

Insight of the effect of chitosan modification on the photocatalytic properties of metal-based and metal-free photocatalysts

Article history:

Received: 01-07-2022 Revised: 21-08-2022 Accepted: 12-09-2022

- ^a School of Advanced Chemical Sciences, Faculty of Basic Sciences, Shoolini University, Solan (HP), India-173229.
- ^b School of Advanced Chemical Sciences, Faculty of Basic Sciences, Shoolini University, Solan (HP), India-173229.
- School of Advanced Chemical Sciences, Faculty of Basic Sciences, Shoolini University, Solan (HP), India-173229.
- ^d Advanced Materials and Processes Research Institute, Hoshangabad Road, Bhopal (MP), India 462026.
- ^e Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia.
- ^f Center of Excellence for Advanced Materials Research, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia.
- ⁹ Department of Biotechnology, School of Chemical and Biotechnology, SASTRA Deemed University, Thanjavur, 613401, Tamilnadu, India.
- ^h School of Advanced Chemical Sciences, Faculty of Basic Sciences, Shoolini University, Solan (HP), India-173229 Corresponding author: pardeepchem@gmail.com

© The Author(s), 2022

Rohit Kumarª, Anita Sudhaik[®], Pankaj Raizada[°], Archana Singh⁴, Tansir Ahamad[®], Aftab Aslam Parwaz Khan^f, S. Rangabhashiyam^g, Pardeep Singh[®]

Abstract: Chitosan is a polymeric material having properties such as adsorption and hydrophilicity. Chitosan itself is almost photocatalytically inactive, but it can couple with other photocatalysts to improve their photocatalytic activity. Chitosan significantly enhances photocatalysts' adsorption and lowers the charge carrier recombination, which ultimately aids in the enhanced photocatalytic activity. In this review, we have discussed chitosan's basic structural, electronic, and chemical properties. We have also explored the photocatalytic properties of chitosan and chitosan-based materials. Since metal-based and metal-free semiconductors are the two major classes of semiconductor photocatalysts, so we have described how chitosan can be used to enhance the limitations of metal-based and metal-free semiconductor photocatalysts. This review will help to develop a better understanding of chitosan and chitosan-based materials for photocatalysis. We have also explored the future aspects of chitosan-based photocatalytic materials to improve the research in the future.

Keywords: Photocatalysis; Chitosan; Support materials; Metal-free photocatalysts; Metal-based photocatalysts; Pollutant degradation.

Highlights:

- The basic mechanism for photocatalysis is discussed
- The physical and chemical properties of chitosan are explored
- Explained the effect of chitosan modification on photocatalysts
- Chitosan with metal-based and metal-free semiconductors is debated

INTRODUCTION

With rapid economic and industrial development, environmental pollution and energy shortages are now major worldwide issues that seriously limit sustainable human development (Ge *et al.*, 2019; Mills *et al.*, 1993; Sudhaik *et al.*, 2022). To solve these problems, industrial technology development must focus on meeting the demand for clean energy and solving the problem of environmental pollution (Crini and Lichtfouse, 2019; Kumar *et al.*, 2022a). Wastewater treatment is costly because the contaminant present needs to be effectively removed before the water can be safely reused. Materials such as membranes, ozone, adsorbents, catalysts, etc. are used to treat polluted water but exhibit poor efficiency and sometimes leave secondary pollutants in the system. Even with conventional methods such as biological and physical treatments, removing the contaminants effectively would still require more advanced technology with lower cost and shorter time requirements (Khan *et al.*, 2021; Yahya *et al.*, 2018). Therefore, photocatalysis is an emerging technique for water treatment that uses solar light for pollutant degradation, energy conversion, and fuel generation (Akhundi *et*

al., 2019; Habibi-Yangjeh et al., 2020; Akhundi

et al., 2020). In photocatalysis, a semiconductor photocatalyst is used to degrade the pollutants present in water or air (Hariganesh et al., 2020; Soni et al., 2022). When a photocatalyst is added to polluted water, pollutants get adsorbed on the surface of the photocatalyst. When light of suitable wavelength/ energy (hv > band gap energy of semiconductor) falls on the semiconductor, electrons excite from the valance band (VB) to the conduction band (CB), leaving behind holes in VB (Kumar et al., 2022b; Rana et al., 2022). These photogenerated electrons and holes interact with water and dissolved oxygen to generate highly oxidative species (viz. 'OH, 'O₂⁻). These highly oxidative species impart high oxidative stress to adsorbed pollutant molecules and ultimately degrade them. The schematic illustration of the photocatalysis process is shown in Figure 1(a). To date, many semiconductors photocatalysts have been explored to achieve high efficiency in degrading the pollutant under solar light (Asadzadeh-Khaneghah et al., 2020; Kumar et al., 2022c). Metal-based and metal-free semiconductors are the two main classes of semiconductors. Still, they both have some limitations, such as poor adsorption ability, high charge recombination, a poor lifetime of charge carriers, etc. To overcome these limitations, and various changes such as heterojunction composite formation, defect engineering, etc., have been done to these photocatalysts.

Moreover, adsorption is well known to be a requirement for a photocatalysis process to occur, and numerous papers have shown that high adsorption could lead to an effective photocatalytic activity (Natarajan *et al.*, 2018; Zhang *et al.*, 2020; Ngah *et al.*, 2011). Some photocatalysts also have a low surface area limiting the available active sites for the degradation of the pollutants. Along with the limitation of poor adsorption and surface area of photocatalysts, water has a strong tendency to

adsorb on the surface of photocatalytic materials, decreasing the adsorption sites for pollutants and ultimately decreasing the photocatalytic activity (Li et al., 2019). Thus, modifying photocatalysts by forming a composite with materials having high adsorption ability and hydrophilicity can greatly enhance photocatalytic activity (You et al., 2022; Zhu et al., 2013). Many types of adsorbent materials available, such as activated carbon, zeolite, graphene oxide, silica oxide, carbon nanotubes (CNT), polymeric adsorbents, etc. (Kyzas et al., 2015). Out of all, chitosan can be a good choice due to its good adsorption ability, abundance, and non-toxicity (Adnan et al., 2020). Chitosan is a biopolymer-based adsorbent material that can be used for immobilization and can be coupled with other semiconductor materials to form a composite having enhanced photocatalytic properties (Verma et al., 2020; Bahrudin and Nawi, 2019). It is biocompatible, biodegradable, non-toxic, and has multiple functional groups providing more active sites for photocatalytic reaction. Chitosan can enhance selectivity, mechanical strength, surface area, surface chemistry, and regeneration of a photocatalyst (Gusain et al., 2019; Khan et al., 2020). Chitosan-based composites are reported to show enhancement in chemical stability, hydrophilicity, biocompatibility, and pore size. The properties of chitosan and its effect on the photocatalytic properties of metal-based and metal-free photocatalysts are briefly explained in this review.

This review will be a good insight for understanding chitosan, and it is composite for photocatalysis. A few reviews have already been published based on chitosan, but none of them have broadly explored chitosan with metal-based and metal-free photocatalysts (Adnan et al., 2020; Lee et al., 2015; Nithya et al., 2014). In this review, we have discussed chitosan, its properties, and chitosan-based modifications to metal-free and metal-based photocatalysts. To write this review, we went through various articles published in Scopus from 2010 to 2022 using the keywords "Chitosan + photocatalysis", "metal-based photocatalysts + chitosan", and metal-free photocatalysts + chitosan". We have selected the data, which is written in the English language and includes photocatalysis. We have neglected the data written in a language other than English. We have also failed the data which does not contain chitosan. The graphical representation of the articles selected for review of literature is shown in Figure 1(b).

Insight of the effect of chitosan modification...

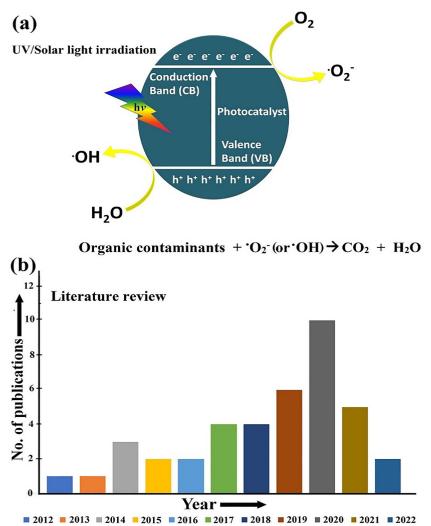


Figure 1. (a) Schematic illustration of the basic mechanism of photocatalysis, (adapted with permission from Elsevier, copyright 2020 with license number: 5342390501031) (Hariganesh *et al.*, 2020)
 (b) Graphical representation of articles selected for literature review.

CHITOSAN

Chitosan is a poly [(1-4)- β -linked 2-amino 2-deoxy-D-glucose] compound that has applications in pharmaceutical, cosmetic, biomedical, agriculture, biotechnology, textile, food, and water treatment (Mourya and Inamdar, 2008). The structure of chitosan resembles cellulose and is the 2nd most abundant polysaccharide on Earth after cellulose (Adnan *et al.*, 2020; Nithya *et al.*, 2014). Chitosan is present in the cell wall of fungi and arthropods. Chitosan has some excellent properties, such as non-toxicity, biodegradability, chemical reactivity, biocompatibility, and hydrophilicity. Chitosan is generally prepared from chitin which is also a biopolymer, through N-deacetylation in the presence of hot

alkali. To remove the acetyl group from chitin, chitin is treated with concentrated alcoholic or aqueous NaOH in absence of oxygen and in the presence of nitrogen or sodium borohydride to avoid depolymerization. The deacetylation in chitin is reported to be < 10%, whereas it is 40% - 90% in chitosan (Mourya and Inamdar, 2008). The structures of chitin and chitosan are shown in Figure 2(a-b). The structures of chitin and chitosan are pretty similar, but still, they have differences in their chemical properties. Chitosan is more accessible to the reagents due to its less crystalline nature than chitin; hence, they have a strict difference in their solubilities. Chitosan also has high chemical and biological reactivity compared to chitin due to regularly distributed amino groups in its molecular chain (Ogawa et al., 2004).

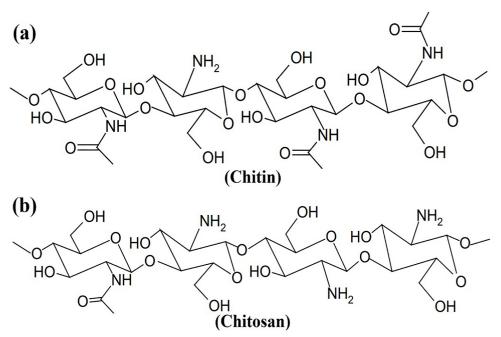


Figure 2. Structure of (a) chitin and (b) chitosan, (Adapted with permission from Elsevier, copyright 2008 with license number: 5342390642174) (Mourya and Inamdar, 2008).

Chitosan has a strong affinity toward the metal ions due to its cationic behaviour in an acidic medium which describes its potential for heterogeneous photocatalysis (Lee et al., 2015). Properties such as low cost, eco-friendly, stability (up to 280 °C), non-toxicity, and easily modified physical and chemical properties make chitosan a good support material for functionalization and immobilization in photocatalysis. Chitosan is reported as a good support material in heterogeneous photocatalysis by many researchers. Chitosan is an excellent material of choice for making efficient heterojunction photocatalyst due to; i) its ability to control active agent release, ii) the presence of large amino groups for crosslinking, and iii) it is cationic nature to interact with multivalent anions. Xiong and his peer group explored the advantages of forming a heterojunction with chitosan to enhance the photocatalytic activity of Ag₃PO₄ photocatalyst (Xiong et al., 2018). On the introduction of chitosan, there was a significant enhancement in visible light absorption of Ag₂PO₄. Ag₂PO₄ had an absorption edge at 520 nm, which was improved to 500-800 nm with chitosan. SEM images of chitosan and Ag₂PO₄/chitosan composite clearly indicated the deposition of Ag₂PO₄ on chitosan fibres. Photocatalytic activities of pure chitosan and Ag₂PO₄/chitosan were also compared, where chitosan showed almost negligible photocatalytic activity against methyl orange dye under visible light. Ag₂PO₄/chitosan composite showed almost ~95% degradation efficiency methyl orange under visible light irradiation within 80 minutes, whereas chitosan showed only 10% degradation under similar conditions. Here, chitosan made Ag₂PO₄ nanoparticles immobilized for better photocatalytic activity. Similarly, Preethi et al. also explored chitosan as a support material to enhance the photocatalytic activity of ZnO for Cr(VI) reduction (Preethi et al., 2017). Chitosan/ZnO composite showed 52.6% of chromium reduction within 60 minutes in the dark, which was improved to 99.2% under UV light. This photocatalytic efficiency decreases with an increase in pH beyond 8 and increases with an increase in irradiation time. Catalytic dose strongly affects the efficiency of the photocatalyst. With the increase in catalyst concentration up to 100 mg, photocatalytic removal of Cr(VI) increases due to the increased adsorption and reduction of Cr(VI). The two major factors responsible for photocatalytic activity enhancement are improved adsorption and lowered electron-hole pair recombination due to chitosan. Chitosan is quite an efficient tool for enhancing of photocatalytic activity of semiconductor photocatalysts. Chitosan is reported to improve the photoactivity for various metal-based and metal-free semiconductor photocatalysts, which we will discuss further in this review.

CHITOSAN WITH METAL-BASED SEMICONDUCTOR PHOTOCATALYSTS

TiO₂ is a widely explored metal-based photocatalyst in metal-based semiconductors due to its easy availability, cheapness, and non-toxicity (Bahrudin and Nawi, 2019; Škorić et al., 2016). Moreover, the high redox potential of TiO, photocatalyst is also a key factor for the high mineralization ability of TiO₂. But, the band gap of TiO_2 is also high (3.2 eV), and it absorbs in the UV region, limiting its practical applications. Moreover, high charge recombination and poor adsorption ability of TiO₂ are some other significant drawbacks of metal-based TiO₂ photocatalyst (Chen et al., 2020). Besides TiO2, many other metal-containing semiconductors are explored, such as metal-oxides, metal-sulphides, oxy(nitrides), oxy(sulphides), etc.. Still, they also have poor efficiency, high charge recombination, and poor absorption of pollutants on the catalyst surface. Chitosan is reported to use as a support material for metal-based semiconductor photocatalysts to overcome the limitations mentioned above. Chitosan support is photocatalytically inactive, but the NH₂ amino groups present in chitosan are responsible for better adsorption and degradation of pollutant molecules (Bergamonti et al., 2019). Chitosan helps immobilise metal-based photocatalysts for better photocatalytic activity, recovery, and reuse (Haldorai and Shim, 2013). Chitosan is reported to dope with CuO, which showed enhanced photocatalytic activity for bacterial inactivation. The high photocatalytic activity of Chitosan/CuO was attributed to the strong interaction of chitosan with the highly electronegative surface of the microbe. Hybrid chitosan/CuO photocatalyst interaction with bacterial membranes blocked the nutrient intake of the cell by changing the permeability of the cell membrane. Moreover, reactive oxidative species generated by chitosan/ CuO nanocomposite increased the oxidative stress on bacterial cells and ultimately led to the inactivation of the bacterial cell. Figure 3 (a-b) compared the picture before and after treatment of Escherichia coli (E. coli) with chitosan/CuO hybrid for 12 hours.

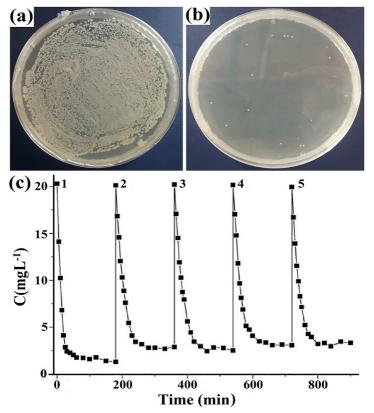


Figure 3. Picture of (a) before and (b) after treatment of *E. coli* with chitosan/CuO hybrid for 12 hours (Adapted with permission from Hindawi, copyright 2013 with (CC BY 3.0)) (Haldorai and Shim, 2013).
(c) Recyclability and efficiency of CdS/chitosan after 5 cycles, (Adapted with permission from Elsevier, copyright 2009 with license number: 5342430321088) (Zhu *et al.*, 2009).

The amino groups at chitosan can be easily protonated in an acidic medium (or low pH), therefore, pollutants can quickly adsorb on chitosan/metal-based photocatalyst (Zhu *et al.*, 2009). The effect of pH on chitosan/CdS composite was examined, and rate constant k_{app} values were evaluated for 6, 8, 10, and 12 pH. The trend in k_{app} values was observed as 6>8>10>12, where the lowest k_{app} value was 5.5 x 10⁻³ min⁻¹ for pH 12, and the highest k_{app} value was 11.8 x 10-3 min⁻¹ for pH 6. These chitosan/ CdS photocatalysts showed 93.6% degradation of Congo red dye within 180 minutes under visible light. Chitosan/CdS also showed good reusability after 5 cycles (Figure 3(c)). Chitosan generally forms a coordination complex with metal ions like Zn, decreasing the composite's free amine groups (Mansur *et al.*, 2014). A schematic illustration of the chitosan/ZnO composite is shown in Figure 4(a). The Chitosan/ZnO composite exhibited 87% degradation efficiency for methylene blue dye under UV light within 120 minutes. The schematic mechanism of pollutants degradation via chitosan/ZnO composite is shown in Figure 4(b). Chitosan is also reported to enhance the photoactivity of magnetic photocatalysts. Due to the presence of amino group (-NH₂) and hydroxyl group (-OH) on chitosan, magnetic metal ions (e.g., Fe) get chelated on chitosan (Cao *et al.*, 2014).

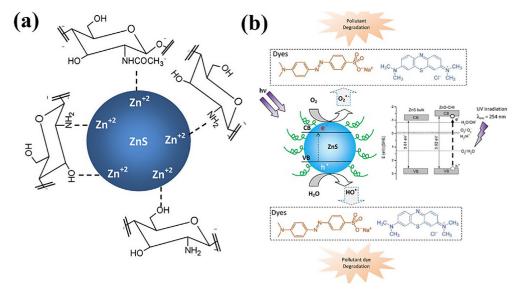


Figure 4. (a) Schematic illustration of the chitosan/ZnO composite. (b) Mechanism of pollutants degradation via chitosan/ZnO composite (Adapted with permission from Elsevier, copyright 2014 with license number: 5342430476679) (Mansur *et al.*, 2014).

Conjugated nanoparticles of magnetic Co, Ni, and Fe were prepared and compared by Khan et al. for the degradation of bromophenol blue (Khan et al., 2016). Out of all, Co-based chitosan nanocomposite showed the highest crystallinity, whereas Fe-based showed the lowest. But, Fe-chitosan nanocomposite showed the highest degradation efficiency (94.5%) for bromophenol blue under UV light within 10 hours. Here, chitosan is highly responsible for this photocatalytic activity and acts as a photocatalyst to electron-hole pairs for the generation of highly oxidative species. The photocatalytic degradation of bromophenol via metal-based chitosan composites is -dependent and increases with irradiation time. For a photoinduced chemical transformation, the catalyst surface is a crucial factor, and chitosan can enhance the surface properties effectively. Fe-based chitosan nanocomposite also showed high reusability (Adnan *et al.*, 2020). Metal-based chitosan composite showed some excellent characteristics for improved photocatalysis, but still, some important factors are crucial in this process, such as,

- Particle size significantly affects the photocatalytic activity
- Interfacial of metal-based semiconductors which are responsible for intermolecular forces such as van der Waals forces, hydrogen bonding, electrostatic attractions/repulsions, etc.
- Dispersion of metal-based semiconductors with chitosan required for good bonding

Although chitosan and metal-based hybrid semiconductors exhibit good and enhanced photocatalytic activity, they still have some drawbacks of high cost, large band gap, high recombination, and high energy absorption (UV light). Moreover, the interaction of pollutants with these photocatalysts occurs via chelation, coprecipitation, and electrostatic interaction with protonated $\rm NH_2$ group. Protonation of $\rm NH_2$ highly depends upon pH. Also, recovery of some metal-based semiconductor composites is a big issue.

CHITOSAN WITH METAL-FREE SEMICONDUCTOR PHOTOCATALYSTS

Metal-free photocatalysts are an ultimate class of photocatalysts that are mainly derived from elements like Si, Se, P, S, B, Te, etc. (Li *et al.*, 2017).

Carbon-based materials such as carbon quantum dots, SiC, graphitic carbon nitride, graphene oxide, and other organic photocatalysts are also good for metal-free photocatalysts. But, some of the significant drawbacks of some metal-free photocatalysts are poor charge separation, poor adsorption, instability, and poor charge transfer. Doing and heterojunctions are some of the highly explored modification techniques to overcome the limitations of the photocatalyst. Chitosan has a high Nitrogen content (~7%) due to nitrogen-containing amine and acetamide groups, making it a suitable precursor for synthesising N-doped carbon materials (Khan et al., 2020). The schematic illustration of the synthesis of N-doped carbon-based graphene oxide is shown in Figure 5(a). For materials like silicon, chitosan can be used to control its expansion and conduction behaviour (Khan et al., 2020).

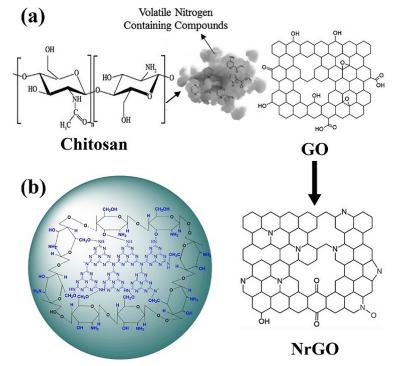


Figure 5. (a) Schematic illustration of the synthesis of N-doped carbon-based graphene oxide (Adapted with permission from ACS, copyright 2020 with CC-BY-NC-ND) (Khan *et al.*, 2020) and (b) structure of chitosan/GCN composite, (Adapted with permission from Elsevier, copyright 2019 with license number: 5342430613474) (Vigneshwaran *et al.*, 2019).

Chitosan is a polymer matrix to hold the photocatalysts (Shen *et al.*, 2021). g- C_3N_4 (GCN) in chitosan matrix can develop self-cleaning surfaces. The schematic illustration of the chitosan/GCN composite is shown in Figure 5(b) (Vigneshwaran *et al.*, 2019). Studies revealed that reactive oxidative species generated by GCN/Chitosan photocatalyst are comparable to GCN, which clearly showed that the formation of composite with chitosan doesn't affect the formation of reactive oxygen species. Doping the GCN with chitosan also blue-shifts the absorption edge from 480 nm to 450 nm, but it also

lowers the photoluminescence (PL) intensity (Zhao et al., 2018). Lower PL intensity of GCN/Chitosan composites compared to GCN and chitosan is the direct indication of enhanced charge separation and an improved lifetime of charges. GCN/chitosan composite synthesized by Zhao and coworkers showed enhanced photocatalytic activity for methylene blue (MB) dye degradation. ~100 % of MB was reported to remove by GCN/chitosan composite within 120 minutes under visible light irradiation. Percentage of chitosan in the composite significantly affects the photocatalytic activity. With the increased chitosan concentration, adsorption increases, but it also hinder photocatalytic performance. Along with photocatalytic activity, GCN/chitosan photocatalysts also show good recyclability and stability, which offers an excellent practical application. Even after 5 cycles, the composite showed ~97% degradation efficiency and <10% mass change. Chitosan is also reported to coat with polymers such as Polyvinylidene fluorides, Polyethersulfone, etc., and make the surface of other polymers positively charged (Gharbani and Mehrizad, 2022). NH₂ group of chitosan changed to NH₂⁺ in acidic pH. This NH₂⁺ group interacts with the carboxylic (COO-) and -O- groups of pollutants like rhodamine B through hydrogen bonding and improve the photocatalysis process. At higher pH, NH, remains neutral and poor interaction of chitosan with pollutant molecule occurs. Ternary composite of chitosan/lactose/GCN was synthesized by Karimi *et al.* and compared its photoactivity for the degradation of methyl orange, methyl blue, and methyl red at different concentrations under visible light irradiation at 6.5, 7.8, and 8.8 pH (Karimi et al., 2021). Among all, this photocatalyst exhibited a higher photocatalytic at pH 6.5. Figure 6 shows the chitosan/lactose/GCN photocatalysts efficiency at different pH and concentrations.

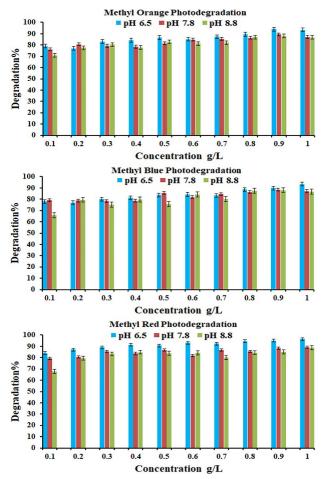


Figure 6. The efficiency of chitosan/lactose/GCN photocatalyst at different pH and concentrations, (Adapted with permission from John Wiley and Sons, copyright 2021 with license number: 5342430816942) (Karimi *et al.*, 2021).

Thus, metal-based and metal-free semiconductors are two different classes of semiconductors. Metal oxides have unique electronic and optical properties. Metal-based semiconductors offer good charge mobility, separation, and reusability. But, low light-harvesting, metal pollution, and leaching are some of the significant drawbacks of metal oxides. Adding chitosan to metal-based semiconductors can reduce electron-hole pair recombination, enhance the polarity of semiconductors, improve the lifetime of charge carriers, and boost the adsorption ability of semiconductors. Similarly, metal-free semiconductors are low-cost and offer good light-harvesting ability and non-toxicity. But, poor stability, low charge transfer ability, and high recombination are some of the significant issues of metal-free semiconductors. Chitosan improves pollutant adsorption on photocatalyst surfaces when introduced to metal-free semiconductors. It also lowers the PL intensity, confirming the low recombination and high photocatalytic activity. The comparison of photocatalytic activity of chitosan/metal-based and chitosan/metal-free semiconductors is shown in Table 1.

Photocatalyst	Pollutant	Light source	Photocatalyst / pollutant concentration	Efficiency	Reference (s)
Ag ₂ O/TiO ₂ / chitosan	Ampicillin	Visible light	80 mm film / 40 mL of 20 mg/L	~100% in 200 minutes	(Zhao <i>et al.,</i> 2017)
Ag ₂ O/TiO ₂ / chitosan	Methyl orange	Visible light	80 mm film / 40 mL of 10 mg/L	~100% in 60 minutes	(Zhao <i>et al.,</i> 2017)
Ag/AgCl/chitosan	Rhodamine B	Visible light	50 mg / 50 mL of 10 mg/L	~100% in 60 minutes	(Wang <i>et al.,</i> 2017)
TiO ₂ /ZnO/chitosan	Methyl Orange	Solar Light	50 mg / 100 mL of 15 mg/L	~100% in 240 minutes	(Zhu <i>et al.,</i> 2012)
Chitosan/ZnO	Malachite Green	Visible light	50 mg / 5 mg/L	~100% in 270 minutes	(Saad <i>et al.,</i> 2020)
Chitosan/Ce-ZnO	Malachite Green	Visible light	50 mg / 5 mg/L	~100% in 90 minutes	(Saad <i>et al.,</i> 2020)
Chitosan/g-C ₃ N ₄	Chlorpyrifos	Visible light	100 mg / 50 mL of 50 mg/L	~85%	(Vigneshwaran <i>et al.,</i> 2019)
Polypyrrole/ chitosan/ZnO	Reactive Orange-16	UV light	300 mg / 300 mL of dye	~90% in 70 minutes	(Ahmad <i>et al.,</i> 2019)
Chitosan/g-C ₃ N ₄ / TiO ₂	Cr(IV)	Visible light	30 mg / 30 mL of 100 mg/L	~75% in 240 minutes	(Li <i>et al.,</i> 2021)

 Table 1. Comparison of photocatalytic activity of different chitosan-based

 metal-free and metal-based photocatalysts.

CONCLUSION AND FUTURE ASPECTS

Based on the current research result, chitosan is an excellent support material for metal-based and metal-free semiconductors due to its high sorption capacity, stability of metal anions, and physical and chemical versatility properties. Chitosan makes the photocatalysts immobilize, stable, and highly effective. Chitosan improves the adsorption ability of modified photocatalysts due to the presence of the $\rm NH_2$ group on the surface. Chitosan also enhances the lifetime of charge carriers when attached to some semiconductors. Chitosan highly decreases the charge-carriers recombination and improves the overall photocatalytic process. In this review, we have discussed the properties of chitosan with metal-based and metal-free semiconductors. Despite its advantages, the study of chitosan-based materials is still in its early stages. Future aspects in the field of chitosan-based materials are discussed below,

- Chitosan modification is generally reported to blue-shift the absorption edge. Improved methods should be developed to improve the light-harvesting ability of chitosan-based materials.
- Chemical modifications can be done to chitosan to attach various functional groups to control the adsorption ability, cationic-anionic properties, and hydrophilic nature.

- Density functional theory-based studies should be performed to understand the mechanism of chitosan-based photocatalysts more clearly.
- Implementation of chitosan-based photocatalysts for the large-scale treatment of wastewater should be focused on.

This review will be an effective tool for a better understanding and improvement of chitosan-based photocatalytic materials. Chitosan exhibited a significant application potential in the field of photocatalysis. Unique properties of chitosan, such as adsorption and hydrophilicity, make it a suitable choice for investment in heterogeneous photocatalysis.

Acknowledgment

The corresponding author Dr Pardeep Singh and co-author Dr Pankaj Raizada are thankful to H.P. Council for Science, Technology & Environment (HIMCOSTE) for financial support through research project proforma for monitoring the progress of research project no. HIMCOSTE (R&D)/2019-20-2.5(4).

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

- ADNAN, M. A. M., PHOON, B.L., JULKAPLI, N. M. (2020). Mitigation of pollutants by chitosan/metallic oxide photocatalyst: a review. Journal of Cleaner Production, 261, 121190.
- AHMAD, N., SULTANA, S., FAISAL, S. M., AHMED, A., SABIR, S., KHAN, M. Z. (2019). Zinc oxide-decorated polypyrrole/chitosan bionanocomposites with enhanced photocatalytic, antibacterial and anticancer performance. RSC Advances, 9(70), 41135-41150.
- AKHUNDI, A., HABIBI-YANGJEH, A., ABITORABI, M., RAHIM POURAN, S. (2019). Review on photocatalytic conversion of carbon dioxide to value-added compounds and renewable fuels by graphitic carbon nitride-based photocatalysts. Catalysis Reviews, 61(4), 595-628.

- AKHUNDI, A., BADIEI, A., ZIARANI, G. M., HABI-BI-YANGJEH, A., MUNOZ-BATISTA, M. J., LUQUE, R. (2020). Graphitic carbon nitride-based photocatalysts: toward efficient organic transformation for value-added chemicals production. Molecular Catalysis, 488, 110902.
- Asadzadeh-Khaneghah, S., & Habibi-Yangjeh, A. (2020). g-C₃N₄/carbon dot-based nanocomposites serve as efficacious photocatalysts for environmental purification and energy generation: a review. Journal of Cleaner Production, 276, 124319.
- BAHRUDIN, N., NAWI, M. (2019). Mechanistic of photocatalytic decolorization and mineralization of methyl orange dye by immobilized TiO₂/chitosan-montmorillonite. Journal of Water Process Engineering, 31, 100843.
- BERGAMONTI, L., BERGONZI, C., GRAIFF, C., LOTTICI, P. P., BETTINI, R., ELVIRI, L. (2019). 3D printed chitosan scaffolds: A new TiO₂ support for the photocatalytic degradation of amoxicillin in water. Water Research, 163, 114841.
- CAO, C., XIAO, L., CHEN, C., SHI, X., CAO, Q., GAO, L. (2014). In situ preparation of magnetic Fe_3O_4 / chitosan nanoparticles via a novel reduction– precipitation method and their application in adsorption of reactive azo dye. Powder Technology, 260, 90-97.
- CHEN, D., CHENG, Y., ZHOU, N., CHEN, P., WANG, Y., LI, K., HUO, S., CHENG, P., PENG, P., ZHANG, R. (2020). Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review. Journal of Cleaner Production, 268, 121725.
- CRINI, G., LICHTFOUSE, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters, 17(1), 145-155.
- GE, J., ZHANG, Y., PARK, S.-J. (2019). Recent advances in carbonaceous photocatalysts with enhanced photocatalytic performances: a mini review. Materials, 12(12), 1916.
- GHARBANI, P., MEHRIZAD, A. (2022). Preparation and characterization of graphitic carbon nitrides/ polyvinylidene fluoride adsorptive membrane modified with chitosan for Rhodamine B dye removal from water: Adsorption isotherms, kinetics and thermodynamics. Carbohydrate Polymers, 277, 118860.
- GUSAIN, R., GUPTA, K., JOSHI, P., KHATRI, O. P. (2019). Adsorptive removal and photocatalytic degradation of organic pollutants using metal

oxides and their composites: A comprehensive review. Advances in colloid and interface science, 272, 102009.

- HABIBI-YANGJEH, A., ASADZADEH-KHANEGHAH, S., FEIZPOOR, S., ROUHI, A. (2020). Review on heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses: can we win against pathogenic viruses?. Journal of Colloid and Interface Science, 580, 503-514.
- HALDORAI, Y., SHIM, J.-J. (2013). Multifunctional chitosan-copper oxide hybrid material: photocatalytic and antibacterial activities. International Journal of Photoenergy, 2013.
- HARIGANESH, S., VADIVEL, S., MARUTHAMANI, D., RANGABHASHIYAM, S. (2020). Disinfection by-products in drinking water: Detection and treatment methods, In Disinfection By-products in Drinking Water, 279-304.
- KARIMI, M.A., RANJBAR, M., MOHADESI, A. (2021). One-step ultrasonic production of the chitosan/ lactose/g- $C_{3}N_{4}$ nanocomposites with lactose as a biological capping agent: Photocatalytic activity study. Journal of the Chinese Chemical Society, 68(7), 1205-1213.
- KHAN, A., GOEPEL, M., COLMENARES, J. C., GLÄSER, R. (2020). Chitosan-based N-doped carbon materials for electrocatalytic and photocatalytic applications. ACS Sustainable Chemistry & Engineering, 8(12), 4708-4727.
- KHAN, A. A. P., SINGH, P., RAIZADA, P., ASIRI, A. M. (2021). Converting Ag₃PO₄/CdS/Fe doped C₃N₄ based dual Z-scheme photocatalyst into photo-Fenton system for efficient photocatalytic phenol removal. Journal of Industrial and Engineering Chemistry, 98, 148-160.
- KHAN, H., KHALIL, A. K., KHAN, A., SAEED, K., ALI, N. (2016). Photocatalytic degradation of bromophenol blue in aqueous medium using chitosan conjugated magnetic nanoparticles. Korean Journal of Chemical Engineering, 33(10), 2802-2807.
- KUMAR, A., SINGH, P., KHAN, A. A. P., VAN LE, Q., THAKU, S., RAIZADA, P. (2022a). CO₂ photoreduction into solar fuels via vacancy engineered bismuth-based photocatalysts: Selectivity and mechanistic insights. Chemical Engineering Journal, 439, 135563.
- KUMAR, R., RAIZADA, P., AHAMAD, T., ALSHEHRI,
 S. M., VAN LE, Q., ALOMAR, T. S., NGUYEN, V.H., SELVASEMBIAN, R., THAKUR, S., NGUYEN, D.
 (2022b). Polypyrrole-based nanomaterials: A novel strategy for reducing toxic chemicals and

others related to environmental sustainability applications. Chemosphere, 134993.

- KUMAR, R., SUDHAIK, A., KHAN, A.A.P., RAIZADA, P., ASIRI, A. M., MOHAPATRA, S., THAKUR, S., THAKUR, V. K., SINGH. P. (2022c). Current status on designing of dual Z-scheme photocatalysts for energy and environmental applications. Journal of Industrial and Engineering Chemistry, 106, 340-355.
- KYZAS, G. Z., FU, J., LAZARIDIS, N. K., BIKIARIS, D. N., MATIS, K. A. (2015). New approaches on the removal of pharmaceuticals from wastewaters with adsorbent materials. Journal of Molecular Liquids, 209, 87-93.
- LEE, M., CHEN, B.-Y., DEN, W. (2015). Chitosan as a natural polymer for heterogeneous catalysts support: a short review on its applications. Applied Sciences, 5(4), 1272-1283.
- LI, C., XU, Y., TU, W., CHEN, G., XU, R. (2017). Metal-free photocatalysts for various applications in energy conversion and environmental purification. Green Chemistry, 19(4), 882-899.
- LI, Q.-H., DONG, M., LI, R., CUI, Y.-Q., XIE, G.-X., WANG, X.-X., LONG, Y.-Z. (2021). Enhancement of Cr (VI) removal efficiency via adsorption/ photocatalysis synergy using electrospun chitosan/g-C₃N₄/TiO₂ nanofibers. Carbohydrate Polymers, 253, 117200.
- LI, X., ZHANG, Z., FAKHRI, A., GUPTA, V. K., AGAR-WAL, S. (2019). Adsorption and photocatalysis assisted optimization for drug removal by chitosan-glyoxal/Polyvinylpyrrolidone/MoS₂ nanocomposites. International journal of biological macromolecules, 136, 469-475.
- MANSUR, A. A., MANSUR, H. S., RAMANERY, F. P., OLIVEIRA, L. C., SOUZA, P. P. (2014). "Green" colloidal ZnS quantum dots/chitosan nano-photocatalysts for advanced oxidation processes: study of the photodegradation of organic dye pollutants. Applied Catalysis B: Environmental, 158, 269-279.
- MILLS, A., DAVIES, R. H., WORSLEY, D. (1993). Water purification by semiconductor photocatalysis. Chemical Society Reviews, 22(6), 417-425.
- MOURYA, V., INAMDAR, N. N. (2008). Chitosan-modifications and applications: Opportunities galore. Reactive and Functional Polymers, 68(6), 1013-1051.
- NATARAJAN, S., BAJAJ, H. C., TAYADE, R. J. (2018). Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process. Journal of Environmental Sciences, 65, 201-222.

- NGAH, W. W., TEONG, L. C., HANAFIAH, M. M. (2011). Adsorption of dyes and heavy metal ions by chitosan composites: a review. Carbohydrate polymers, 83(4), 1446-1456.
- NITHYA, A., JOTHIVENKATACHALAM, K., PRABHU, S., JEGANATHAN, K. (2014). Chitosan based nanocomposite materials as photocatalyst–a review, Materials Science Forum. Trans Tech Publ, 79-94.
- OGAWA, K., YUI, T., OKUYAMA, K. (2004). Three D structures of chitosan. International Journal of Biological Macromolecules, 34(1-2), 1-8.
- PREETHI, J., FARZANA, M. H., MEENAKSHI, S. (2017). Photo-reduction of Cr (VI) using chitosan supported zinc oxide materials. International Journal of Biological Macromolecules, 104, 1783-1793.
- RANA, A., SUDHAIK, A., RAIZADA, P., NGUYEN, V. H., XIA, C., KHAN, A. A. P., THAKUR, S., NGUYEN-TRI, P., NGUYEN, C. C., KIM, S. Y., VAN LE, Q., SINGH, P. (2022). Graphitic carbon nitride based immobilized and non-immobilized floating photocatalysts for environmental remediation. Chemosphere, 297, 134229.
- SAAD, A. M., ABUKHADRA, M. R., AHMED, S. A.-K., ELZANATY, A. M., MADY, A. H., BETIHA, M. A., SHIM, J.-J., RABIE, A. M. (2020). Photocatalytic degradation of malachite green dye using chitosan supported ZnO and Ce-ZnO nano-flowers under visible light. Journal of Environmental Management, 258, 110043.
- SHEN, H., DURKIN, D. P., AIELLO, A., DIBA, T., LAF-LEUR, J., ZARA, J. M., SHEN, Y., SHUAI, D. (2021). Photocatalytic graphitic carbon nitride-chitosan composites for pathogenic biofilm control under visible light irradiation. Journal of Hazardous Materials, 408, 124890.
- ŠKORIĆ, M. L., TERZIĆ, I., MILOSAVLJEVIĆ, N., RA-DETIĆ, M., ŠAPONJIĆ, Z., RADOIČIĆ, M., KRUŠIĆ, M. K. (2016). Chitosan-based microparticles for immobilization of TiO₂ nanoparticles and their application for photodegradation of textile dyes. European Polymer Journal, 82, 57-70.
- SUDHAIK, A., RAIZADA, P., KHAN, A. A. P., SINGH, A., & SINGH, P. (2022). Graphitic carbon nitride-based upconversion photocatalyst for hydrogen production and water purification. Nanofabrication, 7.
- VERMA, M. L., KUMAR, S., DAS, A., RANDHAWA, J. S., CHAMUNDEESWARI, M. (2020). Chitin and chitosan-based support materials for enzyme immobilization and biotechnological applications. Environmental Chemistry Letters, 18(2), 315-323.

- VIGNESHWARAN, S., PREETHI, J., MEENAKSHI, S. (2019). Removal of chlorpyrifos, an insecticide using metal free heterogeneous graphitic carbon nitride $(g-C_3N_4)$ incorporated chitosan as catalyst: Photocatalytic and adsorption studies. International Journal of Biological macromolecules, 132, 289-299.
- WANG, H., WU, Y., WU, P., CHEN, S., GUO, X., MENG, G., PENG, B., WU, J., LIU, Z. (2017). Environmentally benign chitosan as reductant and supporter for synthesis of Ag/AgCl/chitosan composites by one-step and their photocatalytic degradation performance under visible-light irradiation. Frontiers of Materials Science, 11(2), 130-138.
- XIONG, S., LIU, M., YAN, J., ZHAO, Z., WANG, H., YIN, X., WANG, L., CHEN, S. (2018). Immobilization of Ag_3PO_4 nanoparticles on chitosan fiber for photocatalytic degradation of methyl orange. Cellulose, 25(9), 5007-5015.
- YAHYA, N., AZIZ, F., JAMALUDIN, N., MUTALIB, M., ISMAIL, A., SALLEH, W., JAAFAR, J., YUSOF, N., LUDIN, N. (2018). A review of integrated photocatalyst adsorbents for wastewater treatment. Journal of Environmental Chemical Engineering, 6(6), 7411-7425.
- YOU, J., LIU, C., FENG, X., LU, B., XIA, L., ZHUANG, X. (2022). In situ synthesis of ZnS nanoparticles onto cellulose/chitosan sponge for adsorption– photocatalytic removal of Congo red. Carbohydrate Polymers, 288, 119332.
- ZHANG, M., XIONG, J., YANG, H., WEN, Z., CHEN, R., CHENG, G. (2020). Surface Potential/Wettability and Interface Charge Transfer Engineering of Copper-Oxide (Cu–MO_x, M=W, Ti, and Ce) Hybrids for Efficient Wastewater Treatment through Adsorption–Photocatalysis Synergy. Industrial & Engineering Chemistry Research, 59(35), 15454-15463.
- ZHAO, C., YAN, Q., WANG, S., DONG, P., ZHANG, L. (2018). Regenerable g-C₃N₄-chitosan beads with enhanced photocatalytic activity and stability. RSC advances, 8(48), 27516-27524.
- ZHAO, Y., TAO, C., XIAO, G., SU, H. (2017). Controlled synthesis and wastewater treatment of Ag_2O/TiO_2 modified chitosan-based photocatalytic film. RSC advances, 7(18), 11211-11221.
- ZHU, H., JIANG, R., FU, Y., GUAN, Y., YAO, J., XIAO, L., ZENG, G. (2012). Effective photocatalytic decolorization of methyl orange utilizing TiO₂/ZnO/chitosan nanocomposite films under simulated solar irradiation. Desalination, 286, 41-48.

ZHU, H., JIANG, R., XIAO, L., CHANG, Y., GUAN, Y., LI, X., ZENG, G. (2009). Photocatalytic decolorization and degradation of Congo Red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation. Journal of Hazardous Materials, 169(1-3), 933-940.

Zhu, H., Jiang, R., Xiao, L., Liu, L., Cao, C., Zeng, G. (2013). CdS nanocrystals/TiO₂/crosslinked chitosan composite: Facile preparation, charadsorption-photocatalytacterization and ic properties. Applied surface science, 273, 661-669.





Publisher's note: Eurasia Academic Publishing Group (EAPG) remains neutral with regard to jurisdictional claims in published maps and institutional affiliations. Open Access. This article is licensed under a Creative Commons Attribution-NoDerivatives 4.0 International (CC BY-ND 4.0) licence, which permits copy and redistribute the material in any medium or format for any purpose, even commercially. The licensor cannot revoke these freedoms as long as you follow the licence terms. Under the following terms you must give appropriate credit, provide a link to the license, and indicate if changes were made. You may do so in any reasonable manner, but not in any way that suggests the licensor endorsed you or your use. If you remix, transform, or build upon the material, you may not distribute the modified material. To view a copy of this license, visit https://creativecommons.org/licenses/by-nd/4.0/.