



RESEARCH ARTICLE

Photocatalytic oxygenation of sulfide using solar light and ingenious GQDs@AQ catalyst: Mechanistic and synthetic investigations

Rahnuma Siddique¹ | Rajesh K. Yadav¹ | Satyam Singh¹ | Rehana Shahin¹ | Arun K. Dubey¹ | Alok Kumar Singh² | Atresh K. Singh² | Navneet Kumar Gupta³ | Jin-Ook Baeg⁴ | Tae Wu Kim⁵

¹Department of Chemistry and Environmental Science, Madan Mohan Malaviya University of Technology, Gorakhpur, India

²Department of Chemistry, Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur, India

³Centre for Sustainable Technologies, Indian Institute of Science, Bengaluru, India

⁴Korea Research Institute of Chemical Technology, Daejeon, South Korea

⁵Department of Chemistry, Mokpo National University, Yeongson-ro, Cheonggye-myeon, Muan-gun, South Korea

Correspondence

Rajesh K. Yadav, Department of Chemistry and Environmental Science, Madan Mohan Malaviya University of Technology, Gorakhpur 273010, India. Email: rajeshkr_yadav2003@yahoo.co.in

Navneet Kumar Gupta, Centre for Sustainable Technologies, Indian Institute of Science, Gulmohar Marg, Mathikere, Bengaluru 560012, India. Email: nkgupta@iisc.ac.in

Jin-Ook Baeg, Korea Research Institute of Chemical Technology, N3, 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, South Korea. Email: jobaeg@kriict.re.kr

Tae Wu Kim, Department of Chemistry, Mokpo National University, 1666, Yeongson-ro, Cheonggye-meon Muan-gun, Jeollanam-do 58554, South Korea. Email: twkim@mnu.ac.kr

Abstract

The combination of excellent electronic properties and thermal stability positions orange-derived graphene quantum dots (GQDs) as promising materials for solar light-based applications. Researchers are actively exploring their potential in fields such as photovoltaics, photocatalysis, optoelectronics, and energy storage. Their abundance, cost-effectiveness, and eco-friendly nature further contribute to their growing relevance in cutting-edge scientific research. Furthermore, only GQDs are not much more effective in the UV-visible region, therefore, required band gap engineering in GQDs material. In this context, we designed GQDs-based light harvesting materials, which is active in UV-visible region. Herein we synthesized GQDs coupled with 2,6-diaminoanthraquinone (AQ), that is, GQDs@AQ light harvesting photocatalyst the first time for the oxidation of sulfide to sulfoxide under visible light. For the integrating reactions of sulfide in aerobic conditions under visible light by GQDs@AQ photocatalyst exhibit utmost higher photocatalytic activity than simple GQDs due to low molar extinction coefficient and slow recombination charges. The use of GQDs@AQ light harvesting photocatalyst, showed the excellent organic transformation efficiency of sulfide to sulfoxide with excellent yield (94%). The high efficiency and excellent yield of 94% indicate the effectiveness of GQDs@AQ as a photocatalyst for these specific organic transformations.

KEYWORDS

GQDs, GQDs@AQ photocatalyst, Methyl p-tolyl sulfide, oxygenation reaction, solar light

INTRODUCTION

Solar light utilization for the conversion of organic compounds has become one of the enormous potential research areas based on green nanotechnology.¹ The conversion of organic compounds in the existence of variously reported photocatalysts under solar light illumination due to the effective reaction circumstance to activate substrates along with sequential creation of solar light blocking units via feasible reaction route many researchers have been focusing on these.^{2,3} The preparation of readily processed, metal-free, and effective photocatalysts has been significant for the conversion of organic compounds for industrial applications, to overcome such types of limitations. To do so, the natural mimic artificial photocatalytic system can be another tactic for the conversion of organic compounds into useful solar-made products because of the use of eco-friendly and environmentally friendly, and maintainable solar lights.⁴ In 1972, a few metal-based organic complexes have been utilized as a general platform for a photocatalytic system since well-known scientists⁵ employed the photo anode that is made from inorganic materials for solar fuel formations and hydrogen evolution.^{6–8}

Nevertheless, in the use of a few metal-based organic complexes for mimicking natural synthesis through artificial photo-catalysis pathways, there were utmost restrictions due to the wide optical energy gap and tuning the capability of molar extinction coefficient in the presence the solar light.⁹ To improve the UV-visible properties of photocatalysts, expensive semiconducting solar light active materials have been reported for the transformation of organic compounds.¹⁰ To facilitate the photo-catalysis based on the with and without metal graphene quantum dots (GQDs) has been utilized on a large scale and it has exhibited good applications in different research fields due to good solar light absorption properties in the spectral window and thermal stability.^{11,12} Based on these properties and stability, GQDs with metal and without metal photocatalysts have been extensively and briefly utilized for the fixation of carbon dioxide (CO₂) into low-cost value-added chemicals and water splitting.¹³

Currently, it was explained that the GQDs-modified materials can be utilized for light-induced photo-catalysis for the transformation of organic compounds such as C-H, C-S, C-N bond activation, and so on.¹⁴ In this context, the use of GQDs photocatalyst has a limitation for photocatalytic applications to cover the wide spectral spectrum of solar light. Therefore, we developed a metal-free new type of GQDs solar light absorbing materials. As a means to attain this goal, we herein developed GQDs covalently coupled to a solar light harvesting AQ molecule (2,6-diamino anthraquinone) that indeed exhibit excellent ability for

oxygenation of sulfide compared to graphene-based photocatalysts.¹⁵ The unique properties of GQDs and the synergistic effect between GQDs and AQ contribute to their enhanced performance in this process. Overall, the covalent coupling of GQDs with AQ molecules enhances the performance of the photocatalyst by combining the light-harvesting properties of GQDs with the strong oxidizing ability of AQ. This synergistic effect leads to improved oxygenation of sulfide, making GQDs coupled with AQ an excellent choice for such applications. The solar light platform was developed using GQDs@AQ as photocatalyst utilities in a highly selective and efficient pathway, leading to high oxygenation of sulfide (~99%) under solar light (Scheme 2 and Table 1). The current solar light active fundamental research endeavor highlights the improvement and application of a GQDs-based photocatalyst for direct oxygenation reaction^{16,17} Scheme 2.

MATERIALS AND METHODS

Materials

Orange peel, glycerol, aqueous medium, 2,6-diamino anthraquinone, triethanolamine (TEA), ortho dichlorobenzene (ODCB), dimethylformamide (DMF), HATU (for selective coupling), methyl *p*-tolyl sulfide, hydrochloric acid (HCl), and ethyl alcohol were acquired from Sigma-Aldrich and further utilized as such.

Synthesis of GQDs

According to the previous study, GQDs were synthesized by the condensation method. Orange peel was gently scrubbed and washed with clean water and allowed to air dry. The dried Orange peel was crushed into a fine powder. Firstly, 10g of dried orange peel-based powder was thoroughly mixed with 100 mL of distilled water along with 20 mL of glycerol. Secondly, the prepared solution was refluxed at 100°C. Thirdly, the color of the refluxed solution was changed into dark brown color from yellow color, which showed the formation of graphene-like material. Finally, the solution was filtered and washed with 100 mL water and

TABLE 1 Oxygenation of methyl *p*-tolyl sulfide by AQ, GQDs, and GQD@AQ photocatalyst.

Entry	Photocatalyst	Solvent	Yield (%)	Selectivity (%)
1	AQ	C ₂ H ₅ OH	41	41
2	GQD	C ₂ H ₅ OH	30	30
3	GQD@AQ	C ₂ H ₅ OH	99.9	99.6

50 mL acetone. After that final product was dried at 70°C. In totality, 1 g graphene-like material was heated in the muffle furnace at 500°C, for 4 h. After cooling we achieved 86% GQDs as per the reported method (Scheme 1).¹⁸

Synthesis of GQDs coupled with AQ (GQDs@AQ) photocatalyst for organic transformation reaction

The GQDs@AQ photocatalyst was synthesized via the co-polymerization method.¹⁵ First, 80 mg graphene quantum dot (GQDs), 160 mg 2,6-diamino anthraquinone (reddish in color), (0.5 mL) tri-ethyl-amine, (10 mL) ortho-dichlorobenzene, and HATU (catalytic amount) were dissolved in (1 mL) dimethyl-formamide (DMF). This prepared solution was refluxed at 183°C for 4 days. After work-up,¹⁹ the received organic compound was dried at 100°C. Finally, the resultant product is shown in Scheme 2.

RESULT AND DISCUSSION

Instruments and Measurements

UV instrument, FT-IR instrument, and thermogravimetric analysis (TGA) were used for the calculation of the optical band gap, molecular structure elucidation, and stability of the photocatalyst. The zeta potential and particle size were used for the coupling of GQD with AQ and enhanced the photocatalytic efficiency. Raman spectra were used for the coupling of the GQD with AQ.

Optical band gap and structure elucidation of newly designed photocatalyst through UV and FTIR techniques

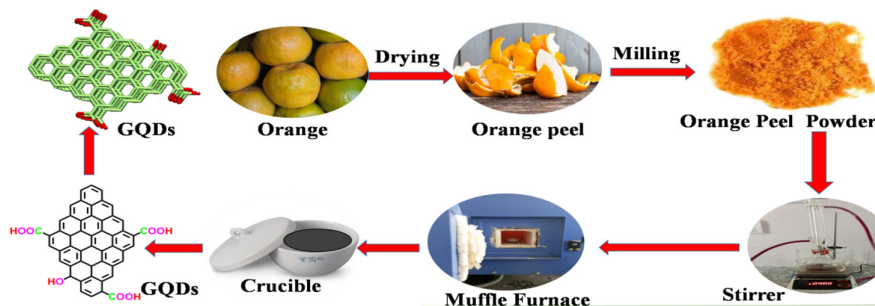
The UV-visible light absorption ability spectra of GQDs, AQ, and GQDs@AQ photocatalyst have been recorded in DMF solution, which is shown in Figure 1A. In the case

of GQDs, it has no band absorption in the UV-visible region. Therefore, we coupled GQDs with 2,6-diamino anthraquinone via the condensation method. After attaching AQ from GQDs, it absorbed the UV-visible light from 400 to 500 nm. So, the absorption spectra of GQDs@AQ photocatalyst clearly show that light-harvesting molecule.²⁰ Therefore, the GQDs@AQ photocatalyst has an extraordinary solar light absorption ability along with a suitable optical band gap, which is calculated by the Scherrer method. Oxygenation of sulfide by newly designed GQDs@AQ photocatalyst has a slow recombination charge and excellent light-harvesting ability. Therefore, the GQDs@AQ photocatalyst has excellent capability for oxygenation reaction.

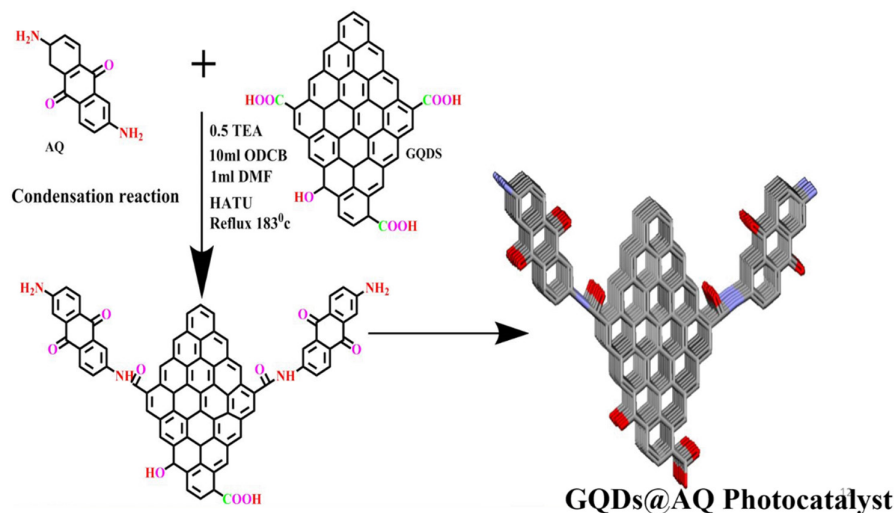
The FTIR spectra were used to determine the molecular structure elucidation of the newly designed GQDs@AQ photocatalyst. In Figure 1B, FTIR spectra of GQDs, AQ, and GQDs@AQ photocatalyst were synthesized by the reported method.²¹ In Figure 1B, GQDs@AQ photocatalyst has a strong peak at 1260 cm⁻¹, which can be attributed to the stretching mode of -C-O, and the additional peak at 1696 cm⁻¹ confirms the stretching mode of an amide bond. In Figure 1B, the spectrum of GQDs showed characteristic peaks near about 1050 and 1365 cm⁻¹, indicating the presence of carbonyl and hydroxyl groups. In addition, the characteristic peak near about at 1700 cm⁻¹ was allocated to the carbonyl stretching of the acidic group. In the characteristic spectrum of GQDs@AQ photocatalyst, the non-existence of a peak near about 1710 cm⁻¹ and concomitant appearance of new bands at 1610 cm⁻¹ and 1280–1210 cm⁻¹ allocated to the carbon–nitrogen, and carbonyl stretching, respectively, of the group of amides confirmed the coupling of AQ to GQDs.²² Additionally, as per the reported article,²³ the surface morphology of GQDs@AQ photocatalyst is similar to flower-like morphology.

Thermogravimetric and X-ray diffraction studies for stability and crystallinity

Figure 2A represents the thermal stability of the GQDs@AQ photocatalyst, which is investigated by the TGA



SCHEME 1 Schematic illustration for preparation of GQDs.



SCHEME 2 Synthesis of GQDs@AQ from 2,6-diamino anthraquinone and GQDs materials respectively.

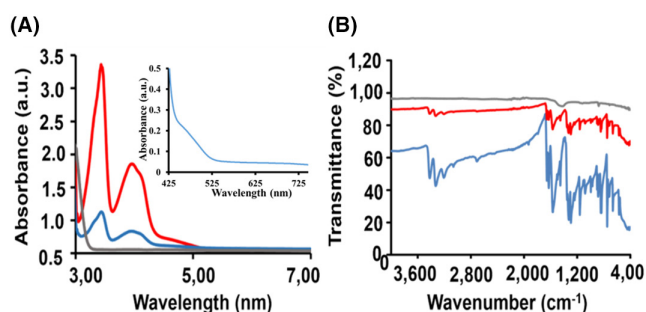


FIGURE 1 (A) UV-Visible spectra of GQDs@AQ photocatalyst (red) with an inset of the λ_{max} region between 425 and 525 nm, AQ (blue), and GQDs (gray) respectively. (B) FTIR spectra of GQDs@AQ photocatalyst (red), AQ (blue), and GQDs (gray).

technique. The TGA (heating rate: $5^{\circ}\text{C min}^{-1}$ under an inert atmosphere) curve for GQDs@AQ exhibits very slow weight loss with the rise in temperature of the muffle oven up to 800°C . The TGA curve of the GQDs@AQ photocatalyst shows a major weight loss at near about 400 and 420°C corresponding to the characteristic arrangement of sidewall functionalization, which confirms the newly designed GQDs@AQ photocatalyst is more stable than others.²⁴ The TGA curve can indicate that the temperature is increased with a decrease in weight loss percentage, thus displaying that the mass is exchanging nonstop due to thermal treatment.²⁵ Due to thermal stability, the newly designed GQDs@AQ photocatalyst is superior to individual materials. Therefore, the yield of oxygenation products is higher in comparison to GQDs and AQ.

In **Figure 2B**, the sharp line in the X-ray diffraction (XRD) spectra of the GQDs@AQ photocatalyst confirmed its crystalline nature. As per the reported paper,²⁵ the

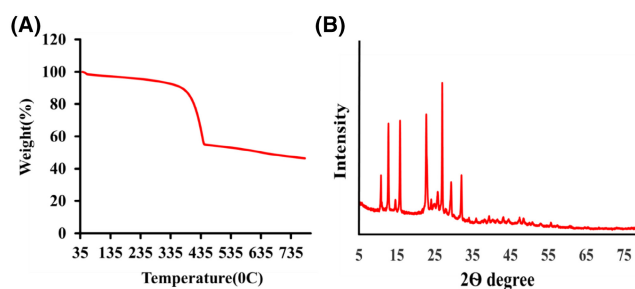


FIGURE 2 (A) Thermogravimetric analysis and (B) XRD patterns of GQDs@AQ photocatalyst.

XRD pattern of GQDs has a 2θ value at 26° . After attaching GQDs with 2,6-diaminoanthraquinone, a new peak appeared at 27° . Therefore, the existence of new peaks belonging to the amide bond was confirmed by using characterization techniques in the manuscript, as described in detail previously.²⁶

DLS analysis and Raman spectroscopy studies for coupling of the donor-acceptor materials and improved efficiency

The zeta potential (ZP) and particle size (PS) were observed through the dynamic light scattering (DLS) technique. The ZP value of GQDs@AQ photocatalyst (-26.9 eV) is less positive than GQDs (-24.1 eV), which designates that the attachment of highly efficient GQDs with AQ as per described literature routes.²⁷⁻²⁹ From the same technique, we measured the PS of the GQDs and GQDs@AQ photocatalyst (**Figure 3**), respectively. The PS of the GQDs@AQ photocatalyst was (190 nm) higher

than that of the GQDs as per the reported method.²⁷ The change in the size confirms the formation of the GQDs@AQ photocatalyst.²⁶ Therefore, after the formation of the GQDs@AQ photocatalyst, it showed an excellent solar light harvesting ability for the photocatalytic oxygenation of sulfide under solar light at ambient temperature.

Raman spectroscopy is an influential technique to examine the structure of GQDs and GQDs@AQ photocatalysts (Figure 3D). As reported Raman spectra of GQDs have two strong peaks at 1367 and 1611 cm^{-1} , corresponding to the disorder (D) and graphitic (G) bands, respectively. In addition, D and G bands in newly prepared GQDs@AQ appeared near about 1374 and 1638 cm^{-1} , respectively. The characteristic shift in the peak position of the D (7 cm^{-1}) and G (27 cm^{-1}) bands confirmed the attachment of GQDs with AQ through the condensation method.³⁰ There are various issues such as strains, defects, and coupling, which distress the position of the D and G bands.²⁹ However, it should be distinguished that both bands are shifting due to the generation of new amide bond groups and these changes are improved with an increase in the atomic ratio of N–C atomic in GQDs@AQ photocatalyst.^{30,31}

Transformation of sulfide to sulfoxide by newly designed GQDs@AQ photocatalyst

The combination of GQDs@AQ photocatalyst (10 mg), and methyl *p*-tolyl sulfide (0.134 mL) were mixed in 4 mL of ethyl alcohol along with 0.05 M HCL. The prepared reaction mixture was irradiated under blue LED light (5 W, wavelength 450 nm) in the aerobic condition at ambient

temperature. Later, the progress and completion of the pathway of reaction were monitored through thin-layer chromatography. After the completion of the reaction, the reaction mixture was removed from the LED condition and the mixture was washed with 50 mL water and 20 mL alcohol. The filtrate was concentrated and evaporated by the rota-evaporator technique. After that, the end product was purified by the reported method.³² Finally, the yield of the oxygenated product was received at 99.9%. Newly designed photocatalyst material is more efficient than the reported materials¹⁵ (Scheme 3 and Table 1). The combination of GQDs and AQ molecules leads to synergistic effects, where the unique properties of each component complement and enhance the overall catalytic performance. The GQDs act as electron acceptors, while the AQ molecules serve as electron donors, promoting efficient redox reactions. In contrast, the earlier reported¹⁵ photocatalyst may have limitations in terms of its oxygenation ability for sulfide compounds. Without further information on the specific properties and composition of the reported photocatalyst,¹⁵ it is challenging to directly compare its performance to the GQD-AQ composite. However, the advantages of GQD-AQ, as mentioned above, make it a promising candidate for efficient oxygenation of sulfide compounds in photocatalytic applications. Overall, the covalent coupling of GQDs with AQ molecules offers a promising and cost-effective approach for developing efficient photocatalysts. These hybrid materials combine the advantages of GQDs and AQ molecules, leading to enhanced photocatalytic properties and providing a viable alternative to the more complex and potentially expensive reported photocatalyst.¹⁵

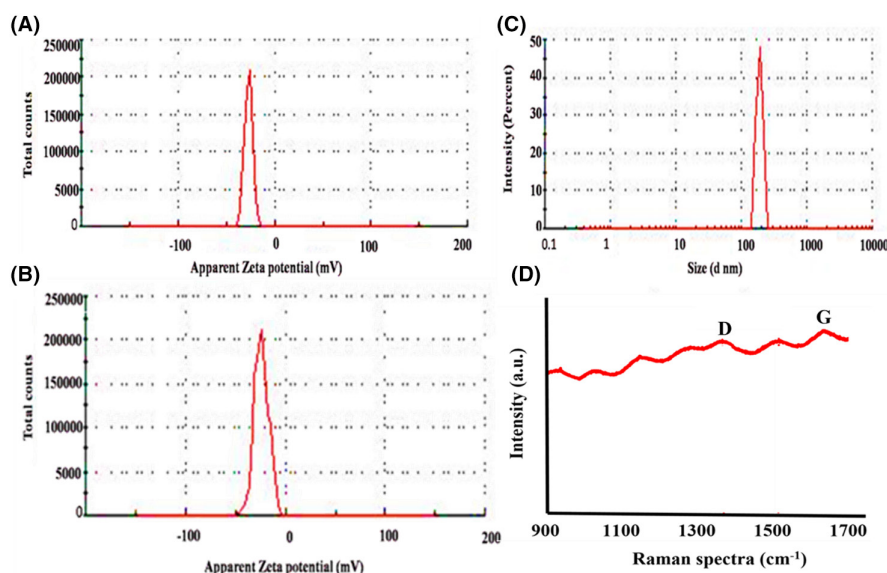
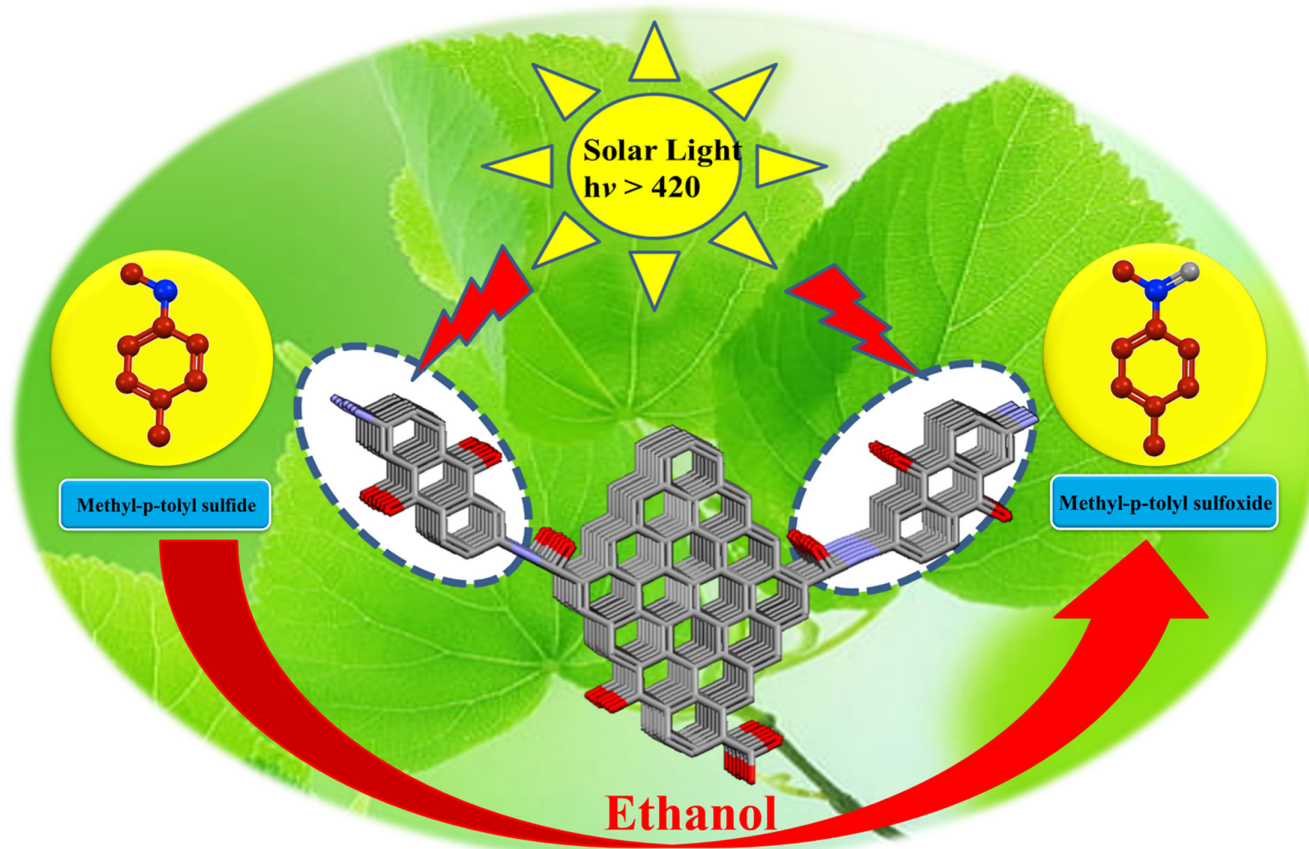


FIGURE 3 Zeta Potential of (A) GQDs and (B) GQDs@AQ photocatalyst respectively. PS of (C) GQDs@AQ photocatalyst respectively. (D) Raman spectra of GQDs @AQ photocatalyst.



SCHEME 3 Pictorial diagram for representation of the oxygenation of methyl *p*-tolyl sulfide through GQDs@AQ photocatalyst under visible light.

Reaction conditions

GQDs@AQ photocatalyst (10 g), methyl *p*-tolyl sulfide (0.134 mL), and 0.05 M hydrochloric acid in 4 mL ethyl alcohol (C_2H_5OH), Blue LED light (5 W, wavelength 450).

Mechanistic study for photocatalytic oxygenation of sulfide to sulfoxide under solar light

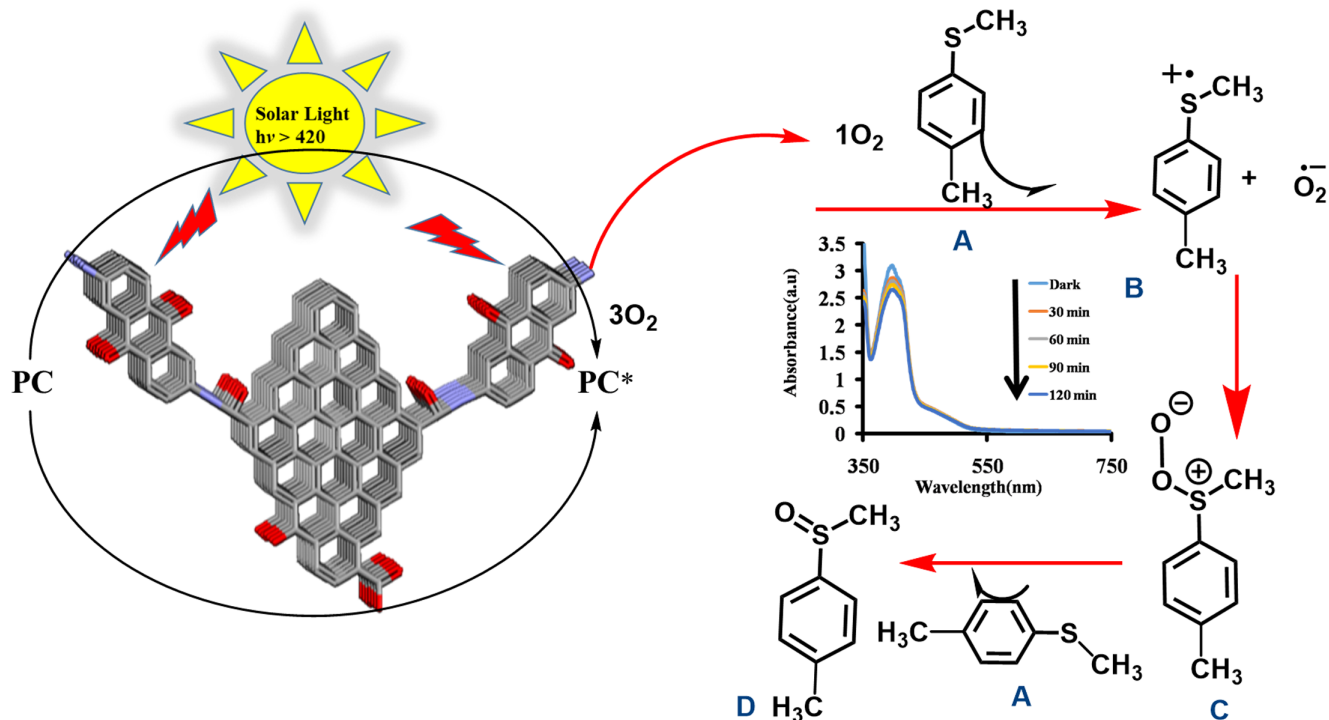
A reasonable mechanism was proposed for the oxygenation of methyl-*p*-tolyl sulfide over GQDs@AQ photocatalyst in aerobic conditions under solar light (Scheme 4). It is well-known that the oxygenation reaction in aerobic conditions was carried out by the conversion of triplet oxygen (3O_2) into reactive singlet oxygen (1O_2) species (inset in Scheme 4). As per the reported paper, GQDs@AQ (PC) photocatalyst formed the singlet excited state of GQDs@AQ (PC*), which converted 3O_2 to the 1O_2 (inset in Scheme 4). Subsequently, the singlet excited state of PC* was created from the triplet excited state of PC* via intersystem crossing (ISC). Then, the reactive species of 1O_2 reacts with methyl-*p*-tolyl sulfide (A) to generate (B) as a cation of sulfur radical. Finally, sulfur

radical cation (B) leads to the development of key intermediate persulfoxide (C) after the reaction with O_2^- . The persulfoxide nucleophilic (C) undergoes a similar nucleophilic reaction to give the oxygenated end product (D).³³

To lengthen the photocatalytic presentation of produced GQDs@AQ photocatalyst, the photocatalyst was used as specified 1O_2 quencher (inset in Scheme 4). Here, the inset of Scheme 4 shows the model set of UV-visible quenching spectra of GQDs@AQ in DMF solution. This clearly shows the decrease in the absorbance of the GQDs@AQ photocatalyst, which confirms the conversion of triplet oxygen into singlet oxygen by a newly designed photocatalyst.^{34–36}

CONCLUSION

Graphene quantum dots coupled with 2,6-diaminoanthraquinone to generate the artificial photo-system known as GQDs@AQ photocatalyst that is utilized in the oxygenation of sulfide in aerobic conditions. Because GQDs@AQ photocatalyst has high light harvesting ability, thermal stability, and high molar extinction coefficient instigating from the reticular type structure.



SCHEME 4 Mechanism of metal-free covalent GQDs@AQ photocatalyst for selective oxygenation of sulfides under solar light. The oxygenation quenching experiment of sulfide is mentioned in the inset.

Therefore, high oxygenation end product received 94% by outstanding GQDs@AQ photocatalyst than AQ and GQDs respectively. Additionally, the generation of singlet oxygen ($^1\text{O}_2$) from triplet oxygen ($^3\text{O}_2$) was carried out by UV-visible spectroscopy in the presence of GQDs@AQ photocatalyst. Herein, we established the more effective approach for the utilization of solar light and a cost-effective photocatalyst for the oxygenation of sulfide in aerobic conditions. Such type of oxygenated end product was achieved by GQDs@AQ photocatalyst, which has a significant role in chemotherapy as well as reducing pain.

ACKNOWLEDGMENTS

The authors are thankful for the kind research support of the Madan Mohan Malaviya University of Technology, Gorakhpur-273010, and the Centre for Sustainable Technologies, Indian Institute of Science, Gulmohar Marg, Mathikere, Bengaluru 560012, India.

ORCID

Rajesh K. Yadav <https://orcid.org/0000-0002-5320-5259>
 Satyam Singh <https://orcid.org/0000-0001-8537-4594>
 Jin-Ook Baeg <https://orcid.org/0000-0003-0074-4758>
 Tae Wu Kim <https://orcid.org/0000-0002-6370-0907>

REFERENCES

- Marin ML, Santos-Juanes L, Arques A, Amat AM, Miranda MA. Organic photocatalysts for the oxidation of pollutants and model compounds. *Chem Rev.* 2012;14:1710-1750. doi:10.1021/cr2000543
- Li W, Feng C, Dai S, Yue J, Hua F, Hou H. Fabrication of sulfur-doped g-C₃N₄/Au/CdS Z-scheme photocatalyst to improve the photocatalytic performance under visible light. *Appl Catal B.* 2015;168:465-471. doi:10.1016/j.apcatb.2015.01.012
- Deng Y, Tang L, Zeng G, et al. Insight into highly efficient simultaneous photocatalytic removal of Cr(VI) and 2,4-dichlorophenol under visible light irradiation by phosphorus doped porous ultrathin g-C₃N₄ nanosheets from aqueous media: performance and reaction mechanism. *Appl Catal B.* 2017;203:343-354. doi:10.1016/j.apcatb.2016.10.046
- Ran J, Ma TY, Gao G, Du XW, QSZ. Porous P-doped graphitic carbon nitride nanosheets for synergistically enhanced visible-light photocatalytic H₂ production. *Energy Environ Sci.* 2015;8:3708-3717. doi:10.1039/x0xx00000x
- Marpani F, Pinelo M, Meyer AS. Enzymatic conversion of CO₂ to CH₃OH via reverse dehydrogenase cascade biocatalysis: quantitative comparison of efficiencies of immobilized enzyme systems. *Biochem Eng J.* 2017;127:217-228. doi:10.1016/j.bej.2017.08.011
- Yu D, Ilango PR, Han S, et al. Metal-organic framework derived Co@NC/CNT hybrid as a multifunctional electrocatalyst for hydrogen and oxygen evolution reaction and oxygen reduction reaction. *Int J Hydrog Energy.* 2019;44(60):32054-32065.
- Manikandan A, Ilango PR, Chen CW, et al. A superior dye adsorbent towards the hydrogen evolution reaction combining active sites and phase-engineering of (1T/2H) MoS₂/α-MoO₃ hybrid heterostructured nanoflowers. *J Mater Chem A.* 2018;6(31):15320-15329.
- Ilango PR, Huang H, Li L, Yang S, Peng S. Facile synthesis of self-organized single crystalline TiOF₂ nanotubes for photocatalytic hydrogen evolution. *Solid State Sci.* 2021;117:106627.

9. Zhang Z, Muschiol J, Huang Y, et al. Efficient ionic liquid-based platform for multi-enzymatic conversion of carbon dioxide to methanol. *Green Chem.* 2018;20:4339-4348. doi:10.1039/c8gc02230e
10. Wu Y, Ward-Bond J, Li D, Shi J, Zhang S, Jiang Z. G-C₃N₄@#-Fe₂O₃/C photocatalysts: synergistically intensified charge generation and charge transfer for NADH regeneration. *ACS Catal.* 2018;8:5664-5674. doi:10.1021/acscatal.8b00070
11. Yang D, Zou H, Wu Y, et al. Constructing quantum dots@flake graphitic carbon nitride isotope heterojunctions for enhanced visible-light-driven NADH regeneration and enzymatic hydrogenation. *Ind Eng Chem Res.* 2017;56:6247-6255. doi:10.1021/acs.iecr.7b00912
12. Li X, Yu J, Jaroniec M, Chen X. Co catalysts for selective photo reduction of CO₂ into solar fuels. *ACS Catal.* 2019;119:3962-4179. doi:10.1021/acs.chemrev.8b00400
13. Liu J, Antonietti M. Bio-inspired NADH regeneration by carbon nitride photocatalysis using diatom templates. *Energy Environ Sci.* 2013;6:1486-1493. doi:10.1039/C3EE40696B
14. Wang S, Li M, Patil AJ, et al. Design and construction of artificial photoresponsive protocells capable of converting daylight to chemical energy. *J Mater Chem A.* 2017;5:24612-24616. doi:10.1039/C7TA08999F
15. Chaubey S, Singh C, Singh P, et al. Solar light-assisted rod-shaped CPTF@FACC photocatalyst: an efficient platform for oxygenation reactions and coenzymes regeneration. *Int J Energy Res.* 2022;46:16643-16657. doi:10.1002/er.8327
16. Kinastowska K, Liu J, Tobin JM, et al. Photocatalytic cofactor regeneration involving triethanolamine revisited: the critical role of glycolaldehyde. *Appl Catal B.* 2019;243:686-692. doi:10.1016/j.apcatb.2018.10.077
17. Wang J, Tang L, Zeng G, et al. Plasmonic Bi-metal deposition and g-C₃N₄ coating on Bi₂WO₆ microspheres for efficient visible-light photocatalysis. *ACS Sustain Chem Eng.* 2016;5:1062-1072. doi:10.1021/acssuschemeng.6b02351
18. Hu X, Li Y, Xu Y, et al. Green one-step synthesis of carbon quantum dots from orange peel for fluorescent detection of *Escherichia coli* in milk. *Food Chem.* 2021;339:127775. doi:10.1016/j.foodchem.2020.127775
19. Wu H, Huo Y. One-step synthesis of efficient photocatalysts by TCAP doped g-C₃N₄ for enhanced visible-light photocatalytic activity. *New J Chem.* 2020;44:1127-1137. doi:10.1039/C9NJ05270D
20. Wazir AH, Kundi IW. Synthesis of graphene Nano sheets by the rapid reduction of electrochemically exfoliated graphene oxide induced by microwaves. *J Chem Soc Pak.* 2016;38:1-7. <https://www.researchgate.net/publication/298710601>
21. Çiplak Z, Yildiz N, Çalimli A. Investigation of graphene/Ag nanocomposites synthesis parameters for two different synthesis methods. Fuller. Nanotub. carbon nanostructure, 2014;23:361-370. doi:10.1080/1536383X.2014.894025
22. Yadav RK, Baeg JO, Oh GH, et al. A photocatalyst-enzyme coupled artificial photosynthesis system for solar energy in production of formic acid from CO₂. *J Am Chem Soc.* 2012;134:11455-11461. doi:10.1021/ja3009902
23. Singh A, Yadav RK, Yadav U, Kim TW. Highly efficient flower-like graphene quantum dots-based Fuschin photocatalyst for selective NAD(P)H cofactor regeneration under solar light irradiation. *Photochem Photobiol.* 2021;98(2):412-420.
24. Yang D, Velamakanni A, Bozoklu G, et al. Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and micro-Raman spectroscopy. *Carbon.* 2009;47:145-152. doi:10.1016/j.carbon.2008.09.045
25. Yang Q, Xu W, Tomita A, Kyotani T. The template synthesis of double coaxial carbon nanotubes with nitrogen-doped and boron-doped multiwalls. *J Am Chem Soc.* 2005;127:8956-8957. doi:10.1021/ja052357e
26. Singh S, Yadav RK, Kim TW, et al. Rational design of a graphitic carbon nitride catalytic-biocatalytic system as a photocatalytic platform for solar fine chemical production from CO₂. *React Chem Eng.* 2022;7:1566-1572. doi:10.1039/d2re00079b
27. Kumru B, Antonietti M, Schmidt BVKJ. Enhanced dispersibility of graphitic carbon nitride particles in aqueous and organic media via a one-pot grafting approach. *Langmuir.* 2017;33:9897-9906. doi:10.1021/acs.langmuir.7b02441
28. Dodd AC, McKinley AJ, Saunders M, Tsuzuki T. Effect of particle size on the photocatalytic activity of nanoparticulate zinc oxide. *J Nanopart Res.* 2006;8:43-51. doi:10.1007/s11051-005-5131-z
29. Singh S, Yadav RK, Kim TW, et al. In situ prepared NRCPFs as highly active photo platforms for in situ bond formation between aryldiazonium salts and heteroarenes. *Photochem Photobiol.* 2021;7:1-6. doi:10.1111/php.13639
30. Singh C, Chaubey S, Singh P, et al. Self-assembled carbon nitride/cobalt (III) porphyrin photocatalyst for mimicking natural photosynthesis. *Diam Relat Mater.* 2020;101:107648. doi:10.1016/j.diamond.2019.107648
31. Singh C, Kim TW, Yadav RK, Baeg JO, Gole V, Singh AP. Flexible covalent porphyrin framework film: an emerged platform for photocatalytic C single bond H bond activation. *Appl Surf Sci.* 2021;554:148938. doi:10.1016/j.apsusc.2021.148938
32. Chhabra VA, Kaur R, Kumar N, Deep A, Rajesh C, Kim KH. Synthesis and spectroscopic studies of functionalized graphene quantum dots with diverse fluorescence characteristics. *RSC Adv.* 2018;8:11446-11454. doi:10.1039/c8ra01148f
33. Pua Q, Pua M, Mohammadi M. Application of transition metals in sulfoxidation reactions. *Mini Rev Org Chem.* 2020;17:423-429. doi:10.2174/1570193X16666190430154835
34. Singh C, Kim TW, Yadav RK, Kumar K, Yadav BC. Anthracene-based g-C₃N₄ photocatalyst for regeneration of NAD(P)H and sulfide oxidation based on Z-scheme nature. *Int J Energy Res.* 2021;45:1-13. doi:10.1002/er.6638
35. Singh P, Yadav RK, Kumar K, et al. Eosin-Y and sulfur-Co doped g-C₃N₄ composite for photocatalytic applications: regeneration of NADH/NADPH and oxidation of sulfide to sulfoxide. *Cat Sci Technol.* 2021;7:313-534. doi:10.1039/D1CY00991E
36. Etacheri VK, Valentin CD, Schneider J, Bahnemann D, Pillai SC. Visible-light activation of TiO₂ photocatalysts: advances in theory and experiments. *J Photochem. Photobiol. C* 2015;25:1-29. doi:10.1016/j.jphotochemrev.2015.08.003

How to cite this article: Siddique R, Yadav RK, Singh S, et al. Photocatalytic oxygenation of sulfide using solar light and ingenious QDs@AQ catalyst: Mechanistic and synthetic investigations. *Photochem Photobiol.* 2023;00:1-8. doi:10.1111/php.13859