

The effect of P +3 , Bi +3 and Zr +4 substitution in Mo_{1-x-y-z}P_xBi_yZr_zO₂/g-C₃N₄ nanocomposite: Microstructure, optical properties and improvement of photocatalytic behavior in the visible light range

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Research Article

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Posted Date: September 2nd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10578987/v1>

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Additional Declarations: No competing interests reported.

**The effect of P^{+3} , Bi^{+3} and Zr^{+4} substitution in $Mo_{1-x-y-z}P_xBi_yZr_zO_2/g-C_3N_4$ nanocomposite:
Microstructure, optical properties and improvement of photocatalytic behavior in the
visible light range**

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Abstract

In recent years, $MoS_2/g-C_3N_4$ heterojunction have attracted significant attention due to their narrow band gap and reduced recombination of electron-hole pairs. These composites as photocatalyst show great promise in various applications such as water purification, pollutant degradation, hydrogen and oxygen fuel generation, solar cells, drug release, and more. In this study, MoS_2 was synthesized by hydrothermal method and P^{+3} , Bi^{+3} and Zr^{+4} ions were doped in it at molar ratios of 0.4, 0.4 and 0.3 individually, double and triple. A binary heterojunctions MoS_2 (pure samples and those containing dopants)/ $g-C_3N_4$ were synthesized via hydrothermal. The crystal structure, morphology, band structure of heterojunction, identification of various functional groups, behaviors of charge carriers and Catalytic degradation of organic dye (Methylene Blue) were characterized by X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), DRS, FTIR, PL and UV-Vis. Experimental results indicated that the $PBiZr-MoS_2/g-C_3N_4$ heterojunction with 1.68 eV band gap and 99.9% degradation efficiency in 20 min under visible light displayed the best photocatalytic activity. The high degradation rate of methylene blue (MB) by this sample can be attributed to its narrow band gap, the formation of bismuth sulfide phase as an electron trapper, and the low recombination rate.

Keyword: $MoS_2/g-C_3N_4$ heterojunction, photocatalyst, Bismuth cation dopant, Phosphor cation dopant, Zirconium cation dopant, hydrothermal, triple dopant.

1. Introduction

The lack of accessible clean drinking water is a worldwide environmental issue. With the ongoing increase in global population, around 750 million individuals are facing challenges in obtaining safe and drinking water [1]. Various industrial discharge like cosmetics, paper, textiles, and chemicals contributes to the pollution and diminish of our limited clean water resources, posing a threat to both the environment and various life forms. [2]. Considering these circumstances, it's crucial to develop new methods for degradation pollutants in water to expand its accessibility, particularly in developing nations where the need is urgent. Various techniques such as precipitation, reverse osmosis (RO), and adsorption have been employed towards this end [3].

Nevertheless, these approaches face limitations due to their high costs, high energy consumption, and the potential for secondary pollution [4]. Therefore, the critical necessity for advanced technologies in environmental remediation and sustainable energy production drives research into the innovation of high-performance photocatalysts [5]. This environmental and cost-effective photocatalytic technology relies on photo-induced carriers activated by irradiation. These carriers could react with O_2 and H_2O , producing $\cdot OH$ and $\cdot O_2^-$ free radicals, respectively [6]. Subsequently, the $\cdot OH$ and $\cdot O_2^-$ radicals play a crucial role in eliminating organic pollutants from contaminated water through an advanced redox reaction process [7].

Recently, there has been a significant interest focused on two-dimensional (2D) nanomaterials in the field of catalysis, photocatalysis, optoelectronics, and energy-related fields [3]. MoS_2 stands out as a highly effective transition metal chalcogenide (TMD) in 2D nanomaterials, particularly as a photocatalyst for degradation of various substances such as pharmaceutically active compounds (PhACs), synthetic dyes (including rhodamine B, methylene blue, methyl orange, and Novacron red Huntsman), pesticides, and herbicides. Its applications extend beyond pollutant degradation, encompassing tasks like photocatalytic oxygen evolution, nitrogen fixation, ammonia synthesis, and water electrolysis [3]. MoS_2 -based materials find various applications, including energy storage [8], hydrogen production [9], pollutant degradation [10], disinfection [11], etc.

MoS_2 possesses a range of advantageous features, including its natural layered structure, high absorbance in the visible spectrum, narrow band gap, high carrier mobility, robust surface adsorption capacity, controllable morphologies, excellent chemical and thermal stability, non-toxic properties, large surface area, and abundant active sites. These properties, along with its cost-effectiveness and abundance, make MoS_2 highly desirable for applications as a photocatalyst [3,12-18]. Similar to graphene, MoS_2 features a layered structure. MoS_2 nanomaterial consists of three stacked atomic layers i.e. Mo atomic layer

sandwiched between two sulfur layers (S-Mo-S). The bonding between these layers is facilitated by weak van der Waals forces, ensuring their cohesion across the structure [3].

Belonging to the TMDCs group, MoS₂ shows a band gap that varies with the number of layers, attributed to quantum confinement effects. The monolayer configuration of MoS₂ has a direct band gap of approximately 1.8 eV, while the indirect band gap becomes about 1.2 eV, in multilayered structures (>8 L) [19]. Consequently, MoS₂ has attracted significant attention in recent years due to its distinctive electrical and optical properties [12]. MoS₂ exists in three crystal phase structures, namely 2H-MoS₂ and 1T-MoS₂, and the third phase, 3R-MoS₂, is present in less than 3% of molybdenite ore [20].

However, the photocatalytic efficiency of pure MoS₂ is often hindered by its narrow light absorption range and the high recombination rate of photogenerated holes and electrons. As a result, increasing the light absorption capabilities of MoS₂ and accelerating the separation and transport of carriers becomes necessary to meet the practical requirements for its application [21,22].

To address the mentioned challenges, several practical approaches have been proposed. These include modification of MoS₂ through doping of metallic or non-metallic elements (such as Zr [3], Al, P, Si [23], Bi [24], Co [25], etc.), preparing innovative nanostructures, and constructing heterojunctions by incorporating MoS₂ with suitable catalysts. Among these strategies, constructing a p-n junction at the semiconductor interface is known as an effective and promising method to accelerate the separation and transfer of photogenerated electrons and holes [26].

Graphitic carbon nitride (g-C₃N₄) was innovatively introduced in 2009 for photocatalytic hydrogen evolution due to its advantageous properties, including a narrow band gap (2.8 eV), nonmetallic properties, nontoxicity, and easy availability, low cost and high thermal and chemical stability has become the focal point of research. [26-28]. The n-type conductivity characteristic of nanostructured g-C₃N₄ makes sheet-like g-C₃N₄ a suitable candidate for coupling with p-type nanostructured MoS₂ [26,29,30]. Despite the close contact caused by the morphological compatibility, the MoS₂/g-C₃N₄ heterojunction not only minimizes lattice mismatch but also effectively enhances the extraction of photo-induced electrons.

Furthermore, heteroatom doping stands out as another promising method for enhancing photocatalytic activity, achieved by regulating the electronic structure and conductivity of the catalyst. Phosphorus is frequently chosen as a candidate for heteroatom doping due to its distinctive properties. Intriguingly, several electrocatalysis studies have demonstrated that incorporating phosphorus into MoS₂ can effectively improve photocatalytic activity by fine-tuning the electron structure and increasing the reductive sites [21,31].

The introduction of transition metals such as Zirconium and post-transition metals like Bismuth through doping has been found to decrease the charge-transfer impedance of MoS₂, leading to heightened efficiency in photocatalytic reactions. Substituting sulfur atoms with P, Zr, and Bi atoms not only increases the count of unsaturated sulfur atoms but also significantly enhances the electrocatalytic capabilities of MoS₂. Enhancing the catalytic capacity is effectively achieved through two key factors: increasing the number of unsaturated sulfur atoms along the edges within the MoS₂ layers and improving the electric conductivity of MoS₂ [25].

Nevertheless, there has been limited studies on directly enhancing the photocatalytic activity of MoS₂ through heteroatom doping in MoS₂/g-C₃N₄. In this study, a set of novels (P, Zr, and Bi)-doped MoS₂/g-C₃N₄ photocatalysts were prepared with single and triple dopants through a hydrothermal process.

2. Experimental section

2.1 synthesis of g-C₃N₄

Urea powder (10 g) was weighed in an alumina crucible with foil cover and placed in the muffle furnace at 550°C for 3 hours, with a heating rate of 2.5 °C.min⁻¹. The obtained powder is naturally cooled to room temperature. Then, it was centrifuged for 5 minutes at 5000 rpm and washed 3 times with dilute nitric acid (0.1 mol.lit⁻¹) and deionized water to remove any alkaline compounds (for example, ammonia) adsorbed on the surface [32]. After washing, powder was placed in an oven at a temperature of 60°C for 10 hours, finally a gray powder of g-C₃N₄ was obtained.

2.2 synthesis of MoS₂

The MoS₂ sample was prepared using a hydrothermal method. Specifically, 1 mmol of ammonium molybdate and 45 mmol of thiourea were mixed in 60 mL of deionized water and stirred for 30 minutes. Subsequently, the solution was transferred into a Teflon-lined stainless-steel autoclave and maintained at 200 °C for 18 hours. The autoclave was then allowed to cool to room temperature. The resulting products were collected by centrifugation at 5000 rpm for 5 minutes, washed with ethanol and water, and finally dried in an oven at 80 °C for 10 hours. In the end, a black-colored MoS₂ powder was obtained.

2.3 Synthesis of MoS₂/g-C₃N₄ and (P, Zr, and Bi)-doped MoS₂/g-C₃N₄

0.5 grams of g-C₃N₄ powder were dispersed in 60 ml of deionized water and subjected to ultrasonication for 30 minutes. Subsequently, 1.74 grams of ammonium molybdate and 3.22 grams of thiourea were added into the above dispersion and stirred for an additional 10 minutes. The entire suspension was then subjected to another 30 minutes of ultrasonication and subsequently transferred into a Teflon-lined stainless-steel

autoclave. The autoclave was maintained at 200°C for 18 hours. Following the process, the suspension underwent centrifugation at 5000 rpm for 5 minutes. The resulting products were washed with deionized water and ethanol before being collected. The precipitated products were then dried in an oven at 80°C for 12 hours.

The synthesis method for the MoS₂/g-C₃N₄ composite in the presence of dopants is quite similar to the MoS₂/g-C₃N₄ nanocomposite (MSCN) in the absence of dopants. with the difference that after adding ammonium molybdate and thiourea to g-C₃N₄ powder solution and deionized water amounts of 500 mg, 70 mg and 10 mg, respectively, sodium hypophosphite (P source), bismuth nitrate (III) (Bi source), and zirconium oxychloride (Zr source) were added separately for composites with single dopants and simultaneously for PBiZr-MoS₂/g-C₃N₄ nanocomposite (at molar ratios of 0.4, 0.4 and 0.3 individually, double and triple). Subsequently, the remaining steps were carried out as described previously.

2.4 Photocatalytic activity evaluation

The photocatalytic activities of MSCN composites were evaluated through the degradation of Methylene Blue (MB) under visible light irradiation. In each experiment, 20 mg of the photocatalyst powder was dispersed in a 40 mL solution of MB (10 mg/L). Before exposure to light, the suspensions were stirred in the dark for 30 minutes to facilitate the adsorption of MB by the catalysts [33].

At predefined time intervals (every 20 minutes), 2 mL of the reaction solution was collected and centrifuged at 10000 rpm for 2 minutes for further analysis. The concentration of MB was examined using a 50-watt LED lamp with irradiation between 400 and 780 nm, and its absorbance was measured at 464 nm. MB concentration was determined using an ICP instrument (SHIMADZU CORPORATION). The degradation efficiency (D%) was calculated using following equation [33],

$$D\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C₀ represents the original absorbance value of MB, and C_t is the absorbance value of MB at any given moment.

2.5 Characterization

In order to study crystal phase of as-prepared photocatalysts were analyzed using an X- ray diffractometer (Bruker -D8 ADVANCE Cu K α radiation ($\lambda=0.15406\text{nm}$)), The measurement was conducted at room temperature in the 2 θ range of 10–90°. Field emission scanning electron microscope (FESEM, Mira3, TESCAN) were used to characterize the morphologies and microstructures. The presence of different functional groups was detected by Perkin Elmer Fourier transform spectra (FT-IR) and the optical

properties were analyzed using UV-vis spectrophotometer (Shimadzu Corporation) in the range of 200-800 nm to obtain the absorption spectra. The photoluminescence (PL) spectra of the photocatalysts was measured using a fluorescence spectrophotometer and the excitation wavelength was 400 nm.

3. Results and discussion

3.1 Structural and compositional analysis

The phase purity, structural parameters, and layer spacing of pure MoS₂, g-C₃N₄, MoS₂/g-C₃N₄(MCN), Zr-MCN, P-MCN, Bi-MCN and PBiZr-MCN heterojunctions were assessed through XRD, and the diffraction pattern was plotted from 10°–90° as portrayed in Fig. 1a. Diffraction of pure MoS₂ showed visible reflectivity at 14.1°, 32.5°, and 57.6° which is set as (002), (100) and (110) planes respectively. These results confirm the development of hexagonal phase (2H-MoS₂) belongs to the P6₃/mmc space and corresponds good with standard spectrum (JCPDS 01-075-1539 No impurity peak was observed in the sensitivity of the device, which indicated the presence of pure 2H-MoS₂. [34]. For the (002) crystal plane, an interlayer spacing of MoS₂ layers was equal to 0.62 nm according to Bragg's equation ($2d \sin\theta = n\lambda$). The following diffraction pattern shows that MoS₂ with hexagonal structure is well synthesized [35].

As can be seen in the pattern related to graphite carbon nitride (Fig. 1a), the two main peaks are located at 13.2° and 27.5°. These two peaks corresponded well with the hexagonal crystal structure pattern of graphite carbon nitride (JCPDS 087-1526-01). The strongest diffraction peak at the 27.5° can be attributed to the diffraction of the (002) formed crystal plane, which is caused by the accumulation or stacking of g-C₃N₄ conjugated aromatic systems and indicates formation of a layered structure of graphite like g-C₃N₄. Diffraction peak at 13.2° due to polycondensation of tri-s-triazine unites in crystal plane (100) [36]. The interlayer spacing was equal to 0.33 nm for the crystal plate (002).

As it is clear from the X-ray diffraction pattern of the MoS₂/g-C₃N₄(Fig. 1a) heterojunction sample, the intensity of the main diffraction peak of g-C₃N₄ i.e. 27.5 is very low in the composite so that it is not well observed. This issue can have two reasons, one is that the large dispersion of g-C₃N₄ occurred on the surface of the MoS₂ photocatalyst, and the second reason can be the low percentage of g-C₃N₄ for detection by XRD patterns [37-41].

As shown in the XRD pattern of heterojunction (Fig. 1b and 1c) photocatalysts in the presence of dopant, the three main peaks of molybdenum disulfide shifted to lower angles of 57.5°, 32.2° and 13.6°. The reason for this is the substitution of phosphorus, zirconium and phosphorus ions in the structure instead of sulfur and the difference in the atomic radius they have with sulfur. Because the atomic radius of phosphorus with 1.23Å, zirconium with 1.6Å and bismuth with 1.43Å are greater than the atomic radius of sulfur with 1.04Å, and for this reason, with the introduction of these ions in the structure of MoS₂, interlayer spacing increase

from 0.62 nm to 0.64 nm [21,42,43]. The average crystallite size was estimated for MCN, P-MCN, Zr-MCN, Bi-MCN and PBiZr MCN samples using the Debye-Scherrer equation

$$D = \frac{0.94 \times \lambda}{\beta \cos \theta} \text{ (nm)} \quad (2)$$

where, D is crystallite size, λ is X-ray wavelength (nm), β is full width half maximum of diffraction peak and θ is Diffraction angle. The average crystallite sizes were evaluated at 17.3, 4.3, 4.6, 5.1 and 6.4 nm for MCN, P-MCN, Zr-MCN, Bi-MCN and PBiZr MCN heterojunctions, respectively. As it can be seen, the average crystallite size of the composites with dopant in their structure has decreased significantly compared to the composite without dopant. The doped ions were substituted in the host sites, which leads to a decrease in nucleation and subsequently the growth rate of these composites. When decreasing the average crystallite size, surface area of the samples has been increased which helps to increase the efficiency Photocatalytic activity [44].

In the Bi-MCN heterojunction, two peaks related to the new Bi_2S_3 structure are also observed, which is caused by the reaction of bismuth with sulfur [24]. The intensity of peaks in the PBiZr-MoS₂/g-C₃N₄ heterojunction is less than the others, which could be the reason that the presence of three ions together significantly reduced the crystallinity intensity of the MoS₂/g-C₃N₄ composite [45].

FT-IR technique was used to assess the functional groups with different vibrational modes. The schemed spectra between 4500-500 cm⁻¹ are plotted in Fig.2 for MCN, Zr-MCN, P-MCN, Bi-MCN and PBiZr-MCN heterojunctions. As shown, a strong absorption peak at 3430 cm⁻¹ wavenumber is seen for all samples with almost the same intensity, which is related to the O-H hydroxyl bond in physically or chemically adsorbed water [19,40,46].

In all samples, there is a peak related to C-H bond in the range of 2900 cm⁻¹ wavenumber, and the intensity of this peak is stronger in PBiZr-MCN composite as it is clear from the figure [47]. At the wavenumber of 2030 cm⁻¹, which is related to the stretching vibrations of the $\text{C} \equiv \text{C}$ bond [48], this peak is present in the photocatalysts of Zr-MCN, P-MCN and Bi-MCN. In all samples, absorption peaks in the range of 1600 to 1090 cm⁻¹ wavenumber, which is related to C-N, can be seen well. While in two samples of MCN and P-MCN, an absorption peak at about 880 cm⁻¹ is observed, which belongs to tri-s-triazine units [49].

In the absorption spectrum of all nanocomposites, an absorption peak in the wavenumber range of 560 cm⁻¹ is observed, which is related to the Mo-S bond [50]. Also, in the absorption spectrum of Bi-MCN and PBiZr-MCN heterojunctions, an absorption peak with low intensity in the

wavenumber range of 830 cm^{-1} along with a shoulder related to the Bi-S bond is observed [51]. Therefore, according to Fig.2, it was concluded that there are C-N and Mo-S bonds in the structure of nanocomposites, and as mentioned, the O-H peak in nanocomposites is due to water or moisture that the samples absorb physically or chemically.

Field emission scanning electron microscope (FESEM) was used to investigation the microstructure and morphology of MoS_2 , $\text{g-C}_3\text{N}_4$, MCN, P-MCN, Bi-MCN and PBiZr-MCN photocatalysts in as shown in fig.3. As can be seen from Fig.3a, $\text{g-C}_3\text{N}_4$ is formed with a porous layer, and the formation of this structure is due to the synthesis temperature being higher than the polymerization temperature ($525\text{ }^\circ\text{C}$) which causes the decomposition and evaporation of urea during heat treatment [52]. Fig.3b shows the flower-like structure of molybdenum disulfide with a high specific surface area [53].

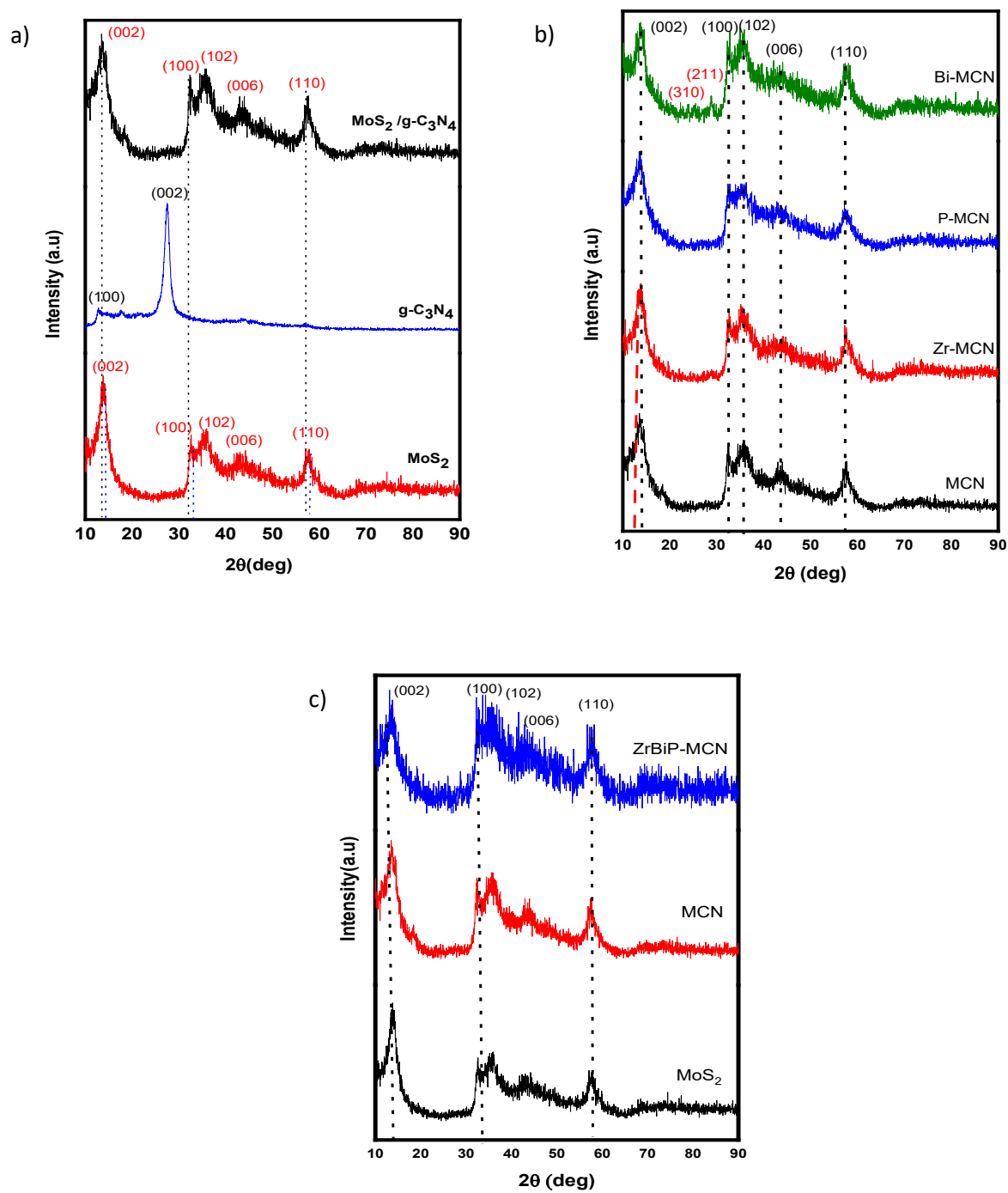


Fig. 1. XRD patterns of pure a) MoS_2 , $\text{g-C}_3\text{N}_4$, $\text{MoS}_2/\text{g-C}_3\text{N}_4(\text{MCN})$, b) Zr-MCN , P-MCN , Bi-MCN and c) PBiZr-MCN heterojunctions.

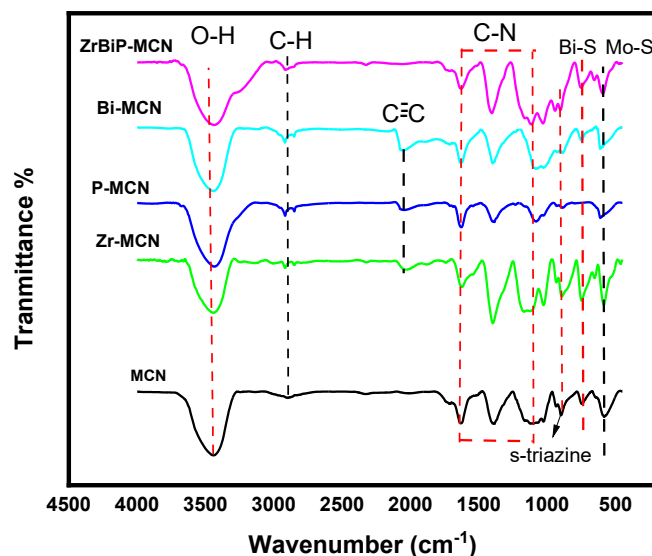
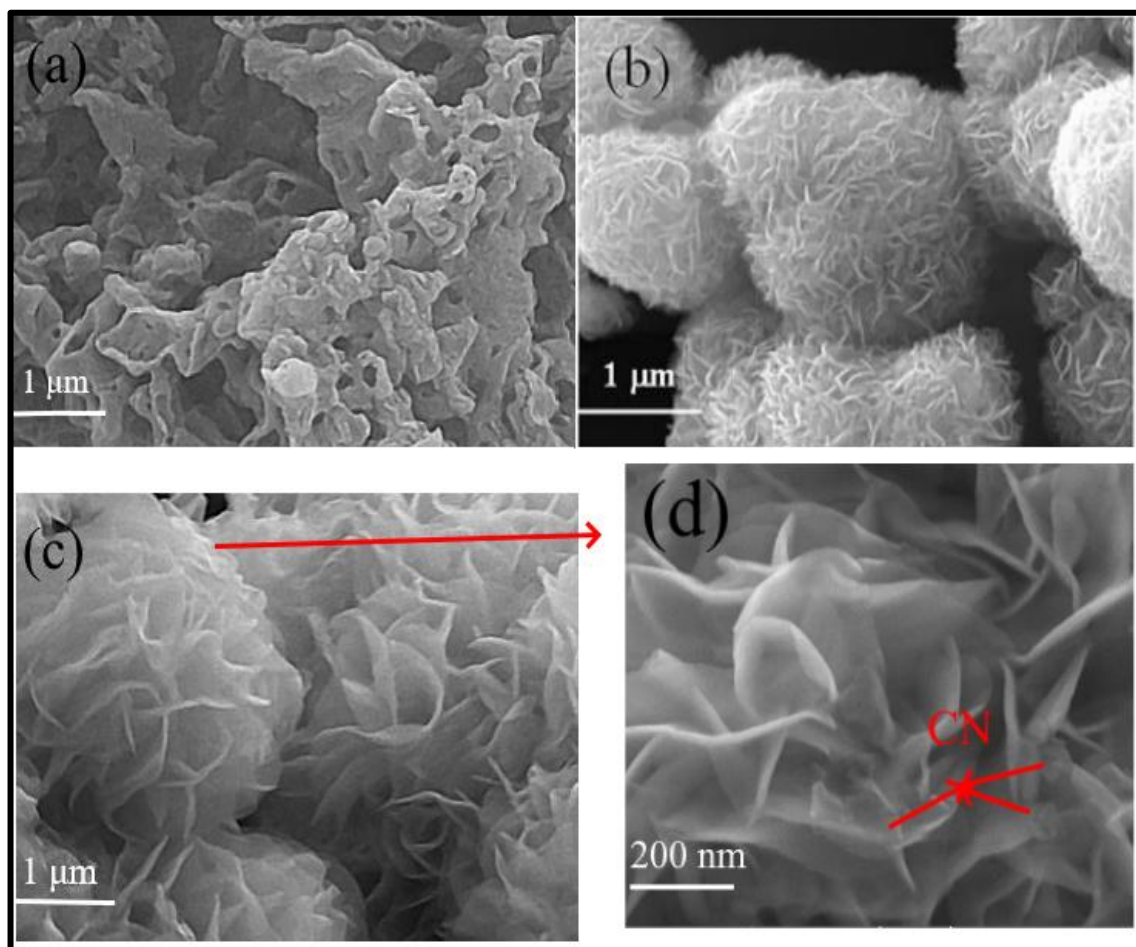


Fig. 2. FTIR spectra of MoS₂/g-C₃N₄(MCN), Zr-MCN, P-MCN, Bi-MCN and ZrBiP-MCN heterojunctions.

In the morphology of the MoS₂/g-C₃N₄ nanocomposite (fig.3c), it can be seen that the g-C₃N₄ particles are well dispersed [53] on MoS₂ layers, and this dispersion can be well seen in Fig. 4d. The layered nature of both MoS₂ and g-C₃N₄ structures makes them well bonded due to the dispersion of these two components [26,54] and as can be seen, both morphologies are seen in the composite. As shown in Fig.3e and fig.3g P-MCN and PBiZr-MCN heterojunctions planes are smaller [21], and in the Bi-MCN heterojunction(fig.3f), the nanofiber microstructure of the new Bi₂S₃ phase [51,54] can be seen, which is consistent with the diffraction pattern results of this sample.



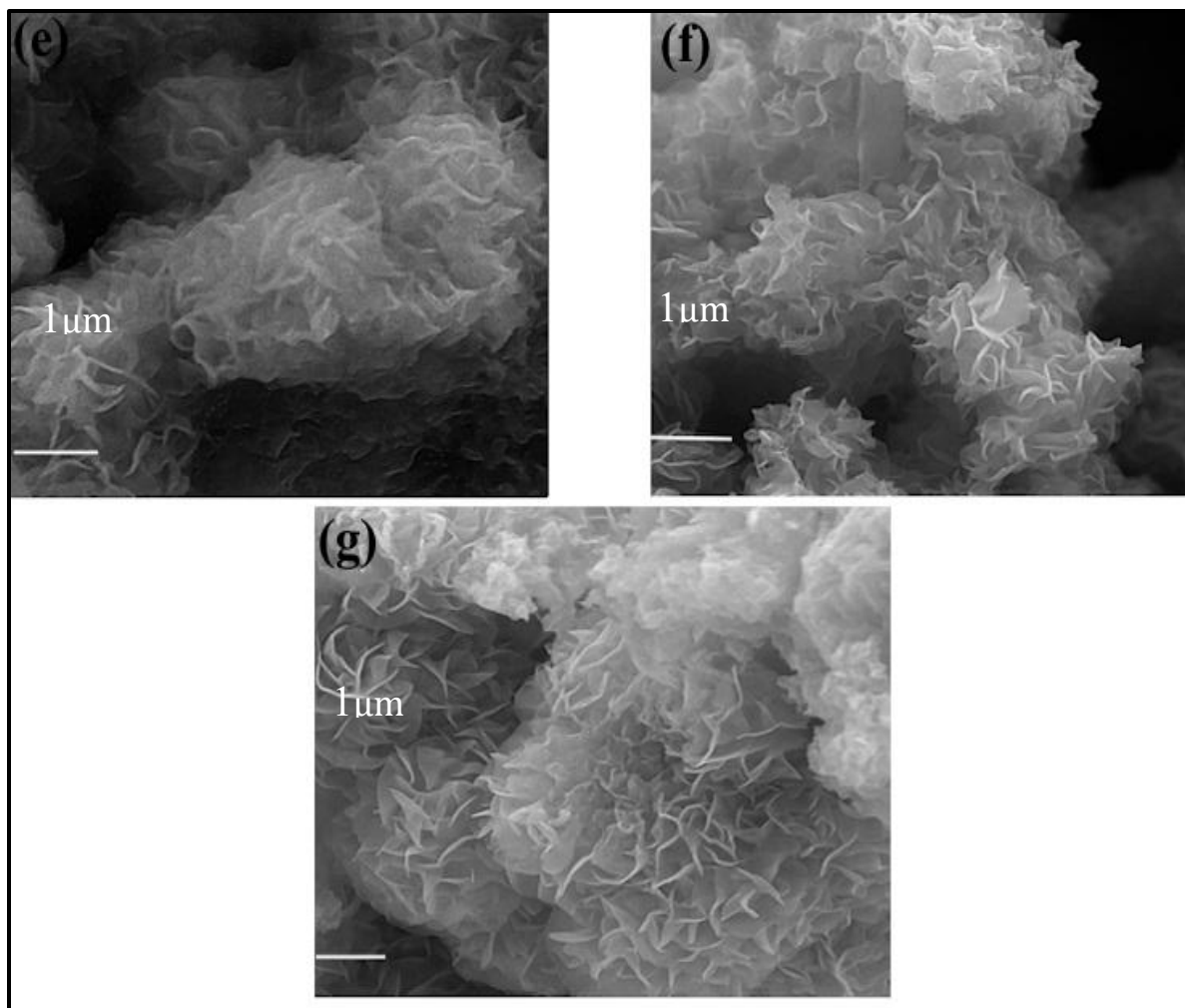


Fig. 3. FESEM images (a,b,c,e,f) g-C₃N₄, MoS₂, MCN, P-MCN, Bi-MCN and ZrBiP-MCN in 1 μ m , d) FESEM image of MCN.

Table.1 lists the particle sizes of MoS₂, P-MCN, Bi-MCN and PBiZr-MCN photocatalysts. According to the results of Table.1, the particle sizes of MoS₂, P-MCN, Bi-MCN and PBiZr-MCN have decreased respectively, which means that the specific surface area of Bi-MCN and PBiZr-MCN samples has increased Compared with pure MoS₂, respectively [55]. Materials with larger surface area are more suitable to achieve higher photocatalytic performance. Because many active sites can be generated on the photocatalyst surface using these materials, which leads to the generation of more radical reactive species for effective photodegradation [56].

Table1. particle size of MoS₂, P-MCN, Bi-MCN and PBiZr-MCN.

Photocatalyst	Particle size (μm)
MoS ₂	1.5
P-MCN	0.2
Bi-MCN	0.15
PBiZr-MCN	0.14

3.2 optical characterization

UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was used to analyze the absorption behavior of MoS₂, g-C₃N₄, MCN, P-MCN, Bi-MCN and PBiZr-MCN photocatalysts in the ultraviolet-visible light region as well as their band gap. As shown in Fig.4a, pure MoS₂ has a strong absorption edge at 380 nm wavelength and enters the visible region, which has shown good absorption in this region. This issue can be directly related to the black color of molybdenum disulfide; Because the darker the photocatalyst powder is, it will have a higher absorption in the visible light region and vice versa [57].

As it is known, the absorption of g-C₃N₄ is high in the ultraviolet light region (250 to 440 nm) and its absorption reaches zero in the visible region. While when carbon graphite nitride forms a composite with molybdenum disulfide its absorption in the visible light region is dramatically improved. The reason for this is the presence of MoS₂ and the change in the color of g-C₃N₄ from gray to black, as well as the formation of new energy levels for electron trapping [26]. PBiZr-MCN nanocomposite has a very high absorption compared to other nanocomposites and has entered a region with a low wavelength (redshift).

The optical band gap of the synthesized samples was calculated by using following equation (Tauc-plots) [58,59,60]

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, A is a constant, ν is frequency, h is Plank's constant, E_g is bandgap energy and n depends to direct or indirect bandgap of the semiconductors [61] which is equal to 2 and 0.5 for the direct and indirect bandgap, respectively [62]. Therefore, the bandgap of the MoS₂, g-C₃N₄, MCN, P-MCN, Bi-MCN and PBiZr-MCN samples were 1.72, 2.80, 1.95, 1.75, 1.89 and 1.68 eV respectively. Meanwhile, the bandgap of the PBiZr-MCN photocatalyst was the smallest, which can be due to the presence of three ions together, which leads to a decrease in the particle size [55], an increase in the specific surface area [47], an increase in the absorption edge, and the formation of energy levels for trapping electrons [61] and finally improved absorption and reduced bandgap.

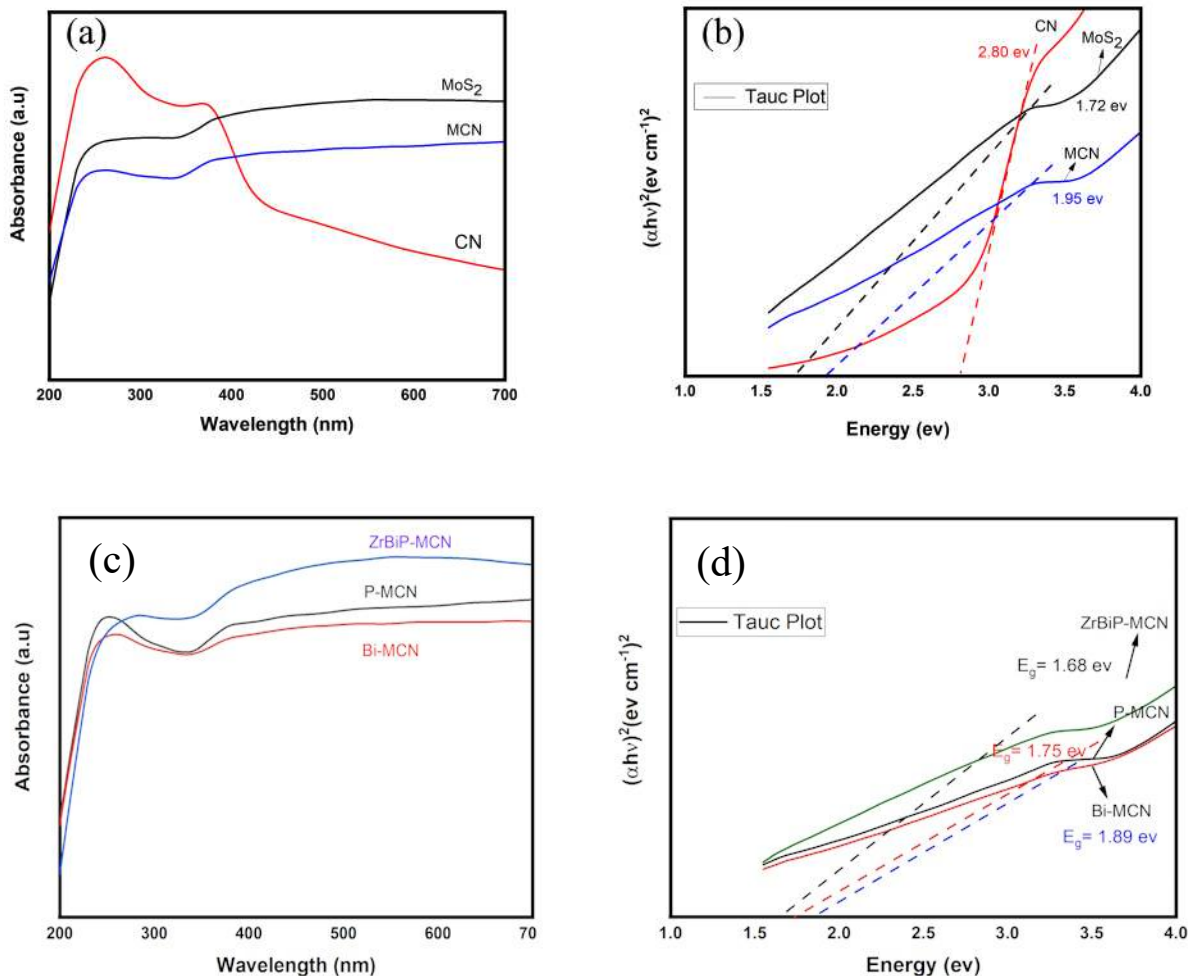


Fig. 4. UV-vis diffuse reflectance spectroscopy a,c and band gap b,d of MoS₂, g-C₃N₄, MCN, P-MCN, Bi-MCN and ZrBiP-MCN

To determine the recombination rate of the excited electrons-holes pair, photoluminescence (PL) spectra of P-MCN, Bi-MCN and PBiZr-MCN were studied at an excitation wavelength of 400nm, as presented in Fig.5. It is generally known that the recombination probability of photogenerated carriers is one of the major factors affecting the photocatalytic activity [26]. By photon absorption, holes and electrons are formed in the valence band and conduction band of the photocatalyst, respectively. Through the interaction of phonons and Coulomb scattering, excitons undergo momentum acceleration and energy relaxation. Therefore, the low-intensity PL spectrum indicates a slow electron-hole pair recombination rate, resulting in longer charge pair lifetimes [63].

As shown, there are two peaks in the emission spectrum of three nanocomposites, the first peak at the wavelength of 530 nm is equivalent to 2.34 eV and the second peak (the main and intense peak) at the wavelength of 607 nm is equivalent to 2.04 eV. These peaks are related to the transfer of electron charge from the valence band to conduction, charge transfer at the interface of composites, and trapping of electrons due to the formation of energy levels by dopants [64,65]. As it is known, in three samples P-MCN, Bi-MCN and PBiZr-MCN, the position of two peaks has not changed and only their intensity has decreased respectively. The reason for the higher peak intensity in P-MCN4.0 sample compared to Bi-MCN4.0 sample can be due to the fact that the crystal size in the first sample is smaller than the second nanocomposite because the smaller crystal size leads to an increase in the recombination rate [58].

Therefore, among the samples, the lowest intensity belongs to the PBiZr-MCN sample, the reason of which can be the high efficiency of electron-hole separation, active absorption edges in visible light and trapping of electrons, which prevents their recombination and helps to increase the photocatalytic efficiency [21,66- 68].

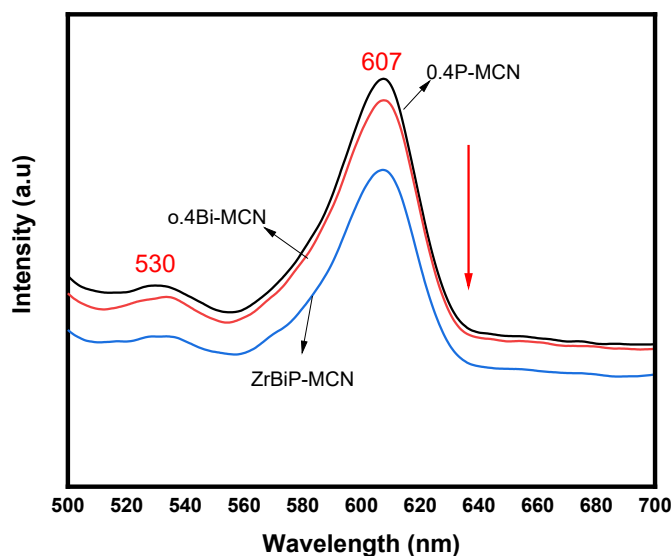
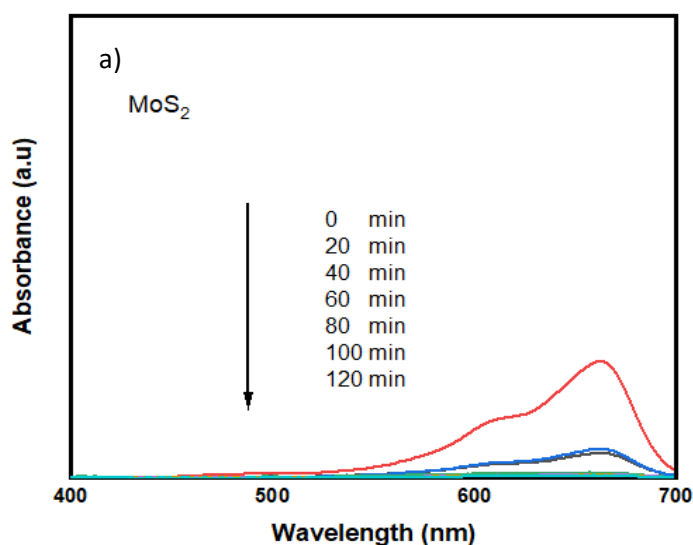


Fig. 5. UV-vis diffuse reflectance spectroscopy a,c and band gap b,d of MoS₂, g-C₃N₄, MCN, P-MCN, Bi-MCN and ZrBiP-MCN

3.3 photocatalytic activity

The photocatalytic activities of MoS₂ and PBiZr-MCN photocatalysts were further examined by measuring the temporal concentration variations of the MB aqueous solution in the presence of photocatalysts dispersion under ~~UV~~ visible light irradiation and the results are shown in Fig. 6. As can be seen in MoS₂, the absorption peak at 670 nm is observed (Fig.6a), and this peak in PBiZr-MCN photocatalyst decreases very strongly after equilibrium and reaches close to zero, which confirms the degradation of methylene blue significantly (Fig.6b).

Fig.7 shows the absorption rate in MoS₂ and PBiZr-MCN photocatalysts for methylene blue degradation. The results of the degradation rate of methylene blue for two photocatalysts using equation (1) after 20 minutes under visible light are equal to 74.8% and, 99.9% respectively (Fig.7). This means the photocatalytic activity of PBiZr-MCN photocatalyst has increased significantly compared to pure molybdenum sulfide, which can be due to increased crystal size, high absorbance in visible light, suitable band gap [49], spherical morphology and compact structure [69], low electron-hole pair recombination [70].



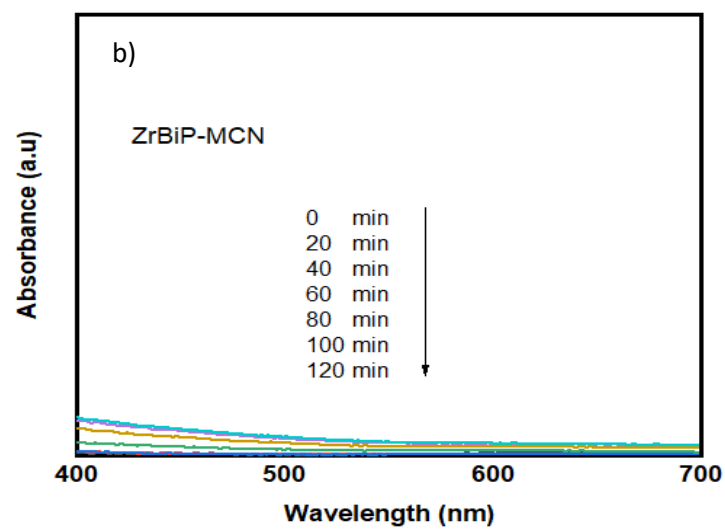


Fig6. Visible absorption spectra of photodegradation of MB dye with a) MoS₂ and b) PBiZr-MCN photocatalysts.

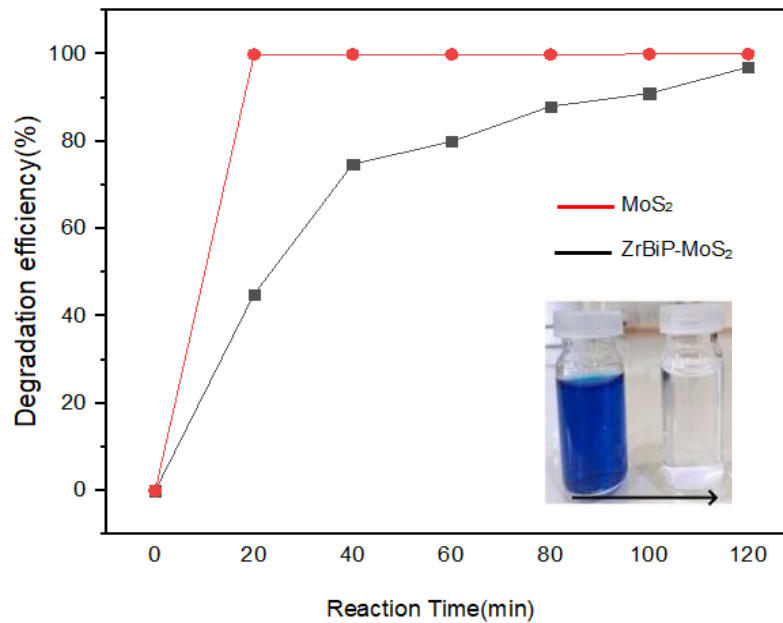


Fig7. MB degradation conversion on MoS₂ and PBiZr-MCN

3.4 mechanism of photocatalyst

The proposed mechanism for the degradation of two-dimensional nanocomposites synthesized in the present research work is the energy levels and migration of charge carriers in the interface, which is shown in the scheme1. According to the scheme, it is clear that the structure type of nanocomposites is type II. The valence band and conduction band of semiconductors can be determined according to the following formula [71,72]:

$$E_{VB} = X - E_e + 0.5E_g \quad (4)$$

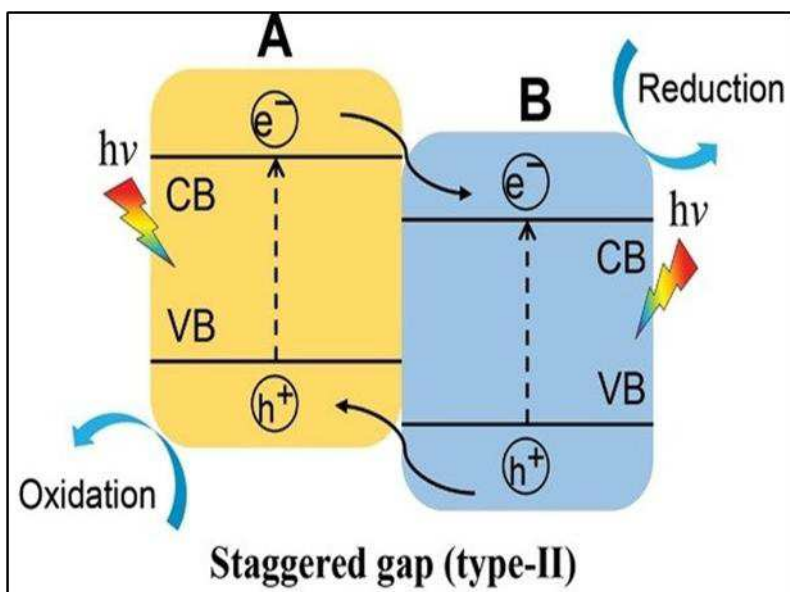
$$E_{CB} = E_{VB} - E_g \quad (5)$$

In the above equation, X is the absolute electronegativity of the semiconductor, which is equal to 4.65 for semiconductor A and 5.33 for semiconductor B [73,74]. E_e is the energy of free electrons in the hydrogen scale (about 4.5 eV), E_{VB} and E_{CB} are respectively equal to the energy of the valence band and conduction band, and E_g is the energy of the semiconductor band gap, which was obtained based on the results of DRS analysis. Based on calculations, the energy range of

conduction band and valence band of semiconductor A (carbon graphite nitride) is equal to -1.23 and 1.57 eV, respectively, and the energy range of conduction band and valence band of semiconductor B (molybdenum sulfide with dopants) is equal to -0.1 and 1.76 eV, respectively.

Electrons in the conduction band of semiconductor B cannot reduce O_2 alone to produce $\bullet O_2$ - due to its more positive edge potential than $O_2/\bullet O_2^-$ ($E(O_2/\bullet O_2^-) = -0.33$ eV) and existing holes. In semiconductor A, it cannot oxidize H_2O to $\bullet OH$ alone ($E(\bullet OH/H_2O) = 2.27$ eV) [71, 72].

Based on the calculations, as shown in scheme1, the potential of the conduction band and the valence band of semiconductor A is more negative and positive, respectively, than that of semiconductor B. Therefore, with visible light irradiation, electrons induced in the valence band of semiconductor A easily transfer through the interface to the valence band of semiconductor B and in a similar way, the holes of semiconductor B move to semiconductor A. Therefore, composite structure causes the effective separation of electrons and holes. In this way, after connecting the two structures of photocatalysts, the rich electrons in the conduction band of semiconductor B and the rich holes in the valence band of semiconductor A play the main role for reduction and oxidation processes, i.e. degradation of methylene blue [65,75,76].



Scheme 1. Schematic diagram of photocatalytic mechanism of the 2D $MoS_2/g-C_3N_4$ composites [77].

4. Conclusion

In this work, the MoS₂ with three dopants (P⁺³, Bi⁺³ and Zr⁺⁴ ions) incorporated g-C₃N₄ heterostructure was successfully fabricated via a hydrothermal method. The PBiZr-MCN photocatalyst presents the highest methylene blue degradation rate and was able to completely degrade methylene blue. The separation of charge carriers, Formation of bismuth sulfide to trap electrons, abundant active sites, broadened optical absorption range and high redox potentials are the five main basic reason for the degradation of methylene blue by this photocatalyst. The optimized Z-scheme PBiZr-MoS₂/g-C₃N₄ heterojunction exhibited significantly enhanced photocatalytic performance, achieving a remarkable 99.99% degradation rate of MB under visible light. Experimental results indicate that the intimate coupling between MS-PBiZr and g-C₃N₄ improving visible-light absorption, Narrow band gap, increasing active sites, increasing electron generation transfer and vastly accelerate photo-induced carriers' separation.

Acknowledgements

No financial support or grants were received from any public, commercial, or not-for-profit entities for the research, authorship, or publication of this article.

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