Promoting Spatial Charge Transfer of ZrO$_2$ Nanoparticles: Embedded on Layered MoS$_2$/g-C$_3$N$_4$ Nanocomposites for Visible-Light-Induced Photocatalytic Removal of Tetracycline

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ABSTRACT: Photocatalytic degradation is a sustainable technique for reducing the environmental hazards created by the overuse of antibiotics in the food and pharmaceutical industries. Herein, a layer of MoS$_2$/g-C$_3$N$_4$ nanocomposite is introduced to zirconium oxide (ZrO$_2$) nanoparticles to form a “particle-embedded-layered” structure. Thus, a narrow band gap (2.8 eV) starts developing, deliberated as a core photodegradation component. Under optimization, a high photocatalytic activity of 20 mg/L TC at pH 3 with ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite was achieved with 94.8% photocatalytic degradation in 90 min. A photocatalytic degradation rate constant of 0.0230 min$^{-1}$ is determined, which is 2.3 times greater than the rate constant for bare ZrO$_2$ NPs. The superior photocatalytic activity of ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ is due to the dual charge-transfer channel between the MoS$_2$/g-C$_3$N$_4$ and ZrO$_2$ nanoparticles, which promotes the formation of photogenerated $e^-$/h$^+$ pairs. Charge recombination produces many free electron–hole pairs, which aid photocatalyst reactions by producing superoxide and hydroxyl radicals via electron–hole pair generation. The possible mechanistic routes for TC were investigated in-depth, as pointed out by the liquid chromatography–mass spectrometry (LC–MS) investigation. Overall, this work shows that photocatalysis is a feasible sorbent approach for environmental antibiotic wastewater treatment.

1. INTRODUCTION

In the past decade, antibiotics- and antiphlogistics-related pharmaceutical wastewater pollution has posed a hazard to human health and the environment. Tetracycline (TC) hydrochloride, a type of TC in general antibiotics, is mainly used in medicine, agriculture, and other fields, and it remains in the soil and groundwater. Improvements in TC can lead to the proliferation of drug-resistant microbes if they are exploited.$^{1-3}$ Currently, many techniques have been developed for the removal of antibiotics from water environments, the most notable of which are photo-Fenton treatment and biological treatments such as ozonation and membrane filtration. Other techniques include electrochemical oxidation, semiconductor photocatalysis, and adsorption.$^{4-6}$ Parallel to these classic technologies, semiconductor photocatalysis has gained significant attention in the field of antibiotic degradation due to its high efficiency and long-term sustainability, which is achieved through the use of solar light and ecologically favorable circumstances. Besides that, it can efficiently digest antibiotics and convert them into readily biodegradable composites with fewer harmful organic or inorganic compounds, diminishing or eliminating their antimicrobial effectiveness. It may be able to alleviate some of the issues associated with some orthodox techniques of antibiotic degradation, such as the problematic biodegradability of antibiotics and the possibility of secondary contamination caused by the intermediates.$^{7-10}$

The most often utilized and investigated materials in heterogeneous photocatalysis are transition-metal oxides and wide-band semiconductors, such as TiO$_2$, SnO$_2$, CeO$_2$, and ZrO$_2$. In particular, the remarkable physicochemical stability of ZrO$_2$ and the unique electronic energy band structure of this photocatalyst have piqued the curiosity of a large number of researchers. Because of their large band gap (>5 eV), ZrO$_2$ photocatalysts can only absorb ultraviolet light, which represents a small percentage of the solar spectrum (less than 5%). As a result, the photocatalytic activity of ZrO$_2$ is limited in its functional application as a photocatalyst. Apart
from that, the poor separation rate between the charged particles generated by photons in ZrO$_2$ restricts the photocatalytic degradation activity of the nanomaterial.$^{11}$ Among the several approaches for overcoming the enhancing light-harvesting and recombination of photogenerated carriers, coupling ZrO$_2$ with another narrow-band-gap semiconductor, for example, TiO$_2$, TiO$_2$−ZrO$_2$, g-C$_3$N$_4$, MoS$_2$, etc.$^{12-14}$ Two-dimensional (2D) layered semiconductors hold several remarkable characteristics, including rapid charge-carrier detachment, electronic conduction, and a vast surface area. It has been discovered that g-C$_3$N$_4$, a nonmetallic polymeric nanomaterial with optimal band-edge position (1.32 V, pH = 7) and a low band gap (2.8 eV), features moderate van der Waals forces between layers and low hydrogen-bonding connectivity bordered by polymeric melon units but strong covalent C−N bonds inside the melon units.$^{15}$ g-C$_3$N$_4$ nanosheets can also help create nanocomposites with rich coupling heterointerfaces and surface-reactive positions. Studies on creating heterojunctions, including g-C$_3$N$_4$/MoS$_2$,$^{16}$ TiOF$_2$/g-C$_3$N$_4$,$^{17}$ MoS$_2$/g-C$_3$N$_4$/Bi$_2$O$_3$Cl$_10$,$^{18}$ and CsPbI$_3$/g-C$_3$N$_4$,$^{19}$ with the goal of overcoming the inherent disadvantages of g-C$_3$N$_4$, were conducted in-depth. This scheme reveals superior visible-light photoinduced activity in the direction of degradation compared to the solitary components.

Individual sandwiched S−Mo−S layers in molybdenum disulphide (MoS$_2$) are intrinsic n-type photocatalysts with a narrow band gap (1.29−1.94 eV) and an anisotropic lamellar structure with weak van der Waals interactions between them. Molybdenum disulphide (MoS$_2$) is a high-productivity cocatalyst for photocatalytic degradation due to the survival of unsaturated Mo and S atoms at the exposed edges, which are capable of encoring photocatalytic degradation. It also enhances visible-light absorption and minimizes reflection, allowing more free charge-transfer carriers for photocatalytic degradation.$^{20,21}$ The layered structures of MoS$_2$ and g-C$_3$N$_4$ help reduce lattice disparity and help form an electronic field at the interface of a 2D−2D nanocomposite, which aids in promoting charge separation and surface reactions. Thus, the nanocomposite charge separation and photoactivity degradation of the intended ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ nanocomposite should be significantly enhanced.

In this work, as mentioned above, a feasible ultrasonic chemical technique was used for the fabrication of ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ nanocomposites. Here, the ZrO$_2$ nanoparticles (NPs) were embedded on the surface of 2D layered MoS$_2$/g-C$_3$N$_4$ nanosheets (NSs). The band alignment of the composite was improved by employing a continuous multistep charge-carrier (e$^-$/h$^+$) transfer path rather than the standard one-step process. This study investigates the photocatalytic degradation of TC over ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ using visible light. A minimum energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) exists due to the delocalized π link between the TC molecule and its connection to the −OH group, leading to the high availability for visible-light absorption. The TC’s π orbital may also create an electronic interaction with the 3d orbital of Zr$^{4+}$, leading to a surface complex between TC and ZrO$_2$. It is expected that visible-light irradiation will cause photoexcitation of the surface complex. The primary goals of this work are to confirm the presence of visible-light photodegradation of TC on ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ and estimate the mechanism of photodegradation. Dependence on the ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ nanocomposite, strong interface effects, relatively short charge-diffusion distance, and numerous close contact interfaces can be obtained simultaneously. The possible mechanistic routes for TC were investigated in-depth, as indicated by LC−MS analysis on the ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ nanocomposites.

2. RESULTS AND DISCUSSION

XRD patterns of the as-synthesized products were obtained to confirm the crystal structure and the phase purity. As shown in Figure 1a,b, bare ZrO$_2$ can be coded for tetragonal (JCPDS card 79-1769); its fundamental diffraction patterns at 28.2, 31.5, 34.1, 35.3, 40.7, 50.1, and 55.3° can be assigned to (011), (111), (002), (211), (202), (013), and (131) planes, respectively. The firm and spire diffraction peaks of ZrO$_2$ confirm the high purity and crystallinity of the sample.$^{22,23}$ The primary peaks of bare g-C$_3$N$_4$ are located at 13.1 and 27.4°, respectively, and correspond to the crystal planes (100) and (002).$^{24}$ It has been observed that there are no distinctive peaks of g-C$_3$N$_4$ and MoS$_2$ in the ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ nanocomposite (Figure 5a,b) even though these peaks can be seen in the transmission electron microscopy (TEM) pictures. According to the results obtained for blank MoS$_2$, the

![Figure 1. XRD patterns of (a) ZrO$_2$, ZrO$_2$/g-C$_3$N$_4$, ZrO$_2$/MoS$_2$/g-C$_3$N$_4$ and (b) MoS$_2$, g-C$_3$N$_4$, MoS$_2$/g-C$_3$N$_4$ nanocomposites.](https://doi.org/10.1021/acsomega.1c06089)
sequences of the diffraction pattern situated at 14.2, 33.2, and 58.9° are ascribable to the diffractions of (002), (100), and (110), corresponding to the usual hexagonal MoS2 structure (JCPDS card 37-1492). Remarkably, the addition of g-C3N4 and MoS2 had no adverse influence on the structure and purity of ZrO2 nanoparticles. However, the intensity of deflection points of ZrO2@MoS2/g-C3N4 is weaker and broader than that of pure ZrO2 due to the low crystallinity and the tiny crystallite size of the ZrO2 nanoparticles.

FT-IR analysis was performed to investigate the surface chemical structure of as-prepared materials. As shown in Figure 2, all of the as-prepared ZrO2, ZrO2@g-C3N4, and ZrO2@MoS2@g-C3N4 nanocomposites retain not only the surface chemical structure of the ZrO2 nanoparticles but also the structure of the g-C3N4 semiconductor. These −NH2 stretching vibrations are responsible for the wide absorption bands in the 3178 cm⁻¹ range. The peaks show the stretching vibration of C–N at 1243 and 1404 cm⁻¹. The peak at 806 cm⁻¹ corresponds to tri-s-triazine stretching vibrations. The bands at 807 and 87 cm⁻¹ as well as 780 cm⁻¹ correspond to the stretching vibration of the Zr–O bond.

Using HR-SEM, the surface morphologies and structural characteristics of ZrO2, g-C3N4, MoS2, and ZrO2@MoS2/g-C3N4 nanocomposite were studied. Figure 3a depicts the irregular spherical nanoparticles of ZrO2 with an average diameter of 15 nm, resulting in a large surface area of 43.2 m² g⁻¹. Due to its unique spherical structure, g-C3N4 has a small surface area of 13.5 m² g⁻¹ compared to pure ZrO2. A shape-free architecture is illustrated in Figure 3b, which has a smooth surface and is in the shape of a platelike structure composed of g-C3N4. It also reveals the strong interaction between the two ZrO2 and g-C3N4 semiconductors. Figure 3c clearly illustrates that pure MoS2 displays a hierarchical-like sheet with adjacent sizes of a limited micrometer and was piled sequentially. As shown in Figure 3d, the ZrO2@MoS2@g-C3N4 structure is not smooth and has grooves because this pattern is formed when ZrO2 nanoparticles are embedded, and more active sites and higher light absorption capacity might be obtained with a product including dispersed nanoparticles, which would be helpful to the formation of reactive free radicals. Figure 4a–f shows evenly distributed Zr, O, C, N, Mo, and S in ZrO2@MoS2@g-C3N4 with a “particle-embedded-layered” structure, demonstrating that the nanocomposite of ZrO2@MoS2@g-C3N4 was successfully constructed. The results are in line with the HR-SEM analysis.

The impact of inserting a 2D cocatalyst layered on recognition of nanocomposite creation using ZrO2 nano-
particles is established by HR-TEM scrutiny in Figure 5. The MoS$_2$/g-C$_3$N$_4$ sheet in Figure 5a,b is embedded with ZrO$_2$ nanoparticles with a regular diameter of 15 nm. The formation of spherical-shaped ZrO$_2$ nanoparticles was confirmed by SAED analysis (Figure 5c). The XRD data show that the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite exhibits good crystallinity, and HR-TEM confirms the tetragonal structure of ZrO$_2$ nanoparticles (101) (JCPDS no. 79-1769), which can be seen in Figure 5d. To define a single-phase growth, the lattice fringes show interplanar spacings ("d" values) of 0.35, 0.32, and 0.62 nm, which correspond to tetragonal ZrO$_2$ (101), g-C$_3$N$_4$, and MoS$_2$ (002) planes, respectively$^{29-32}$; therefore, the evidence presented above suggests that the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite has formed.

The XPS analysis presented in Figure 6 reveals changes in the chemical composition and surface electronic interaction of Zr, O, C, N, Mo, and S components in the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite. As shown in Figure 6a, the Zr 3d$_{3/2}$ and
Zr 3d$_{3/2}$ diffraction peaks in the bare ZrO$_2$ sample appeared to be at 181.9 and 184.3 eV, respectively.$^{33}$ ZrO$_2$ nanoparticles were found to have Zr–O–Zr and Zr–O–H bonding, as shown by their O 1s diffraction values of 529.6 and 531.3 eV, respectively, in Figure 6b.$^{34}$ According to Figure 6c, the electronic states of graphite-like sp$^2$ (C–C) and sp$^3$ (N=C=N) in the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite are denoted by the C 1s deflection patterns at 284.8 and 288.2 eV, respectively, whereas the diffraction patterns at 286.4 eV mimicked a tiny amount of C–O.$^{35,36}$ In the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite, the N 1s diffraction peaks at pyridinic N (398.6 eV), pyrrolic N (399.5 eV), and graphitic N (401.0 eV)

Figure 6. XPS spectra of the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite. (a) Zr 3d, (b) O 1s, (c) C 1s, (d) N 1s, (e) Mo 3d, and (f) S 2p (g) survey profiles and panels.
correlate to the (C$\equiv$N$\equiv$C), (N$\equiv$(C)$\equiv$3), and N$\equiv$H bondings, respectively, as shown in Figure 6d. Among the prominent peaks are Mo 3d$_{3/2}$ (232.4 eV) and Mo 3d$_{5/2}$ (235.7 eV), corresponding to the Mo$^{4+}$ and S 1s states in MoS$_2$, respectively. As shown in Figure 6e,f, the formation of tiny amounts of Mo oxides with an adsorbed oxygen molecule results in a higher binding energy pattern (235.7 eV), which is apparent. However, as shown by XRD, there is no oxide phase in Mo, which does not affect the photocatalytic activity of the ZrO$_2@$MoS$_2$/g-C$_3$N$_4$ nanocomposite. According to Figure 6g, the overall element profile in the ZrO$_2@$MoS$_2$/g-C$_3$N$_4$ nanocomposite is as follows. A considerable amount of interaction between the MoS$_2$/g-C$_3$N$_4$ and the MoS$_2$ would result in this instance. ZrO$_2$ also affected the interfacial contact and charge transport of the material, resulting in the C$\equiv$N pattern in g-C$_3$N$_4$ shifting to a higher binding energy in composites such as MoS$_2$/g-C$_3$N$_4$ and ZrO$_2@$MoS$_2$/g-C$_3$N$_4$. ZrO$_2$ is morphologically restricted, and the addition of MoS$_2$/g-C$_3$N$_4$ prevents the object’s interface communication and charge transfer, altering XPS peaks in the Zr 3d and O 1s spectra. The Zr/O, C/N, and Mo/S ratios of the ZrO$_2@$MoS$_2$/g-C$_3$N$_4$ nanocomposite are shown in the atomic ratio analysis in Table 1.

### Table 1. Atomic Ratios of Zr, O, C, N, Mo, and S Derived from the XPS Data of ZrO$_2@$MoS$_2$/g-C$_3$N$_4$

| element | Zr [atom %] | O [atom %] | C [atom %] | N [atom %] | Mo [atom %] | S [atom %] |
|---------|------------|------------|------------|------------|-------------|------------|
| ZrO$_2@$MoS$_2$/g-C$_3$N$_4$ | 3.21       | 36.12      | 29.13      | 31.17      | 0.13        | 0.24       |

Figure 7. (a) N$_2$ adsorption–desorption isotherms and (b) pore size distribution curves of ZrO$_2$ and ZrO$_2@$MoS$_2$/g-C$_3$N$_4$ nanocomposites.

Figure 8. (a) UV–vis DRS spectra of ZrO$_2$, g-C$_3$N$_4$, MoS$_2$, MoS$_2$/g-C$_3$N$_4$, ZrO$_2@$g-C$_3$N$_4$, and ZrO$_2@$MoS$_2$/g-C$_3$N$_4$ nanocomposites, and (b–d) corresponding Tauc plots of ZrO$_2$, ZrO$_2@$g-C$_3$N$_4$, and ZrO$_2@$MoS$_2$/g-C$_3$N$_4$ nanocomposites.
It is seen that the surface area ($S_{BET}$) of the photocatalyst is essential for determining the number of active sites and the charge-carrier transit distance. Figure 7a,b depicts the isotopes of the nitrogen absorption−desorption and hole size distribution curves of ZrO$_2$ and ZrO$_2$@MoS$_2$/g-C$_3$N$_4$. The ZrO$_2$ sample exhibits the H$_2$-type hysteresis loop with type IV isotherms ($P/P_0 = 0.85–1.0$), which confirms the constant size of the nanoparticles with a mesopore phase morphology. As shown in Figure 7a, the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite shows type IV and H$_2$ hysteresis loops. Two specimens demonstrated the presence of mesopores. According to the BET approach, the $S_{BET}$ values of ZrO$_2$ and ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ are 43.2 and 56.7 m$^2$ g$^{-1}$, respectively. The surface area of the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite is higher than that of ZrO$_2$. To enhance the photocatalytic activity, the wide surface area of the sample provides a sizeable active site for light absorption, contaminant absorption, and photodegradation. The pore size distribution of ZrO$_2$ nanoparticles is 15 nm, while that of the composite ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ is in the 10 nm range, with larger mesopores (Figure 7b). The porous MoS$_2$/g-C$_3$N$_4$ not only served as a supporter but also prevented the ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite from reaggregating as a result of the improved more extensive nitrogen acceptance and $S_{BET}$ of 56.7 m$^2$ g$^{-1}$, which was beneficial because the composite sample’s surface will absorb more visible light, thereby increasing the photocatalytic efficiency by providing more active sites.

To investigate the optical absorbance nature of ZrO$_2$ g-C$_3$N$_4$, MoS$_2$, MoS$_2$/g-C$_3$N$_4$, ZrO$_2@g-C_3N_4$, and the nanocomposite ZrO$_2$@MoS$_2$/g-C$_3$N$_4$, UV−vis diffuse reflectance spectra were obtained (Figure 8a). In the visible range, g-C$_3$N$_4$ has an absorption onset in the visible 460 nm, while bare ZrO$_2$ is absorbed in the UV radiation wavelength range (absorption starts at 275 nm). As expected, the absorption onset of ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ occurs between its constituents at ~490 nm. Additionally, the band gap of ZrO$_2$ (4.88 eV) is in agreement with the reported literature. The addition of MoS$_2$/g-C$_3$N$_4$ resulted in a modest modification in the Tauc plots, as illustrated in Figure 8b−d. As a result of the shift in absorbance edges for the nanocomposite structure, the band gaps for ZrO$_2@g-C_3N_4$ and ZrO$_2@MoS_2@g-C_3N_4$ are 2.82 and 2.8 eV, respectively. The fact that such a modest change in band spacing supports the g-C$_3$N$_4$ and MoS$_2$ sheet production with tight interface contact indicates the presence of ZrO$_2$ nanoparticles and nanocomposite synthesis. Theoretically, the nanosize composite has a larger contact interface area, which allows for a faster charging carrier transit and, as a result, suppresses charge recombination, resulting in increased photocatalytic degradation efficiency.

The photoluminescence spectra were primarily conducted to evaluate the charge transfer and separation behaviors to analyze the starting point of the enhanced photocatalytic activity. Figure 9a shows that, under 325 nm laser stimulation, pure g-C$_3$N$_4$ exhibits an exceptionally bright photoluminescence pattern with the emission wavelength centered at about 460 nm, which can be attributed to its fast charge recombination. The EIS Nyquist plot provides an additional context for exploring spatial charge-transfer assets. The lower the charge-transfer resistance in the broad spectrum, the smaller the semicircle diameter of the EIS Nyquist plot as the spectrum narrows. Following Figure 9b, the relative arc
diameters of the samples can be organized in the following ways: ZrO₂ > ZrO₂@g-C₃N₄ > MoS₂@g-C₃N₄ > ZrO₂@MoS₂@g-C₃N₄, indicating that the nanocomposite interaction between ZrO₂ and MoS₂@g-C₃N₄ will result in the realization of a rapid and effective spatial charge separation process. The above analysis reveals that a more significant number of electrons and holes are used in the photocatalytic process in the ZrO₂@MoS₂@g-C₃N₄ nanocomposite-based reaction compared to the conventional reaction. As illustrated in Figure 9c, transient photocurrent measurements of ZrO₂@MoS₂@g-C₃N₄ reveal a higher photocurrent density than that of pure ZrO₂, indicating a very effective separation of photoexcited charges (electron−hole pairs) and restriction of their recombination. Several repeats of cycles display a similar photocurrent reaction. Significantly, it can be seen that the samples have high photostability.47

The recycle productivity of ZrO₂@MoS₂@g-C₃N₄ was examined by recovering the photocatalyst, and the results are given in Figure 10a. The degradation percentages were 94.8 and 92%, respectively, when compared to the first two recycling cycles. Photocatalytic efficiencies decreased to 91 and 90.1% for the third and fourth recycling cycles, respectively. Until the photocatalyst was used in the fourth cycle, there was little change in the degradation percentage. The absorption of the TC solution on the surface of the photocatalyst may be responsible for the slight divergence in the photodegradation during the recycling experiment. The photocatalytic process is carried out in various sacrificial agents using a ZrO₂@MoS₂@g-C₃N₄ catalyst to identify the active species that participate in TC degradation and remove specific reactive species. Continuous radical scavenging studies are being performed to evaluate the mechanism of ZrO₂@MoS₂@g-C₃N₄ for TC degradation. In the tests, BQ, triethanolamine (TEOA), and isopropanol (IPA) were used as *O₂−, h+, and *OH scavengers, respectively. As illustrated in Figure 10b, the TC degradation efficiency of the ZrO₂@MoS₂@g-C₃N₄ nanocomposite is significantly suppressed in the presence of BQ (30%), which shows the primary quencher of hydroxyl (e−) species in the degradation reaction, compared to a hole (h+) and electron (e−) scavenger. From the absorbed oxygen molecule, photogenerated electrons (e−) form •O₂− radicals, and •OH species form from the hole (h+) in the aqueous solution. In the optimal ZrO₂@MoS₂@g-C₃N₄ nanocomposite [TC = 20 mg/L at pH 3], the TOC technique was used to evaluate TC mineralization. Figure 10c shows that the TC mineralization efficiency was 71%, and the photocatalytic efficiency was 94.7% under 90 min of radiation. These results indicated that the ZrO₂@MoS₂@g-C₃N₄ nanocomposite presents the highest mineralization ability in the TC degradation process.48

The photocatalytic degradation activity of all prepared photocatalysts is determined by monitoring the decomposition of TC in an aquatic solution under visible-light illumination, as illustrated in Figure 11. The primary blank test demonstrated that no degradation could be identified in the absence of light, indicating that the photocatalyst was the main reason for the degradation. The minor decrease in the TC content of ∼4% is due to adsorption in the blank condition. After 90 min, the photocatalytic activity of ZrO₂@MoS₂@g-C₃N₄ is the highest among them, and the degradation rate of TC when using this compound reaches 94.8%. When compared to other photocatalysts, the composite material ZrO₂@MoS₂@g-C₃N₄ was more efficient than ZrO₂, g-C₃N₄, ZrO₂@g-C₃N₄, and MoS₂@g-C₃N₄. The percentages of TC degradation for photocatalysts

![Figure 10. (a) Recycle efficiency of the ZrO₂@MoS₂@g-C₃N₄ photocatalyst for four cycles. (b) Percentage of the photocatalytic degradation of TC with ZrO₂@MoS₂@g-C₃N₄ in the presence of different scavengers (TC conc.: 20 mg/L; ZrO₂@MoS₂@g-C₃N₄ 50 mg; TEOA: (1.6 × 10⁻⁴ mol L⁻¹) in 100 mL/BQ− (4.0 × 10⁻⁴ mol L⁻¹) 100 mL/IPA − (1.0 × 10⁻³ mol L⁻¹) in 100 mL, irradiation time: 90 min). (c) TOC mineralization efficiency for TC of the ZrO₂@MoS₂@g-C₃N₄ catalyst.](https://doi.org/10.1021/acsomega.1c06089)
ZrO$_2$, g-C$_3$N$_4$, ZrO$_2$@g-C$_3$N$_4$, MoS$_2$/g-C$_3$N$_4$, and ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ are 41.9, 68.6, 79.3, 86.9, and 94.8% under visible-light irradiation in 90 min, respectively, as shown in Figure 11a. To determine the optimal dose of ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ in TC degradation, various weight ratios, including 30, 40, 50, and 60 mg of photocatalyst, were used for photocatalytic degradation and examined under comparable test circumstances, as shown in Figure 11b. When comparing the various weight ratios of ZrO$_2$@MoS$_2$/g-C$_3$N$_4$, the photodegradation efficiencies of the various weight ratios were 44.6, 59.4, 94.8, and 74.4%, corresponding to the 30, 40, 50, and 60 mg weight ratios. Increasing the photocatalyst volume enhances the absorption, but increased photocatalyst density accelerates the TC degradation. Under these test conditions, it is reported that 50 mg/100 mL of photocatalyst is the most efficient and optimal for the effective degradation of TC when exposed to visible-light irradiation for 90 min. With an increase in the photocatalyst concentration, the TC degradation rate increases to 50 mg/100 mL, and an increase in the photocatalyst concentration further reduces the degradation rate. When photocatalyst particles are present in quantities more than 60 mg/100 mL (50 mg/100 mL), the dispersion of light by the particles slows down the rate of degradation. The ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ nanocomposite dose and photocatalyst concentrations in Figure 11c,d show the photodegradation kinetics of TC. The pseudo-first-order rate constants are 0.0035, 0.0083, 0.0122, 0.0145, and 0.0230 min$^{-1}$ (in Figure 11e) for ZrO$_2$, g-C$_3$N$_4$, ZrO$_2$@g-C$_3$N$_4$, MoS$_2$/g-C$_3$N$_4$, and ZrO$_2$@MoS$_2$/g-C$_3$N$_4$, respectively. The photocatalyst weights of 30, 40, 50, and 60 mg are represented by the kinetic rate constant values of 0.0060, 0.0084, 0.0236, and 0.0140 min$^{-1}$, respectively. Photocatalytic degradation occurs best under conditions of visible-light illumination, as measured by kinetic rate constants. The determined values are 0.0230 min$^{-1}$ for the composite material and 0.0236 min$^{-1}$ for 50 mg of the photocatalyst. According to Figure 11f, the

Figure 11. Photocatalytic degradation of TC under different conditions: (a) different catalysts (catalysts: 50 mg; TC: 20 mg/L), (b) different dosages of ZrO$_2$@MoS$_2$/g-C$_3$N$_4$ [TC conc.: 20 mg/L], (c) pseudo-first-order kinetic plots of ln($C_0/C$) vs time for different catalysts and (d) different dosages of ZrO$_2$@MoS$_2$/g-C$_3$N$_4$, (e) kinetic constants of different catalysts (TC: 20 mg/L; catalyst dose = 50 mg), and (f) absorbance spectrum (TC: 20 mg/L; catalyst dose = 50 mg).

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absorption band’s intensity reduces in the presence of the ZrO2@MoS2/g-C3N4 catalyst with the intensity of the absorption band decreasing in proportion to the time of visible-light irradiation. The UV absorption at 357 nm decreases over time due to the decay of TC. The effect of different TC concentrations (10, 20, 30, and 40 mg/L TC) on the photocatalytic degradation of TC was studied to establish the optimal state of the catalyst utilized. TC degradation increases from 55.9, 93.8, 69.6, and 79.3%, respectively. Because of the homogeneity of the catalyst and the challenge of light that enters the catalyst surface, the photocatalytic degradation reduces as the TC concentration increases to 40 mg/L. Figure 12a illustrates this phenomenon. When a starting TC concentration of 20 mg/L was used, the photodegradation of TC by ZrO2@MoS2/g-C3N4 was studied at different pH values of 3, 5, 7, and 9, and the degradation percentage is shown in Figure 12b. It takes 90 min of visible-light illumination to significantly reduce the TC degradation percentages to 93.8, 88.3, 70.1, and 60.5% at pH levels of 3, 5, 7, and 9, respectively. The best performance is for TC degradation at pH levels 3 and 5. According to previous reports, TC is amphoteric, with pK_a values of 3.4, 7.7, 9.8, and 12. It is primarily in the neutralized form TC0 from pH 3.4−7.7 and the deprotonated form TC− at pH 7.7−12. The charge intensity of TC increased with pH increasing, resulting in a more intense species attack against molecules. The kinetic curves in Figure 12c,d were used to derive the rate constants for various TC concentrations. Parameters 10, 20, 30, and 40 mg/L TC and pH 3, 5, 7, and 9 are mimicked by pseudo-first-order rate constants of 0.0191, 0.0263, 0.0131, and 0.0179 min^{-1}. The maximal operating rates for maximum decay were 0.0263 and 0.0238 min^{-1} at 20 mg/L and pH 3, respectively.

Table 2. Comparison of Photocatalytic Efficiencies of TC Degradation for Different Photocatalysts

| photocatalyst       | C_{catalyst} dose (mg) | C_{TC} conc. (mg/L) | light source (Xe lamp, W) | kinetic constant (min^{-1}) | degradation (%) (time) | ref |
|---------------------|-----------------------|---------------------|---------------------------|-----------------------------|------------------------|-----|
| Fe3O4@BiOCl/BiVO4   | 50                    | 20 (100 mL)         | 300 (λ > 420 nm)          | 0.0263                      | 87 (90 min)            | 2   |
| SiO2-Fe2O3@TiO2     | 10                    | 10 (50 mL)          | 300 (λ > 420 nm)          | 0.0474                      | 90.6 (60 min)          | 16  |
| g-C3N4/ZrO2         | 2                     | 10 (5 mL)           | 300 (λ > 420 nm)          | 0.0203                      | 85.2 (90 min)          | 20  |
| MoS2/B-rGO          | 20                    | 40 (100 mL)         | 300 (λ > 420 nm)          | 0.4286                      | 93 (180 min)           | 33  |
| Au/Pt@g-C3N4        | 100                   | 20 (100 mL)         | 500 (λ > 420 nm)          | 0.0108                      | 72.2 (120 min)         | 61  |
| WO3@g-C3N4          | 50                    | 25 (100 mL)         | 300 (λ > 420 nm)          | 0.0096                      | 76.2 (150 min)         | 62  |
| g-C3N4/Nb2O5        | 100                   | 20 (100 mL)         | 250 (λ > 420 nm)          | 0.0122                      | 91.2 (180 min)         | 63  |
| Bi/α-Bi2O3@g-C3N4   | 50                    | 10 (50 mL)          | 300 (λ > 400 nm)          | 0.0205                      | 91.6 (120 min)         | 64  |
| BiO1/g-C3N4/Co3O5   | 50                    | 20 (30 mL)          | 300 (λ > 420 nm)          | 0.0302                      | 94.8 (90 min)          | this work |

Figure 12. Photocatalytic degradation of TC under different concentrations: (a) different TC concentrations (catalyst dose = 50 mg), (b) different pH conditions of TC in the presence of ZrO2@MoS2/g-C3N4 (c) first-order kinetic plots of ln(C_0/C) vs time for different concentrations, and (d) different pH of TC in the presence of ZrO2@MoS2/g-C3N4 (TC: 20 mg/L; catalyst dose = 50 mg).

Table 2. Comparison of Photocatalytic Efficiencies of TC Degradation for Different Photocatalysts
Table 2 lists some statistics to compare with other early reports on photodegradation of TC by composite photocatalysts.

The presence of the ZrO₂@MoS₂/g-C₃N₄ nanocomposite degraded the TC in around 90 min, as analyzed by liquid chromatography−mass spectrometry (LC−MS). LC−MS analysis clarified the photodegradation pathway of TC. The uniform mass spectrum obtained after 90 min of reaction with TCs and the resulting mass spectra are shown in Figure 13. Figure 13 shows that TC was reduced to 10 primary photointermediate pathways (I and II), which are denoted as P₁−P₁₀ in the direction of the maintenance period. Additionally, based on the positive m/z ratios discovered and the findings of previous studies, the structural and chemical formulae of restricted byproducts were established, as shown in Figure 13. In addition, a possible photodegradation route was proposed, as revealed in Figure 14. The N-demethylation of TC resulted in the production of Pathway and an intermediate of P₁ with an m/z of 415 (m + 1)⁺. Further photodegradation led to product P₂, which was formed due to the loss of the formamide group and subsequent oxidation, resulting in the construction of the resulting hydroxyl structure. Due to the low C−N binding energy, the carboatomic ring disintegrates. In other words, they can be attributed to the development of product P₂ (m/z 195.10) (m + 1)⁺. Meanwhile, due to the low binding energy of the carbonyl and hydroxyl groups, the carbonyl and hydroxyl groups were removed. As shown in Figure 14, active groups were removed further, resulting in product P₃ (m/z 145.25) (m − 1)⁺. In pathway II, the radicals may initially react with the C=O of TC, resulting in a composite fabrication with an m/z value of P₄ 386.80 (m − 2)⁺. In one photodegradation pathway, additional confronting of free radicals results in the cleavage of the aromatic ring at C=C, which produces the combinations with m/z values of P₇ 316.50, P₈ 209.10 (m + 1)⁺, P₉ 177.10 (m + 1)⁺, and P₁₀ 106.25. Finally, the fragments of this photointermediate were degraded to form CO₂, NH₄⁺, and H₂O.

In a subsequent investigation, the variation of radical species in the photocatalytic mechanism of photodegradation of TC on the catalyst occurring is shown in Figure 15. However, the radical trapping experiments discussed above proved the existence of the element O₂⁻ in the first place. As a result, OH does not participate as an active species. Due to the high probability of O₂/**O₂⁻**, the CBM values of ZrO₂ and g-C₃N₄ are greater than those of O₂. Therefore, O₂ can condense to **O₂⁻**, and the TC is impaired due to the substantial reduction of **O₂⁻** in the atmosphere. Because of the photoinduced VB to CB electron transition in MoS₂/g-C₃N₄, holes appear in the VBM of semiconductors in the ZrO₂@MoS₂/g-C₃N₄ system when exposed to visible light. As a result of the change in the CBM capacity, the photoinduced electrons on the surface of MoS₂/g-C₃N₄ migrate to the CB of ZrO₂, but the holes on the surface of MoS₂/g-C₃N₄ remain on the surface as a result of the change in the CBM capacity. Specifically, when it comes to ZrO₂, the restricted band energy is high, and visible light is insufficient to attract electrons from their current valence band to their current conduction band. The absorption of visible light by g-C₃N₄ allows it to produce the 𝜋−𝜋* transition and transfer the excited-state electrons from the VB
to the CB. Therefore, electrons transferred from g-C₃N₄ to the ZrO₂ conduction band will not be a barrier to the VB when they enter the bar because it is either a type II charge transfer or a type I charge transfer. The scheme can effectively develop the charge separation of photoinduced electron−hole pairs, thereby significantly reducing the chance of e⁻/h⁺ pair recombination. The ZrO₂@MoS₂/g-C₃N₄ nanocomposite exhibits a superior photocatalytic activity because the scheme can effectively develop the charge separation of photoinduced electron−hole pairs, thereby significantly reducing the chance of e⁻/h⁺ pair recombination. In the ZrO₂@MoS₂/g-C₃N₄ mechanism, the overhead photoluminescence and EIS, electron−hole pair recombination, and photocatalytic efficiency all indicate that the recombination of electron−hole pairs has been curtailed, and the straight oxidation capability of holes has been dramatically increased, resulting in the presence of both h⁺ and •O₂⁻ as active species in the ZrO₂@MoS₂/g-C₃N₄ nanocomposite. According to the mechanism (Figure 15), the contact between MoS₂/g-C₃N₄ and ZrO₂ influences the electron−hole pair separation efficiency. Due to the high

Figure 14. Proposed possible degradation pathway and primary intermediate photoproducts of TC in the ZrO₂@MoS₂/g-C₃N₄ nanocomposite with the combined photocatalytic system.
Quantities of ZrO₂, the contact size is reduced, boosting the separation efficiency and photocatalytic efficiency. As a result, MoS₂/g-C₃N₄ is the most effective cocatalyst in the ZrO₂@MoS₂/g-C₃N₄ nanocomposite for photocatalysts in the degradation of TC.

\[
\begin{align*}
\text{MoS₂/g-C₃N₄} & \rightarrow \text{MoS₂/g-C₃N₄(e⁻ + hν⁺)} \quad \text{(1)} \\
\text{MoS₂/g-C₃N₄(e⁻ + hν⁺)} & \rightarrow \text{ZrO₂(e⁻) + MoS₂/g-C₃N₄(hν⁺)} \quad \text{(2)} \\
\text{oxygen molecule (O₂)} + e⁻ & \rightarrow \cdot\text{O₂}⁻ \quad \text{(3)} \\
\cdot\text{O₂}⁻/h⁺ + \text{TC} & \rightarrow \text{intermediates + degradation products} \quad \text{(4)}
\end{align*}
\]

### 3. CONCLUSIONS

In summary, ZrO₂ nanoparticles are embedded in a layered MoS₂/g-C₃N₄ composite to form a “particle-embedded-layered” structure via a feasible ultrasonic chemical method. Under visible-light irradiation, the ZrO₂@MoS₂/g-C₃N₄ nanocomposite has proven to be a viable photocatalyst for tetracycline (TC) degradation. With an apparent kinetic rate constant \( \kappa \) of 0.0230 min⁻¹, the photocatalytic degradation efficiency of TC over ZrO₂@MoS₂/g-C₃N₄ was determined to be around 94.8% in 90 min. The dual charge-transfer channel between the layers of MoS₂/g-C₃N₄ and ZrO₂ nanoparticles is the reason for the superior photocatalytic activity of ZrO₂@MoS₂/g-C₃N₄. It promotes the formation of photoinduced charge carriers while also reducing photoinduced charge recombination, resulting in more free charge carriers available to aid photocatalytic reactions via the production of the \( \cdot\text{O₂}⁻ \) radical. To account for the removal of the tetracycline from the aqueous solution, the LC–MS measurements for the reaction...
intermediates, the reaction pathway, and the mechanism were also carried out. As a result, these photocatalysts may also provide feasible and long-term solutions to the environmental issues that antibiotic-polluted effluents cause.

4. EXPERIMENTAL SECTION

4.1. Synthesis of ZrO2 NPs. About 2.5 mmol of ZrOCl2·8H2O was ultrasonically scattered in 70 mL of deionized water. The ammonia solution was gradually added with vigorous stirring while maintaining a pH between 10 and 11. The sediments above were transferred to a Telfon-lined stainless-steel autoclave and warmed to 200 °C for 12 h before being left to cool to ambient temperature. The deposits were centrifuged and dehydrated at 80 °C after being rinsed with DI water and ethanol numerous times. The completed products were then calcined for 2 h in static air at 400 °C.

4.2. Loading ZrO2 NPs onto Layered MoS2/g-C3N4 NSs. Direct heating in malonate at 540 °C for 4 h in a furnace to obtain a graphite-like C3N4 was accomplished using a muffle furnace. A feasible ultrasonic chemical and self-assembly method (Scheme 1) was used to prepare the ZrO2@MoS2/g-C3N4 nanocomposite. A total of 0.5 g of g-C3N4 powder was generally ultrasonically homogenized in 40 mL of deionized water for 2 h. The sodium molybdate (1 mmol) solution was added to the thiocarbamide (2 mmol) solution, dropped into the above light-yellow suspension, and treated hydrothermally. Following continuous washing and heat-drying, a suitable quantity of stacked MoS2/g-C3N4 and pure ZrO2 NPs (0.1 g) was scattered in 40 mL of methanol for 2 h and then violently agitated continuously in a fume cupboard to eliminate the solution. To improve the contact between the MoS2/g-C3N4 layers and the ZrO2 matrix, the products were ground and then sintered at 350 °C for 2 h under a static airflow to increase the connection between the layers.

4.3. Evaluation of the Photocatalytic Activity and Active Species Capturing Experiments. Using 2 mg of TC and 50 mg of ZrO2@MoS2/g-C3N4 catalyst in 100 mL of DI water, the pH of the suspension was calibrated using diluted H2SO4 and NaOH. Without irradiation, the absorption—desorption equilibrium of the TC pollutant on ZrO2@MoS2/g-C3N4 catalysts can be obtained after 30 min of magnetic stirring in the dark. The light source was used as a visible light with a cutoff filter (420 nm ≤ λ ≤ 760 nm) at 300 W Xe. During photocatalytic irradiation, a small aliquot of 4–5 mL of suspension was taken out at 15 min intervals and centrifuged for 10 min at 5000 rpm. Finally, the concentration was calculated using a UV–vis spectrophotometer and the absorption peak value of λ = 357 nm (TC maximum absorption wavelength).

To detect the active scavenger species, isopropyl alcohol (IPA) (1.0 × 10⁻¹⁻¹ mol L⁻¹) was employed as a hydroxyl radical (·OH) inhibitor. Benzoquinone (BQ) (4.0 × 10⁻¹⁻¹ mol L⁻¹) was utilized to capture the photogenerated superoxide radical (·O₂⁻) and triethanolamine (TEOA) (1.6 × 10⁻¹⁻¹ mol L⁻¹) to react with photogenerated holes (·h⁺). Preliminary tests were carried out to determine the adequate number of scavengers to use in photocatalytic testing.

4.4. LC–MS Analysis. LC–MS analysis was performed in an LC–MS 2020 system equipped with an LC10ADVP binary pump (Shimadzu, Japan). The sample was separated in a Phenomenex column (250 × 4.6 mm², 5 μm) using acetonitrile (B)/water (A) 0.1% formic acid) as the mobile gradient phase. The injection volume was 20 μL, and the flow rate was set at 0.8 mL/min. Detection was done at a wavelength (λ) of 280 nm, with a run time of 20 min. The mass (MS) compartment consisted of a single quadrupole mass spectrometer with an electrospray ionization (ESI) source, and nitrogen gas was used to assist with nebulization at a flow rate of 1.5 L/min. The temperature was set for a curved desolation line (CDL) and heat blocks at 250 and 280 °C. All of the data were collected and processed using Lab Solution software (Shimadzu).

4.5. Analytical Characterization. This study examined the as-prepared materials using a PAN analytical Xpert pro-X-ray diffractometer equipped with a Cu K radiation (=1.54 Å) source at 40 kV and 40 mA at a temperature range of 2 = 5–70° using X-ray diffraction (XRD) patterns. With the support of Agilent Technologies, we were able to acquire the Fourier transform infrared (FT-IR) spectra of the solid sample embedded in the KBr pellets while the sample was still at room temperature. HR-TEM (200 keV, JEOL, JEM-2100F) and HR-SEM (America, FEI: NOVA Nano SEM 450) were employed to examine the morphology and microstructure of the structural applications. X-ray spectroscopy (XPS, EDXS, and ISIS300 Oxford) maps the ZrO2@MoS2/g-C3N4 nanocomposite surface profiles. The XPS binding energy data were calibrated using the carbon peak as a reference. The surface area and textural features were determined using Autosorp IQ (quantachrome instruments version 5.0) and were assessed using the Brunauer—Emmett—Teller (BET) isotherm. The Barrett—Joyner—Halenda (BJH) method was used to determine pore size distributions. The catalyst’s diffuse reflectance spectroscopy (DRS) was carried out at room temperature using a Shimadzu UV 3600 plus in the 200–800 nm wavelength range to determine its UV–vis reflectance. PL measurements were taken with a Fluorolog (Horiba Yvon) spectrophotometer and recorded on a microfilm strip. A three-electrode setup was used to investigate the EIS response of all produced samples (Shanghai Chenhua CH-660D). The photocatalytic performance evaluation was carried out with the help of a lamp source (Xe lamp, 300 (420 nm)). We used LC–MS analysis in the LC–MS 2020 system equipped with an LC10ADVP binary pump (Shimadzu, Japan).

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Notes
The authors declare no competing financial interest.

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