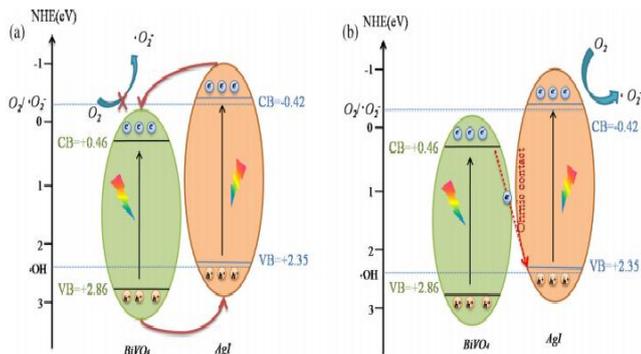
Mojgan Ghanbari et al [5] studied that Ag<sub>2</sub>CdI<sub>4</sub> nanostructures had been made up from reaction of CdI<sub>2</sub> and AgI<sub>2</sub> in solid states reaction. The morphology of product on presence and absence of surfactant have been investigated. Results show that in presence of CTAB nanoparticles shapes prism structures. The photocatalytic properties of nanoparticles un-

der UV light had been investigated for degradation of different dyes and results show that a good catalytic activities.



Chiranjit Kulsi et al. [6] synthesized Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub> by solvothermal method and investigated its photocatalytic performance. The excellent photocatalytic activity of the doped sample can be attributed to the higher light absorption characteristics in the visible region and separation efficiency of electron-hole pair. Complete degradation of malachite green (MG) dye was achieved within five minutes with Ni doped Bi<sub>2</sub>Se<sub>3</sub> in presence of H<sub>2</sub>O<sub>2</sub> with rate constant value 1.21 min<sup>-1</sup> under visible-light illumination. Explanation of the remarkable photocatalytic degradation has been presented based on the modification of band structure of bismuth selenide by doping with nickel. Scavenger test show degradation of MG is dominated by ·OH oxidation process and oxidation action of generated ·O<sub>2</sub><sup>-</sup> radicals.

Dan-Lin Guan et al. [7] synthesized a Z-scheme AgI/BiVO<sub>4</sub> catalyst successfully via a simple deposition-precipitation method. In comparison with other obtained samples and previous reported catalysts (modified with AgI) the BA3 (contained 9.09% of AgI) displayed superior photocatalytic activity towards E. coil and OTC-HCl under visible light, and the corresponding removal rate can reach 100% and 80%, respectively. It is clear that the effective charge separation of the AgI/BiVO<sub>4</sub> and Z-scheme transfer could be responsible for the enhancement of photocatalytic activity. The results of trapping experiments revealed that the O<sub>2</sub> and h<sup>+</sup> were the dominant reactive species during photo-inactivation process, and the leakage of K<sup>+</sup> played a key role for cell membrane destruction and bacteria inactivation. Additionally, the cycle experiments indicated that the catalyst possessed great stability and recyclability. This work suggested that the AgI/BiVO<sub>4</sub> photocatalyst could regard as a promising material for wastewater depuration (especially with highly concentrated pathogenic microorganisms and antibiotics).

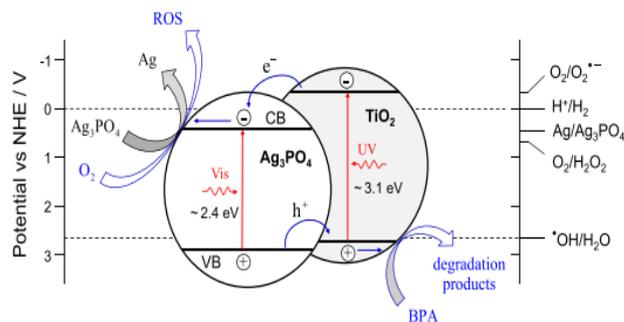


Schematic diagram of the mechanism over AgI/BiVO4 (a) conventional model and (b) Z- scheme heterojunction system

Shrine Maria Nithya and Misook Kang [8] prepared cubic spinel CuCo2O4 with urchin-like architecture by hydrothermal method. The photocatalytic efficiency of CuCo2O4 was explained by the degradation of methyl orange in presence of solar light irradiation. The complete degradation of methyl orange was successfully achieved. Photoelectrochemical measurement supports the photodegradation process. These results explore the new insights in the photocatalytic activity of Cu-Co2O4 for environmental application.

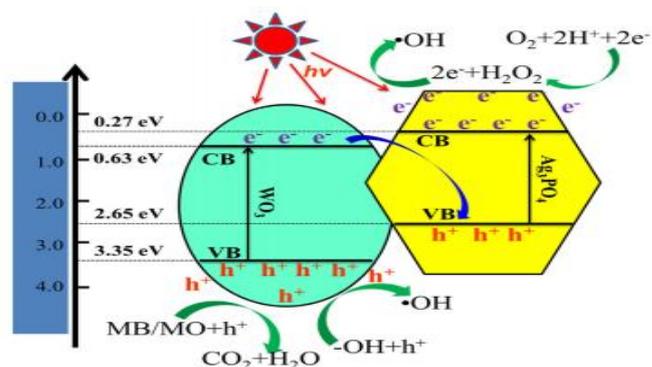
Mir Edris Taheri et al. [9] investigated the degradation of bisphenol A driven by simulated solar radiation over Ag3PO4 and Ag3PO4/TiO2 photocatalysts. The main conclusions extracted from this work are as follows: (1) Ag3PO4 and its composites with P25 TiO2 are highly responsive in the visible spectral region and this renders them particularly suitable for the photocatalytic remediation of waters contaminated by micro-pollutants using solar light as a renewable energy source. (2) The composite photocatalysts consist of relatively large, nearly spherical Ag3PO4 crystallites with an average diameter of ca 2 μm, which are decorated with much smaller P25 TiO2 particles (~20 nm). The two materials are in intimate contact and maintain their individual structural and optical characteristics, implying the absence of chemical interactions between them. (3) The Ag3PO4/TiO2 photocatalysts exhibit substantially greater activity than that of the individual components. This is explained by considering the favourable relative positions of the valence band and conduction band edges of the two semiconductors, which facilitate interfacial charge transfer and, concomitantly, suppression of the electron-hole recombination rate. Evidence is provided that synergy exists between Ag3PO4 and TiO2, which is not the case when Ag3PO4 is combined with photocatalytically inactive metal oxides such as -Al2O3 or ZrO2. (4) Optimal activity for the title reaction was observed for the Ag3PO4/TiO2(75:25) photocatalyst which, under the present experimental conditions, is able to completely degrade BPA (at the μg/L level in pure water) within just few minutes under UV, visible or solar irradiation, with the apparent rate constant being more than 2 and 3.5 times higher than that of pure Ag3PO4 or P25 TiO2, respectively. (5) Typical to most heterogeneous photocatalytic systems, conversion at a given irradiation period increases with increasing catalyst concentration in the range 50–500 mg/L or with decreasing BPA concentration in the range 2200–440 μg/L. The apparent reaction rate is not affected appreciably by the presence of bicarbonate or humic acid in solution but is significantly decreased when the reaction takes place in drink-

ing water or wastewater matrices, presumably due to certain non-target species behaving as scavengers. (6) Prolonged exposure to light results in partial deactivation of both Ag3PO4 and Ag3PO4/TiO2 catalysts due to irreversible reduction of silver orthophosphate to metallic silver by photogenerated electrons. Deactivation is less pronounced for the TiO2-containing samples and seems to depend on the BPA concentration and the water matrix employed.



Simplified diagram showing the band edge positions of the Ag3PO4/TiO2 composite, the energy levels of certain redox couples and the photo-induced reactions that may take place under the present experimental conditions.

Jinsuo Lu et al. [10] successfully synthesized a novel 1W/1Ag composite by hydrothermal method through two steps and employed in degrading two kinds of organic dye contaminant under visible light. Compared with pure Ag3PO4 and WO3, 1W/1Ag exhibited notably excellent photocatalytic efficiency. The degradation of MB and MO obeyed the pseudo-first-order kinetics. The enhanced photocatalytic performance and stability were attributed to the direct Z-scheme heterojunction structure and synergic effect of Ag3PO4 and WO3, which could be benefit to efficient electron-hole separation and enhanced light energy conversion efficiency. Under visible light illumination, the photoexcited electrons in the conduction band of WO3 and retained holes in the valence band of Ag3PO4 are quickly combined. Meanwhile, the photogenerated holes in the valence band of WO3 played a major role in oxidation reactions. Undoubtedly, the developing of 1W/1Ag not only improves the reaction activity, but also effectively reduces the cost of the Ag3PO4 based photocatalyst, which would be a desired alternative as a simple, efficient, and promising photocatalyst material for waste water treatment.



Proposed mechanism for the direct Z- scheme charge carrier transfer process in the 1W/1Ag composite

Mojgan Ghanbari et al. [11] synthesized successfully a novel nanocomposite, Cu<sub>2</sub>CdI<sub>4</sub>/CuI via simple hydrothermal method. XRD analysis showed that the product was mainly composed of Cu<sub>2</sub>CdI<sub>4</sub>/CuI and there are no other materials. Different morphologies of the product were obtained by changing different parameters such as mole ratio, hydrothermal time and temperature. It was found that each parameter has a significant effect on the product size and morphology. The optical property of the product was obtained by DRS spectra and it was found that the product can active in visible range. Finally, due to 2.8 eV band gap of the nanocomposite, the photocatalytic activity of the product was studied using methyl orange, methyl blue and Acid Black as dyes and the results showed that the product can decompose both dyes in high value.

Prem Singh Saud et al. [12] successfully synthesized Carbon quantum dots anchored TiO<sub>2</sub> (CQDs/TiO<sub>2</sub>) composite nanofibers by combining electrospinning and hydrothermal methods. The as-synthesized CQDs/TiO<sub>2</sub> composite nanofibers displayed much enhanced photocatalytic activity in the degradation of MB as well as destruction of E. coli as compared to pristine TiO<sub>2</sub> nanofiber under the visible light irradiation. The above demonstration revealed that as-prepared materials have potential as economically friendly photocatalyst for waste water remediation due to its reusability.

## CONCLUSION

1. Different types of photocatalyst like oxide, iodides, doped, and composites were prepared successfully through hydrothermal, precipitation, solid state, ultrasonication, and solvothermal methods.

2. These catalysts are characterized through different analytical techniques like XRD, EDS, FESEM, and FETEM etc.

3. Harmful substance in water degraded and removed from water by the photocatalyst.

4. The photocatalysis is the best way to clean the waste water for further utilization like irrigation, domestic and industrial purpose.

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