

Latest developments in nano-photoactivation opened up new avenues for organic compounds

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Abstract - This study examines the literature on the usefulness of nano-photocatalysts in the synthesis of organic molecules via fine chemical synthesis. Current laboratory and industrial methods for preparing organic molecules are extremely dependent on nonrenewable energy sources. Additionally, these conventional procedures typically necessitate conditions of severe temperature and pressure. In recent years, there has been a change in emphasis toward photocatalysis due to a greater worldwide awareness of the need to conserve nonrenewable sources of energy. Photocatalysts have been known to catalyze numerous organic reactions, including oxidation, reduction, addition, cyclization, and breakdown, for quite some time. The development of nanotechnology enabled the downscaling of these photocatalytic materials from bulk to nanoscale, hence expanding their use and efficacy. Advances in material chemistry and nanotechnology have also made it possible to produce nano-photocatalysts of novel types, whose molecular characteristics can be tailored and controlled. In this review, an attempt has been made to categorise these various nanophotocatalysts based on their composition and mechanism. Under UV/visible irradiation, these nanomaterials can be employed for a variety of organic transformations, as highlighted in the review. Nanophotocatalysts have considerable potential for the eco-friendly synthesis of extremely valuable chemical molecules. We trust that this review is accurate can provide insights into research done in this field so far, which can pave way for further progress in this topic of far-fetched social significance.

Keywords - Nano-Photocatalysts , Chemical Synthesis, Cyclization , Nanotechnology, Organic Transformations

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1. INTRODUCTION

The modern world is still not very good at keeping environmental and health problems under control, despite the rapid advancements in technology and industrial development that are occurring. The current COVID-19 pandemic is the best example; it has made us realise that the modern world should also take care of the development of novel technologies, materials, and medical innovations to control such health- and environment-related issues [1]. This realisation has made us realise that the modern world should also take care of the development of novel technologies, materials, and medical innovations. Several undesired components that are present in the environment can either directly or indirectly have an impact on human health. In this particular setting, many microbial pathogens that are present in the environment, such as viruses, bacteria, protozoa, and so on, can

sometimes pose a risk to human health and cause deadly infectious diseases [1,2]. Recent developments suggest that methods and materials based on nanotechnology could be alternative options with the huge potential for controlling such bacterial and viral outbreaks [3,4,5,6]. These outbreaks have been a serious problem and have increased at a concerning rate over the past few decades [2].

One of the singular processes that takes place in the presence of sun radiation [7,8] is known as photocatalysis. Photocatalysis makes use of nano-photocatalysts. Due to the fact that there is unused solar energy on Earth, this process holds great potential for the management of environmental problems and the enhancement of the health of the general population [9,10]. In the field of

environmental studies, photocatalysis has a variety of applications, one of which is the photocatalytic degradation of toxic or harmful organic compounds and gases [11,12,13]. Another application is the photocatalytic viral and bacterial disinfection of water, air, or surfaces, which, in the end, protects the environment and improves human health. Under the influence of sunlight, a process known as photocatalytic removal or disinfection of such species is a promising method that is also kind to the environment. The technique uses photocatalysts that are appropriate for the job. In addition to this, it has proven to be very cost-effective and has great promise in open environments [1,9]. In recent years, various different types of metal oxide semiconductor photocatalysts, such as TiO₂, ZnO, CuO, WO₃, and others, have been created to function as visible active photocatalysts. Their properties have been enhanced through a number of changes, which have made it possible for them to function more effectively in the presence of solar light in the photocatalytic degradation and disinfection of chemical and biological species, respectively. These photocatalysts have oxidative capabilities, which are demonstrated by the photocatalytic formation of harmful reactive oxygen species (ROS), as shown in Figure 1. This allows for the photo-degradation and inactivation of such species in both an outdoor and an indoor setting. It has been discovered to be highly helpful for the treatment of a variety of bacterial and viral infections, including measles, influenza, herpes, Ebola, current COVID-19, and many others [1,2], as is schematically represented in Figure 2.

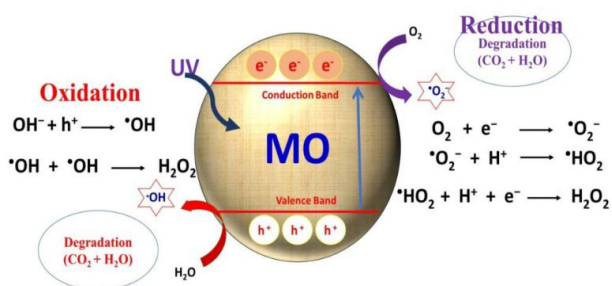


Figure 1. Photocatalytic mechanism of metal oxide nano-photocatalysts towards photocatalytic degradation of chemical species [12].

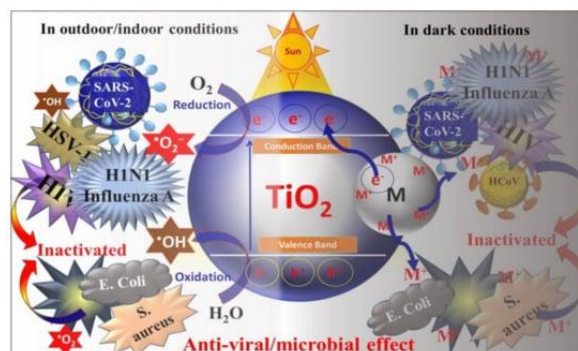


Figure 2. Schematic representation of photodegradation of viruses/microbes in outdoor as well as indoor environment using metal oxide nano-photocatalysts [1].

In depth discussions of each of these photocatalytic substances are provided below.

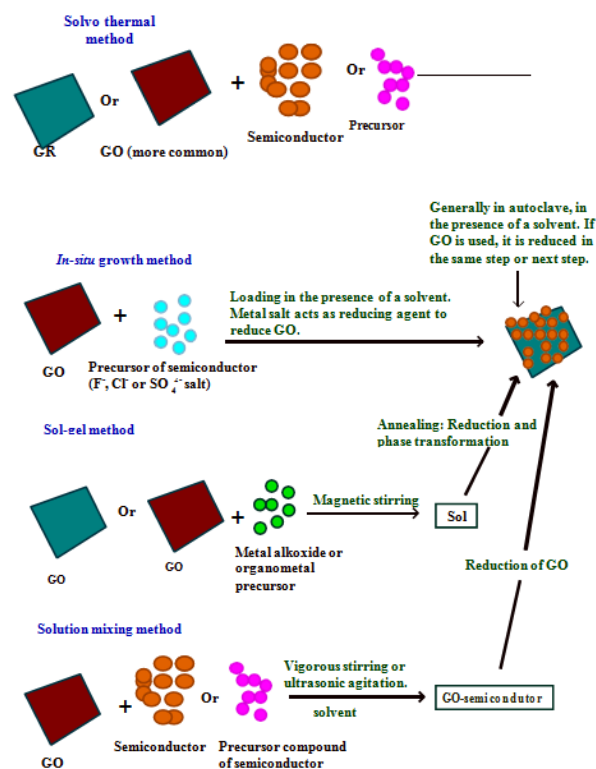


Figure 3 Major synthetic routes to fabricate graphene-semiconductor nanocomposites.

2. NANOPHOTOCATALYST BASED ON A SEMICONDUCTOR

In order to facilitate organic processes via photocatalysis, semiconductor-based materials have been the subject of substantial research. When a semiconductor is exposed to light, it takes it in. The photons elevate electrons from the valence band to the conduction band. The resulting electron-hole pair (e⁻—h⁺) may recombine, resulting in the waste of light energy as heat, or it may interact with electron

acceptors and donors adsorbed on the surface, resulting in the chemical alteration of those species.

A variety of semiconductors (including titanium dioxide (TiO₂), zinc oxide (ZnO), amorphous iron oxide (a-Fe₂O₃), and wolframite (WO₃)) have been studied for use as photocatalysts. Among them, TiO₂ has been the subject of the greatest research into heterogeneous photocatalysis because to its high stability, low toxicity, chemical inertness, and resistance to photocorrosion (Fujishima et al., 2000). But TiO₂ absorbs UV light due to its high band gap (3.0–3.2 eV). Because ultraviolet light makes up such a small percentage of the solar spectrum, researchers have focused on creating visible-light-absorbing photocatalysts.

2.1 Nano-Composite of Semiconductors and Graphene

Graphene (GR) is "a single carbon layer in the graphite structure," whose properties can be described "by analogy to a polycyclic aromatic hydrocarbon of quasi unlimited dimension," according to the official definition (McNaught and Wilkinson, 1997). In this allotrope, sp² hybridised carbon is arranged in a regular hexagonal lattice, making up the structure of the crystalline phase. Novoselov et al. were the first to synthesise it in 2004. Exfoliation of graphite was mechanically separated from the bulk material (Novoselov et al., 2004).

2.1.1 Preparation of graphene-semiconductor nanocomposite

Nanocomposites of graphene and semiconductor materials have semi-conductor nanoparticles uniformly anchored to 2-D graphene. Graphene oxide (GO) or pure graphene (GR) can serve as a precursor (GO). Composites made of graphene have been shown to have superior photocatalytic activity compared to those made of semiconductors and carbon nanotubes. The advantages of GR over CNT were demonstrated in a study that compared the two nanostructures. In terms of controlling the nanocomposite's morphology and increasing TiO₂'s photocatalytic effectiveness, GR proved superior to CNT (Y. Zhang et al., 2011). However, antecedents of the components and the route taken to anchor the components on each other are crucial factors in determining the composite's catalytic activity.

To get to graphene, another option is to employ solvent-exfoliated GR (SEG), which is GR that has been treated with N,N-dimethylformamide (Liang et al., 2011; Y. Zhang et al., 2012b). However, film forming polymers like polyvinylpyrrolidone or ethyl cellulose are required to increase the interfacial contact of SEG with the semiconductor because of the lack of hydrophilic groups in SEG.

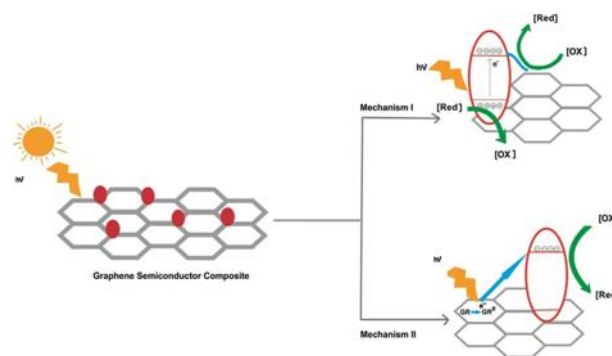


Figure 4: Illustration of mechanism of photocatalytic activity of graphene-semiconductor nanocomposite: [Ox] and [Red] indicate oxidized and reduced species respectively.

2.2.2 Mechanism of action of the graphene-semiconductor nanocomposite in organic photocatalysis

The visible-light photo-catalytic activities of the nanocomposite are improved by the inclusion of graphene for the following reasons:

- (i) Metal-to-carbon (M-C) and metal-oxide-carbon (M-O-C) connections are formed when semiconductors and graphene contact. New energy levels may result from such interactions. Deoxygenation of GO occurs during its reduction to RGO in RGO composites generated from GO precursors. This is counteracted by the diffusion of semiconductor surface lattice oxygen atoms into chemical interactions with RGO as nanoparticle development continues.
- (ii) Graphene's high conductivity and electron mobility lengthen the lifetime of photogenerated holes and electrons that would otherwise recombine in a matter of nanoseconds (An and Yu, 2011; Long et al., 2013; Ng et al., 2010). As a result, the mean free path of electrons is lengthened, allowing them to be conducted across a wider region of the carbon framework, which improves the possibility of the carbon's interplay with substrates.
- (iii) Graphene provides structural integrity and increases the photocatalyst's surface area. Graphene's 2-D conjugated p- electron system enhances substrate adsorption on the nanocomposite through its interactions with the substrate.

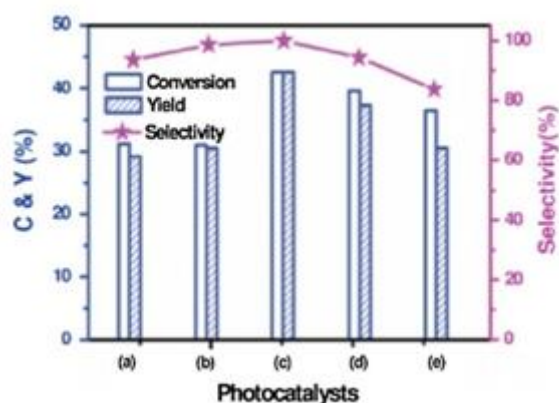
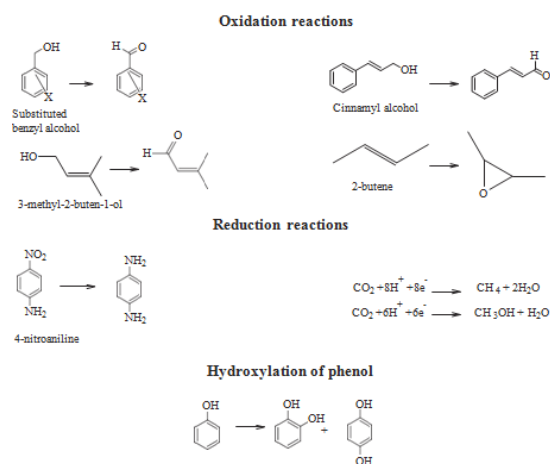


Figure 5: Photocatalytic oxidation of benzyl alcohol to benzaldehyde under visible irradiation of 4 h over different nanocomposites

2.2.3 Photocatalytic selectivity in graphene-semiconductor nanocomposites for organic transformations

To selectively oxidise alcohols to aldehydes and catalyse the epoxidation of alkenes, graphene works as a photosensitizer in GR-ZnS nanocomposite (Y. Zhang et al., 2012a).

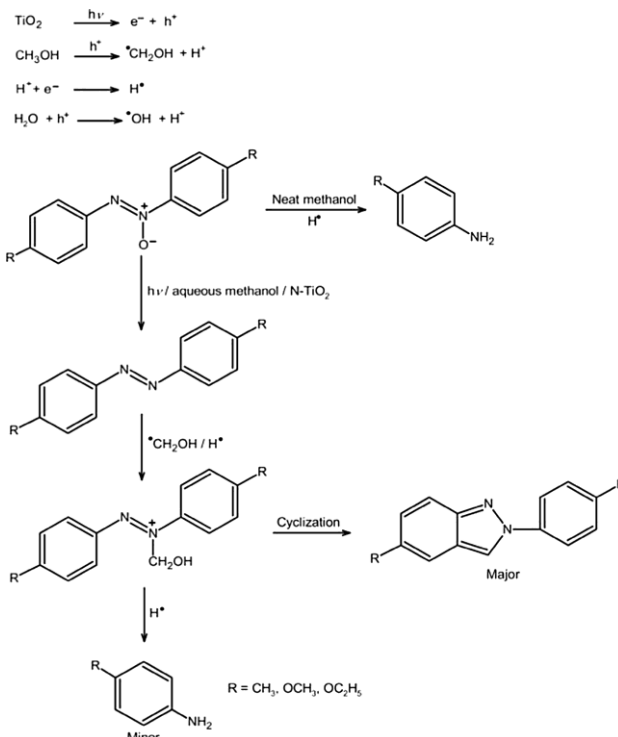


Scheme 1: Selective Organic Transformations Catalyzed by Graphene-Semiconductor Nanocomposites

ii) Selective reduction reactions

The reduction of nitro compounds is a common method for preparing amines. In turn, amines play a crucial role as building blocks in the production of pharmaceuticals and colourants. These are also employed in the removal of CO_2 and H_2S from gas streams. After 7 minutes of irradiation with microwave energy at 108 °C, alumina-supported hydrazine in the presence of Fe(III) compounds has delivered an outstanding yield (89%) for this reaction (Vass et al., 2001). These rapid and substantial yields have not

previously been achieved in the presence of photocatalysts. However, there is ongoing investigation into photocatalysts with the hope of enhancing their functionality. In particular, photocatalysts have garnered the interest of the scientific community due to their ability to facilitate the selective reduction of molecules like 4-nitroaniline, which have seen relatively little use from other types of catalytic systems.



Scheme 2: Possible reaction pathways for reductive cleavage of azoxybenzene on photoirradiation in the presence of nano N-TiO₂ (Selvam et al., 2012).

3. METAL-ORGANIC CHARGE-TRANSFER BASED NANOPHOTOCATALYST: MOF

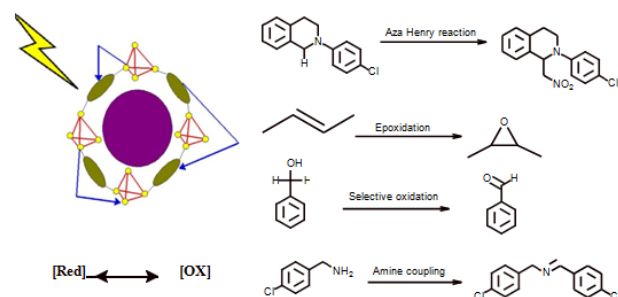
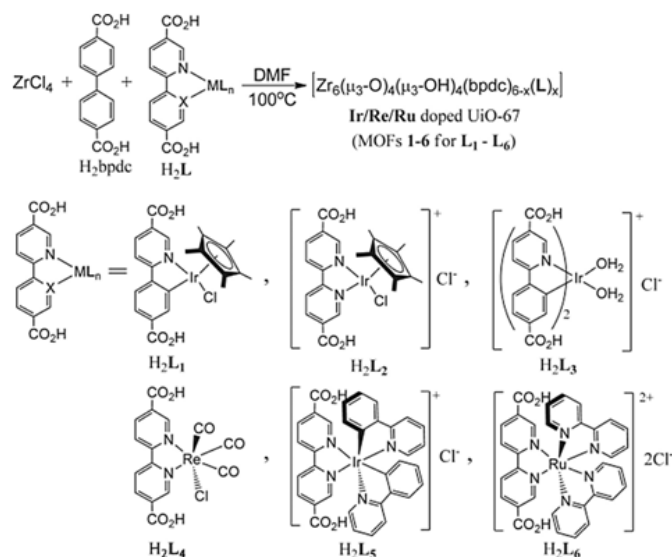


Figure 6. Illustration of mechanism of action of MOF. Yellow spheres indicate the metal ions in the framework. Purple sphere indicates the substrate trapped in pore of MOF. Green ovals denote the bridging ligands. Blue arrows denote metal-metal, metal-ligand, ligand-

ligand charge transfer on irradiation. [Ox] and [Red] denote oxidized and reduced species respectively.



Scheme 3 Synthesis of doped UiO-67 (C. Wang et al., 2011).

4. CONCLUSIONS AND PERSPECTIVES

This review has covered the fabrication, mechanism, and use of nanophotocatalysts for performing selective organic transformations. The vast number of nanophotocatalysts developed thus far for organic conversions were also categorised according to their composition and mechanism to facilitate their study.

Even though the literature review showed that advances are being made to fabricate materials with better photocatalytic properties, much more research is desired in this field. Most importantly, the stability and the performance of these catalysts need to be monitored in natural sunlight. The catalysts have been prominently applied for selective oxidation of alcohols and reduction in nitroaromatics. It cannot be denied that strict vetting criteria were used in conjunction with these conversions. However, more could be done to expand the range of reactions for which these photocatalysts are used. The composition, nature of used support, size of nanoparticles, shape of nanoparticles, polarity of reactant, irradiation intensity, and solvent were found to have the greatest impact on the catalytic activity. Better photocatalysts can be created by keeping an eye on and manipulating these parameters.

Studies on graphene and semiconductor-based nanocomposites dominate the literature, but metal-organic frameworks (MOFs) and plasmon-based photocatalysts are quickly emerging as promising nanophotocatalysts. Newer kinds of arrangements of components in the composites are being developed. The composites are being extended from binary to

ternary structures. Further improvisations can be done by preparing composite materials of different classes of photocatalysts discussed in this review, where the distinct merits of each component can be tapped to the fullest.

It is beyond doubt that the conservation of earth's non-renewable resources is the need of the hour. The development of low-cost, reliable nanophotocatalysts will open up new opportunities to convert solar energy to chemical energy and can prove to be an enormously crucial step toward solving the energy dilemma of the globe.

REFERENCES

- Huang, X.Q., Li, Y.J., Chen, Y., Zhou, H.L., Duan, X.F., Huang, Y., 2013. Plasmonic and catalytic AuPd nanowheels for the efficient conversion of light into chemical energy. *Angew. Chem. Int. Ed.* 52, 6063–6067.
- Huang, Y., Qin, Y., Zhou, Y., Niu, H., Yu, Z.-Z., Dong, J.-Y., 2010. Polypropylene/graphene oxide nanocomposites prepared by in situ Ziegler–Natta polymerization. *Chem. Mater.* 22, 4096–4102.
- Hubesch, B., Mahieu, B., 1985. Conversion of dextrose into hydrogen using aqueous tris(2,20-bipyridine)rhodium(III) complex as a photocatalyst and enhanced by efficient heterogeneous redox catalysts. *Polyhedron* 4, 669–674.
- Inoue, Y., 2009. Photocatalytic water splitting by RuO₂-loaded metal oxides and nitrides with d₀- and d₁₀-related electronic configurations *Energy Environ. Sci.* 2, 364–386.
- Jeong, H.-C., Shim, I.I.-W., Choi, K.Y., Lee, J.K., Park, J.-N., Lee, C.W., 2005. Hydroxylation of phenol with H₂O₂ over transition metal containing nano-sized hollow core mesoporous shell carbon catalyst. *Korean J. Chem. Eng.* 22, 657–660.
- Townsend, T.K., Browning, N.D., Osterloh, F.E., 2012. Nanoscale strontium titanate photocatalysts for overall water splitting. *ACS Nano* 6, 7420–7426.
- Tsai, C.-W., Chen, H.M., Liu, R.-S., Asakura, K., Chan, T.-S., 2011. Ni @ NiO core-shell structure-modified nitrogen-doped InTaO₄ for solar-driven highly efficient CO₂ reduction to methanol. *J. Phys. Chem. C* 115, 10180–10186.

8. Wang, G., Wang, X., Liu, J., Sun, X., 2012. Mesoporous Au/TiO₂ nanocomposite microspheres for visible-light photocatalysis. *Chem. Eur. J.* 18, 5361–5366.
9. Stibal, D., Sa, J., van Bokhoven, J.A., 2013. One-pot photo-reductive N-alkylation of aniline and nitroarene derivatives with primary alcohols over Au–TiO₂. *Catal. Sci. Technol.* 3, 94–98.
10. Stoller, M.D., Park, S., Zhu, Y., An, J., Ruoff, R.S., 2008. Graphenebased ultracapacitors. *Nano Lett.* 8, 3498–3502.
11. Su, Y., Wang, L.C., Liu, Y.M., Cao, Y., He, H.-Y., Fan, K.N., 2007. Microwave-accelerated solvent-free aerobic oxidation of benzyl alcohol over efficient and reusable manganese oxides. *Catal. Commun.* 8, 2181–2185.
12. Li, J., Cushing, S.K., Bright, J., Meng, F., Senty, T.R., Zheng, P., Bristow, A.D., Wu, N., 2013. Ag@Cu₂O core-shell nanoparticles as visible-light plasmonic photocatalysts. *ACS Catal.* 3, 47–51.
13. Du, J., Lai, X., Yang, N., Zhai, J., Kisailus, D., Su, F., Wang, D., Jiang, L., 2011. Hierarchically ordered macro–mesoporous TiO₂– graphene composite films: improved mass transfer, reduced charge recombination, and their enhanced photocatalytic activities. *ACS Nano* 5, 590–596
14. Mori, K., Kawashima, M., Che, M., Yamashita, H., 2010. Enhancement of the photoinduced oxidation activity of a ruthenium(II) complex anchored on silica-coated silver nanoparticles by localized surface plasmon resonance. *Angew. Chem. Int. Ed.* 49, 8598–8601.

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