**1. Introduction**

A clean environment is highly significant for healthy living and sustaining life on earth. As a whole, all living creatures are reliant on the environment for food, air, water, and many other requirements. Consequently, it is significant that each individual must contribute to save and protect the environment from various pollutants. Very important assets for life like water and air are under continuous threat from various organic pollutants and toxic chemicals generated from the chemical, agricultural, food and textile industries that act as poisons.\(^1,2\)

Carcinogenic dyes present in water restrict the path of sunrays and obstruct them from entering the aqueous system. This results in a reduced rate of photosynthesis and damage to aquatic animals.\(^3\) In addition to the impairment of body organs, dyes also affect public health by accumulation in living beings. Nitrophenol compounds are widely used in the synthesis of agrochemicals, fungicides and rubber. These are considered to be persistent pollutants and adversely affect the functioning of various body organs. An eco-friendly approach must be planned to carry out degradation reactions more precisely and efficiently for elimination of these toxic chemicals from waste water. Previously used conventional methods such as biological degradation, membrane filtration, chemical oxidation, and plasma ozonization have not been proved to be appropriate due to their complexity, low efficiency, time consuming mechanisms, disposal problems and being uneconomical.\(^4,5\)

Among all the natural energy resources, solar energy is considered to be the most efficient, easily available and renewable energy source on earth. In the whole solar spectrum, 43% energy is provided by visible light whereas UV region contributes only 4% of energy.\(^6,7\) In this manner, improvement of effective photocatalysts, especially noticeable light responsive systems, is fundamental for the proficient usage of sunlight-based energy in photocatalysis. The general mechanism of photocatalysis involves the generation of activated electron–hole pairs in the valence band of semiconductor, followed by electron transfer from the valence band to the conduction band in the presence of light energy.\(^8\) These charged species play a major role in photocatalysis by providing surface...
for adsorption of species, and generate superoxide and hydroxide radicals which further participate in oxidation-reduction degradation reactions.

In past years, removal of pollutants by the photocatalytic process has become a matter of great interest. Until now, a number of semiconductor photocatalysts have been fabricated to remove toxic chemicals from the environment. TiO₂, ZnO, CuO, SnO₂, ZnS, Cds, BiVO₄, and g-C₃N₄ are considered to be the most common semiconductors utilized for light energy mediated catalytic reactions. Out of all the semiconductor photocatalyst materials, BiVO₄ has gained maximum attraction because of its excellent photocatalytic activity in visible light region, low toxicity and high stability. BiVO₄ has a band gap of 2.44 eV that corresponds to λmax value between 300 and 400 nm. Its photocatalytic behavior promotes removal of toxic dyes, pesticides, disintegration of pollutants and production of hydrogen gas by splitting of water. One major limitation concerning its efficiency was a high rate of recombination of electron–hole pairs which retards its capability. This limitation was overcome by modifying the structure of BiVO₄ by doping with metals and non-metals or coupling with other semiconductors. With these efforts, the structure and morphology of BiVO₄ were tuned for its utilization as a photocatalyst in the presence of visible light. To date, a number of BiVO₄ based hybrid composites have been manufactured which exhibited higher photocatalytic activity towards photo-electrochemical reactions, dye degradation, mineralization of pesticides and, splitting of water as compared to that of pure BiVO₄ semiconductor.

In the present investigation, a sunlight activated heterojunction, MnV₂O₆/BiVO₄, was synthesized by a one pot hydrothermal method. The p-type MnV₂O₆ photocatalyst comprises narrow band gap energy (~1.6 eV) and exhibits high catalytic activity towards redox reactions involving splitting of water into hydrogen and oxygen, elimination of harmful pesticides, and degradation of toxic organic dyes under visible radiation. In addition to this, MnV₂O₆ also acts as an excellent anodic material in lithium-ion batteries, attributed to its continuous recycling activity. The prepared MnV₂O₆/BiVO₄ heterojunction was utilized as a photocatalyst for degrading MB and RhB dyes, and reducing 4-NP in the presence of solar radiation. Photocatalytic experiments under same conditions were performed for sole BiVO₄ and MnV₂O₆ also.

2. Experimental

2.1 Materials and methods

Bi(NO₃)₃·5H₂O, NH₄VO₃, Mn(CH₃COO)₂·4H₂O, NaBH₄, polyvinylpyrrolidone (PVP), 4-nitrophenol, and MB and RhB dyes were purchased from LOBA Chemie Pvt Ltd India.

2.1.1 Synthesis of BiVO₄. Synthesis of pure BiVO₄ was carried out by adding 0.2425 g of Bi(NO₃)₃·5H₂O in 30 mL of distilled water while maintaining the temperature at 50 °C. In another beaker, 10 mL solution was made by adding 0.0585 g of NH₄VO₃. Then, slow mixing of the above solutions was carried out with continuous magnetic stirring for 30 min (pH = 2), followed by addition of PVP surfactant. The obtained mixture was transferred to a steel autoclave that was heated in an oven maintained at 180 °C. The obtained yellow-colored precipitates were thoroughly rinsed with distilled water and dried in an oven at 100 °C for 2 h (sample S-I).

2.1.2 Synthesis of MnV₂O₆. In this hydrothermal synthesis, a solution of 0.306 g of Mn(CH₃COO)₂·4H₂O in 50 mL distilled water was prepared and stirred for 30 min. To this solution, 0.29 g of NH₄VO₃ was added and stirring was continued. Then, PVP was added to prevent agglomeration of particles. The obtained blend was transferred to an autoclave and heated at 80–180 °C in an oven. The precipitates (brown colored) obtained were washed with distilled water and dried at 50 °C for 5 h (sample S-II).

2.1.3 Fabrication of MnV₂O₆/BiVO₄ heterojunction. A one pot hydrothermal method was utilized to prepare the MnV₂O₆/BiVO₄ heterojunction with different molar ratios. A solution of Bi(NO₃)₃·5H₂O in dilute HNO₃ was prepared and magnetically stirred till a clear suspension was obtained. Then, Mn(CH₃COO)₂·4H₂O was added and mixed thoroughly with magnetic stirring. An aqueous solution of NH₄VO₃ (50 mL) was prepared separately and added drop wise to the above mixture with continuous stirring. PVP was also added in the mixture to synthesize the composite with an optimum particle size and structure. After 2 h of continuous stirring, this mixture was transferred to an autoclave and placed overnight in an oven at 180 °C. The obtained precipitates were washed thoroughly with double distilled water (DDW) and dried in an oven for 5 h at 100–120 °C. By following the same procedure, composites with different molar ratios of MnV₂O₆ : BiVO₄ i.e., 0.25 : 1.00, 0.50 : 1.00, 0.75 : 1.00, and 1.00 : 1.00 were synthesized by varying the amounts of reagents and labeled as S-III, S-IV, S-V and S-VI, respectively (Scheme 1).

2.1.4 Characterization of MnV₂O₆/BiVO₄ heterojunction. A Bruker Alpha-T spectrometer was employed to obtain FT-IR spectra of the synthesized heterojunction samples. UV-visible spectra of the fabricated heterojunction and organic dyes were obtained on a Shimadzu/UV-2600 UV-vis spectrophotometer at high resolution in a scan range of 200–800 nm using a transparent quartz cuvette of 1 cm width. An X-ray diffractometer was used to obtain XRD powder patterns of pure as well as doped samples. Topographic details of the heterojunction samples were visualized by using a FESEM, Carl Zeiss Supra 55 equipped with an EDS to perform elemental and chemical analysis of the samples. Highly magnified TEM images of the internal structure and size of particles were obtained using a JEOL JEM 2100 PLUS. The photoluminescence (PL) spectra were obtained at room temperature using a spectrofluorometer (HORIBA Fluoromax plus CP-011).

2.1.5 Photocatalysis experiments. The photocatalytic performance of the synthesized BiVO₄, MnV₂O₆ and MnV₂O₆/BiVO₄ heterojunction samples with different molar ratios was estimated by degradation of organic dyes MB and RhB in natural sunlight. Day light from 9:30 am to 2:30 pm was utilized to perform the photocatalytic experiments. In this typical reaction, 50 mL solution of the organic dye MB (25 mg L⁻¹) was prepared in DDW with continuous magnetic stirring for 20 min. To this solution, 50 mg of the synthesized catalyst was added. Then, the solution was placed in natural sunlight. At standard
time spans, 5 mL of this solution was taken out, filtered to eliminate the catalyst and then centrifuged for 10 min. The progress of degradation was monitored by determining the absorbance of this centrifuged solution. The photocatalytic efficiency of pure BiVO₄ and pure MnV₂O₆ was compared by degrading MB and RhB dyes separately, under identical reaction conditions.

2.1.6 Photocatalytic reduction test of 4-nitrophenol. The catalytic performance of MnV₂O₆/BiVO₄ heterojunction for reduction was investigated using 4-nitrophenol (4-NP). In this process, a freshly prepared solution of NaBH₄ (1.0 mM) in distilled water was thoroughly mixed with a 50 mL solution of 4-NP (0.2 mM) in a beaker, and stirred on a magnetic stirrer. The colour of the solution instantly transformed to colorless from yellow. Subsequently, 15 mg of the heterojunction was put into the above solution. The reaction progress at room temperature was monitored by using a UV-visible spectrophotometer at equal gaps of time.

3. Results and discussion

The as-synthesized MnV₂O₆/BiVO₄ heterojunction was characterized using various sophisticated techniques like UV, FTIR, XRD, FESEM, HRTEM and XPS. UV-vis diffuse reflectance spectroscopy (DRS) of S-I to S-VI samples was performed and the results are displayed in Fig. S1 (ESI†). The band gap (E_g) values of BiVO₄ and MnV₂O₆ were found to be 2.5 eV & 1.60 eV, respectively, which agree with previous findings.22,26 The band gap of MnV₂O₆/BiVO₄ heterojunction samples i.e. S-III to S-VI was found to be 2.2, 2.1, 1.95 and 1.90 eV, respectively, signifying that the incorporation of MnV₂O₆ diminishes the band gap of BiVO₄. Moreover, this diminution affirms electronic coupling between MnV₂O₆ and BiVO₄.

FTIR spectra of pure BiVO₄, MnV₂O₆ and MnV₂O₆/BiVO₄ heterojunctions with varied molar ratios are shown in Fig. 1. The band in the 600–800 cm⁻¹ region was assigned to symmetric and asymmetric vibrations of the VO₄³⁻ group. The peak at 750 cm⁻¹ is attributed to the vibrations of Bi–V bonds, and stretching vibration of the V–O double bond is present at 1366 cm⁻¹.27 The sharp peaks in 600–1000 cm⁻¹ region for MnV₂O₆ are attributed to the vibrations of V–O–V bonds. Short V–O bonds gave an absorption band at 903 cm⁻¹ and that of longer V–O bonds appeared at 815 cm⁻¹. In the FTIR spectra of MnV₂O₆/BiVO₄ heterojunction samples with different molar ratios, some additional peaks were observed as the amount of MnV₂O₆ increased. This observation confirmed that no structural change happened in the synthesized heterojunction composite. Sharp peaks in the region 1500–1550 cm⁻¹ were
observed for all composites and correspond to interactions of two metals. A clear sharp band at 1700 cm\(^{-1}\) could be attributed to the metal–oxygen stretching vibrations. The O–H stretching vibrations of lattice water molecules were observed at 3750 cm\(^{-1}\). Change in the peak intensity of BiVO\(_4\) was noticed which might be due to the interactions of both the semiconductors through the formed interface. IR data of composites with different molar ratios confirmed that both BiVO\(_4\) and MnV\(_2\)O\(_6\) semiconductors coexist in the composite.

The XRD patterns of synthesized BiVO\(_4\), MnV\(_2\)O\(_6\) and MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunctions are shown in Fig. 2. It can be noticed from the XRD pattern of BiVO\(_4\) semiconductor (Fig. 2S-I) that the diffraction peaks can be entirely indexed to a monoclinic phase (JCPDS card-96-901-3438). The corresponding peaks are displayed in the XRD spectrum of BiVO\(_4\) at 2\(\theta\) = 18.7 (4.74 \(\AA\)), 28.9 (3.07 \(\AA\)), 30.7 (2.92 \(\AA\)), 34.6 (2.59 \(\AA\)), 35.3 (2.54 \(\AA\)), 39.7 (2.26 \(\AA\)), 42.3 (2.13 \(\AA\)), 46.7 (1.94 \(\AA\)), 50.3 (1.81 \(\AA\)), 53.5 (1.71 \(\AA\)), 58.7 (1.54 \(\AA\)) and 59.6 (1.43 \(\AA\)). Peaks at 28, 29 and 30 \(\theta\) (Fig. 2S-II) clearly show that the diffraction peaks match the provided data remarkably well (JCPDS card-96-711-9177), and no phase impurity was observed. The corresponding peaks are exhibited in the XRD spectra of MnV\(_2\)O\(_6\) at 2\(\theta\) = 9.5 (9.25 \(\AA\)), 11.5 (7.65 \(\AA\)), 17.5 (5.07 \(\AA\)), 19.2 (3.45 \(\AA\)), 25.8 (3.34 \(\AA\)), 27.1 (3.29 \(\AA\)), 28.3 (3.16 \(\AA\)), 28.9 (2.13 \(\AA\)), 31.5 (2.83 \(\AA\)), 33.4 (2.67 \(\AA\)), 35.0 (2.56 \(\AA\)), 52.1 (1.75 \(\AA\)) and 53.4 (1.71 \(\AA\)) with indices (001), (100), (101), (002), (102), (011), (201), (003), (111), (302), (103), (401) and (121), respectively. When a small amount of MnV\(_2\)O\(_6\) was introduced, no diffraction peaks of MnV\(_2\)O\(_6\) were observed in the XRD pattern of MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction (Fig. 2S-II). With an increase of MnV\(_2\)O\(_6\) content, S-III, S-IV, S-V and S-VI displayed diffraction peaks of both BiVO\(_4\) and MnV\(_2\)O\(_6\), demonstrating the effective fabrication of MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction. In order to find typical crystallite size of the samples, Debye–Scherer equation was employed. The crystallite sizes were observed as 32.7 (S-I), 34.01 (S-II), 31.35 (S-III), 25.49 (S-IV), 40.6 (S-V) and 40.1 nm (S-VI).

FESEM was performed to explore the morphology of synthesized heterojunction (Fig. 3a and b). The MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction demonstrated a belt-like morphology with a length of 8–10 \(\mu\)m (Fig. 3a). Fig. 3b illustrates that the MnV\(_2\)O\(_6\)/BiVO\(_4\) nano-belts were homogeneously mixed to form an interface between the two materials, i.e., MnV\(_2\)O\(_6\) and BiVO\(_4\), and the thickness of nanobelts was tens of nanometers. The FESEM micrograph of pure BiVO\(_4\) nanoparticles displayed a rod-like structure with a high degree of homogeneity. Pure MnV\(_2\)O\(_6\) nanoparticles have a globular structure with agglomeration (Fig. S2†). The morphology of the heterojunction was further explored by HRTEM (Fig. 3c and d). It was revealed that MnV\(_2\)O\(_6\) particles were homogeneously mixed with BiVO\(_4\) nanoparticles, and particle size of the resulting composite material was in 35–45 nm range which is comparable to that obtained from the XRD results. The corresponding SAED pattern showed clear ring patterns confirming the formation of polycrystalline MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction.

The chemical states of as-synthesized MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction were examined by XPS. Elements C, Mn, V, O and Bi were confirmed by the survey scan of XPS spectra (Fig. 4a). The high-resolution C 1s spectrum of MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction (Fig. 4b) may be deconvoluted into two dissimilar peaks at 286.8 eV and 284.5 eV which are attributed to epoxide C (O–C–O) and C=–C sp\(^2\) hybridized material, respectively.\(^{39}\) Peaks at 529.5 and 530.78 eV in the O 1s spectrum (Fig. 4c) are ascribed to the
oxygen bonded inside an oxide crystal (O²⁻) in the composite, and –OH groups adsorbed on the surface, respectively.²¹,²² For the V 2p orbital (Fig. 4d), binding energy peaks at 524.1 eV and 516.7 eV relate to V, 2p₁/₂ and V, 2p₃/₂ which originate from the V 2p orbital (Fig. 4d), binding energy peaks at 524.1 eV and V⁵⁺.

O were also examined by XPS. Elements C, Mn, V and O and C, V, Bi and their wavelength values using the PL technique, and based on intensity of these emissions can be recorded corresponding to band gap energy values of the semiconductor. The to the ground state, various emissions are generated, depending upon band gap energy values of the semiconductor. The intensity of these emissions can be recorded corresponding to their wavelength values using the PL technique, and based on their intensity, the rate of recombination of active charged species can be detected. The PL spectra of pure BiVO₄, pure MnV₂O₆, and BiVO₄/MnV₂O₆ heterojunction are shown in Fig. S4. For the pure BiVO₄ semiconductor material, excitation occurred at 325 nm wavelength and corresponding to this excited energy, a broad band in the region of 550–650 nm was produced in the emission spectrum. Pure MnV₂O₆ showed excitation at 450 nm and delivered a highly intense peak at 562 nm. The intensity of these pure compounds was much higher as compared to that of the hybrid BiVO₄/MnV₂O₆ heterojunction photocatalyst which confirmed successful separation of active charged species (electron–hole pairs) and reduced recombination rate which favored high photocatalytic activity of the heterojunction.

3.1 Photocatalytic reduction of 4-nitrophenol over MnV₂O₆/BiVO₄ heterojunction

The waste water disposed off by industries probably contains hazardous nitrophenols and their derivatives. The main sources of nitrophenols and their derivatives are insecticide, synthetic dye and herbicide manufacturing industries.²⁶ Hence, the elimination of these hazardous chemicals from industrial effluents is vital before it is discharged into water bodies. However, it is hard to remove these compounds by regular microbial degradation due to their natural and artificial stability.²⁷ Thus, it is essential to build up environment responsive strategies to remove such contaminants from waste effluents.²⁸ UV-visible spectra during the reduction of 4-nitrophenol (4-NP) by NaBH₄ using MnV₂O₆/BiVO₄ heterojunction as a catalyst are given in Fig. 6. The absorption peak of the aqueous solution of yellow coloured 4-NP was observed at 317 nm. When an aqueous solution of NaBH₄ was added, a red-shift was noticed at ~400 nm owing to the generation of nitrophenolate anion (Fig. S5†). The absorption peak at 400 nm remained invariable for a prolonged period, suggesting that 4-nitrophenolate ions could not be reduced by sole NaBH₄ in the absence of as-synthesized catalyst. Pure MnV₂O₆ and BiVO₄ nanoparticles illustrated little activity and hence, both of them can’t be considered worthwhile catalysts for 4-NP reduction. However, 4-NP was effortlessly reduced using both, NaBH₄ and MnV₂O₆/BiVO₄ heterojunction. The absorption peak corresponding to 4-NP at 400 nm progressively diminished and almost vanished after 40 min (Fig. 6a). Meanwhile, another absorption peak at ~297 nm corresponding to 4-amino phenol (4-AP) with increasing intensity emerged. This outcome confirmed the comprehensive transformation of 4-NP to 4-AP without the production of intermediates as established in earlier reports also.²⁹ Absorbance and concentration of the solution are proportionate to each other and hence, absorbance Aₜ (t = 0) corresponds to the initial concentration, and absorbance Aₜ corresponds to the concentration at time t (Cₜ). The rate constant (k) was evaluated from the plot of ln(Cₜ/C₀) vs. time (min) and its values were determined to be 0.0118, 0.0120, 0.008, 0.030, 0.12 and 0.045 min⁻¹ for S-I, II, III, IV, V and VI, respectively for reduction of 4-NP (Fig. 6b).
3.2 Photocatalysis of dyes over MnV$_2$O$_6$/BiVO$_4$ heterojunction

The photocatalytic activities of pure MnV$_2$O$_6$ and BiVO$_4$ semiconductors as well as those of MnV$_2$O$_6$/BiVO$_4$ heterojunctions were assessed by degrading MB and RhB dyes in solar light. The photocatalytic performance of MnV$_2$O$_6$/BiVO$_4$ heterojunctions was optimized w.r.t. solution pH, varying photocatalyst dosage and lapse of time, to achieve maximum degradation.

The degradation results were recorded over a wide range of photocatalyst amounts and pH. It was noticed that dye degradation performance varied as a function of the amount of MnV$_2$O$_6$/BiVO$_4$ heterojunction photocatalyst. As expected, the amount of MnV$_2$O$_6$/BiVO$_4$ heterojunction photocatalyst for the degradation of both MB and RhB dyes followed the order: 50 > 40 > 30 and 20 mg. The increase in photocatalyst amount from 20 mg to 50 mg leads to an increase in dye degradation from 25...
to 98.1% and 23 to 96.2%, respectively, for MB and RhB dyes. Evidently, the enhancement of degradation proficiency with an increase in the amount of heterojunction is primarily attributed to the increased number of active sites on the surface of MnV2O6/BiVO4 photocatalyst for UV light absorption.

The pH of solution is another most essential factor in photocatalytic degradation. Fig. S6† presents the effect of pH (range 3–10) on the degradation of both the dyes over MnV2O6/BiVO4 heterojunction photocatalyst. It was observed that both the MB and RhB dyes degraded to a maximum extent at pH 7 compared to lower or higher pH values. This behavior might be due to the formation of Fenton’s reagent at a lower pH and at a higher pH, MnV2O6/BiVO4 photocatalyst could leach into solution and form chemical sludge. Therefore, it was found that the as-synthesized photocatalyst was more efficient at pH 7.

The photocatalytic degradation of aqueous solutions of MB and RhB dyes over MnV2O6/BiVO4 heterojunction photocatalyst as a function of time was examined by UV-visible spectroscopy (Fig. S7†). A drastic decrease in absorption peak intensity with time was noticed, and the peak nearly disappeared within 6 and 35 min, respectively, for MB and RhB dyes.

It is clear from Fig. 7a that pure semiconductors BiVO4 (S-I) and MnV2O6 (S-II), and heterojunction photocatalysts, S-III, IV, V & VI have degraded 56, 45, 70, 86, 98 & 98.5% of MB dye after 6 min of sunlight irradiation. To endorse the self-photosensitization methodology, a blank experiment was likewise accomplished in the absence of catalyst under identical experimental conditions, and negligible degradation was noticed. When the catalyst was added to the dye solution, significant dye degradation was observed, indicating that the photocatalytic measure is largely responsible for dye degradation. To further investigate the photocatalytic efficiency of MnV2O6/BiVO4 heterojunction composite, the COD experiment was performed. The calculated COD value for MB and RhB solutions decreased from 160 to 40 mg L\(^{-1}\) and 115 to 37 mg L\(^{-1}\), respectively. These results showed that the mineralization yield of composite reached a value of 75% and 68%, respectively, for MB and RhB dyes, after irradiation with direct sunlight.

In addition, kinetic models were employed to comprehend the photocatalytic degradation process of MB dye. Similarly, a comparable performance for degradation of RhB dye under solar light in the presence of MnV2O6/BiVO4 heterojunction photocatalyst was observed (Fig. 7b). It was demonstrated from Fig. 7b that the intensity of absorption peak diminished appreciably with the passage of time, signifying the efficient disintegration of RhB dye using the MnV2O6/BiVO4 heterojunction photocatalyst. The debasement productivity of RhB dye over S-I, II, III, IV, V & VI was determined to be 47, 45, 58.7, 96 and 96.1%, respectively, after 35 min of sunlight irradiation.
In the heterogeneous photocatalytic degradation process of organic pollutants, various active species comprising superoxide (\(\cdot \text{O}_2^\cdot\)) anion radicals, hydroxide (\(\cdot \text{OH}\)) radicals, and photogenerated electrons (\(\cdot \text{e}^\cdot\)) and holes (\(h^+\)) are created under appropriate light irradiation. To figure out the active species that assumes a significant role in dye photodegradation utilizing MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction on irradiation by sunlight, different types of examinations on extinguishing active species were carried out by addition of separate scavengers in the reaction mixture. For this purpose, isopropyl alcohol (IPA), potassium iodide (KI) and benzoquinone (BQ) were employed for scavenging \(\cdot \text{OH}\), \(h^+\) and \(\cdot \text{O}_2^\cdot\) radicals, respectively. Due to extinguishing of active species, photocatalytic response is little restrained and prompts modest degradation of both the dyes. The degree of decline brought about by scavengers in degradation demonstrated the role of competing responsive species.

Fig. 7(a) and (b) illustrate that photodegradation of both the dyes over MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunction was considerably influenced on addition of scavengers. The degradation of dyes was significantly suppressed on addition of BQ (\(\cdot \text{O}_2^\cdot\) scavenger) which indicated a crucial role of ‘\(\cdot \text{O}_2^\cdot\)’ in the photodegradation procedure. The photodegradation activity of MnV\(_2\)O\(_6\)/BiVO\(_4\) only marginally decreased on introducing IPA and KI which suggested that both ‘\(\cdot \text{OH}\) and \(h^+\) have a minor but synergistic role in the degradation reaction.\(^{36,42}\)

### 3.3 Plausible mechanism of photodegradation

In the light of results obtained, a tentative mechanism has been suggested to clarify the improved photocatalytic activity of MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunctions (Fig. 8). To perceive the band positions of MnV\(_2\)O\(_6\)/BiVO\(_4\) heterojunctions, the potentials at conduction band (CB) and valence band (VB) edges of MnV\(_2\)O\(_6\) & BiVO\(_4\) semiconductors were designed using the equations below:\(^{23}\)

\[
E_{\text{CB}} = \chi - E^\circ - 0.5E_g
\]

\[
E_{\text{VB}} = E_{\text{CB}} + E_g
\]

where \(E_{\text{CB}}, E_{\text{VB}}, E^\circ\) and \(\chi\) denote the potential of CB & VB bands, energy of free electrons vs. hydrogen (4.5 eV) and electronegativity (\(\chi\)) of the semiconductor, respectively.\(^{41}\) The following equation was used to get the value of \(\chi\):

\[
\chi = \left[\frac{\chi(A)^a \chi(B)^b}{a + b}\right]^{1/2}
\]

The constants \(a\) and \(b\) denote the number of atoms in the compounds.\(^{44}\) \(E_g, \chi, E_{\text{CB}}\) and \(E_{\text{VB}}\) values for BiVO\(_4\) were found to be 2.50 eV, 6.04 eV, +0.29 and +2.79 eV/NHE, respectively and are comparable to the reported values.\(^{45,46}\) The values of \(E_g\) and \(\chi\) for MnV\(_2\)O\(_6\) are 1.60 eV and 5.90 eV, respectively. Consequently, \(E_{\text{CB}}\) and \(E_{\text{VB}}\) values for MnV\(_2\)O\(_6\) were determined to be +0.60 and +2.20 eV/NHE.

In the light of above discussion and knowledge of active species involved, a potential mechanism for the degradation of organic dyes utilizing BiVO\(_4\)/MnV\(_2\)O\(_6\) heterojunction has been projected as follows and is displayed in Fig. 8. When sunlight was

![Fig. 7](image1.png)

**Fig. 7** Plot illustrating the concentration change of the MB and RhB dyes as a function of time of irradiation.

![Fig. 8](image2.png)

**Fig. 8** A plausible mechanism for organic pollutant removal over BiVO\(_4\)/MnV\(_2\)O\(_6\) heterojunction under direct sunlight illumination.
illuminated over BiVO₄/MnV₂O₆ heterojunction, the photons approaching the photocatalyst were hopefully consumed by BiVO₄ and MnV₂O₆ counterparts, prompting the production of a few electron–hole pairs. BiVO₄ has a high negative \( \eta \) at band capability in comparison to MnV₂O₆. As a result, the electrons continue to move towards MnV₂O₆ from BiVO₄ till the Fermi level stability of both is accomplished. Concurrently, OH is generated by oxidation of adsorbed H₂O molecules by the photoinduced holes of the VB of MnV₂O₆ and BiVO₄ semiconductors. Simultaneously, the electrons gathered on the exterior of MnV₂O₆ interact with the adsorbed oxygen to generate \( \cdot O₂⁻ \). Hence, the produced active species like OH⁻, \( h^+ \) and \( \cdot O₂⁻ \) efficiently break down the dye molecules to CO₂, H₂O and non-toxic inorganic

### Table 1: Comparison of heterojunctions for photocatalytic degradation of organic contaminants

| Sr. no. | Photocatalyst/ Method of synthesis | Catalyst dosage (mg) | Pollutant/conc. | Source of light/time in min | Photocatalytic efficiency (%) | Ref. |
|---------|------------------------------------|----------------------|-----------------|----------------------------|-------------------------------|------|
| 1       | ZnO/Ag₂O Photochemical route        | 20                   | MB/3.12 × 10⁻⁵ mol L⁻¹ | 250 W UV, 500 W Xe lamp/4 | 99.5                          | 47   |
| 2       | AgBr/Bi₂WO₆ Hydrothermal           | 200                  | MB/10 mg L⁻¹     | 500 W Xe lamp/30 min       | 100                           | 48   |
| 3       | Ag₂O/TiO₂ Sol gel                 | 10                   | 4-NP/200 ppm     | Solar/210 s                | 100                           | 49   |
| 4       | Ni₃P/Ni₃P Solvothermal             | 15                   | 4-NP/14 mg L⁻¹   | Solar/8 min                | 100                           | 50   |
| 5       | CuO/ZnO Hydrothermal              | 30                   | MB/5 mg L⁻¹      | Solar radiation/210 min    | 97                            | 51   |
| 6       | CuSeSe₂/TiO₂ Microwave method     | 100                  | RbH/MB/100 ppm   | Long UV-A radiation/275 min | 75.93 (MB), 42.72 (RbH)       | 52   |
| 7       | CuO/g-C₃N₄ Ultrasound              | 10                   | 4-NP/20 ppm      | 35 W Xe lamp/100 min       | 92                            | 53   |
| 8       | Ag-CuO/g-C₃N₄ Hydrothermal         | 100                  | 4-NP/100 ppm     | Ni light irradiation/4 min  | 97.8                          | 54   |
| 9       | CeO₂/CuO/ Chemical precipitation  | 125                  | MB (5 mg L⁻¹)/RbH | LED lamp/80 min            | 58.46 (MB), 84.79 (RbH)       | 55   |
| 10      | Bi₂Zr₂O₇/ Hydrothermal             | 50                   | RbH/MB & 4-NP    | Solar light/200 min        | 84 (RbH), 90 (MB), 100 (4-NP) | 56   |
| 11      | WO₃-BPNs Co-precipitation          | 50                   | RbH/10 mg L⁻¹    | 350 W Xe lamp/120 min      | 92                            | 57   |
| 12      | MOF/P-TiO₂ Self-assembly hydrothermal | 10              | RbH/10 ppm       | 300 W Xe/25 min            | 97.6                          | 58   |
| 13      | MnV₂O₆/ BiVO₄ One pot hydrothermal | 50                   | 4-NP, MB & RbH (25 mg L⁻¹) | Direct sunlight, 35 (4-NP), 6 (MB), 35 RbH | 100 (4-NP), 98 (MB), 96 (RbH) | Present work |

### Table 2: Various factors of the kinetic models for degradation of MB dye

| Semiconductor/ heterojunction | First order \( K_1 \) & \( R^2 \) | Second order \( K_2 \) & \( R^2 \) |
|------------------------------|--------------------------------------|--------------------------------------|
| S-I                          | 0.063 & 0.98                         | 3.2 × 10³ & 0.89                     |
| S-II                         | 0.045 & 0.98                         | 11.3 × 10³ & 0.98                    |
| S-III                        | 0.096 & 0.98                         | 4.6 × 10³ & 0.93                     |
| S-IV                         | 0.183 & 0.99                         | 3.0 × 10³ & 0.91                     |
| S-V                          | 0.283 & 0.98                         | 28.3 × 10³ & 0.99                    |
| S-VI                         | 0.374 & 0.97                         | 2.9 × 10³ & 0.86                     |

**Fig. 9** Graph of (a) pseudo first and (b) second order kinetics models for degradation of MB dye over MnV₂O₆/BiVO₄ heterojunction.
products. A comparison of photocatalytic efficiency of some heterojunctions for degradation of organic contaminants is presented in Table 1.

3.4 Photocatalytic degradation kinetics

Furthermore, pseudo first and second order models were used to explore the kinetics of dye degradation. The pseudo first order rate equation of Langmuir is given as: 

\[ \log(q_e - q_t) = \log q_e - k_1 t \]

where \( q_e \) and \( q_t \) denote the concentration of dye adsorbed at equilibrium and at any time \( t \), and the first order rate constant is represented by \( k_1 \).

The plot of \( \log(q_e - q_t) \) vs. \( t \) for pseudo first order kinetics of MB dye is shown in Fig. 9a. The calculated values of \( k_1 \) and \( R^2 \) are given in Table 2.

The pseudo-second order rate equation was also applied to MB dye and is represented as:

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \]

where \( K_2 \) is the second order rate constant. Fig. 9b demonstrates the plot of \( \frac{t}{q_t} \) vs. \( t \) for pseudo second order kinetics of MB dye and \( K_2 \) and \( R^2 \) values are given in Table 2.

A similar process was established for rhodamine B (RhB) for thorough comparison of kinetics. Fig. 10(a and b) presents both the kinetic models for the degradation of RhB dye.

| Semiconductor/heterojunction | First order | Second order |
|------------------------------|-------------|--------------|
|                              | \( K_1 \)  | \( R^2 \)  |
| S-I                          | 0.0006      | 0.993        |
| S-II                         | 0.0044      | 0.993        |
| S-III                        | 0.0111      | 0.993        |
| S-IV                         | 0.0136      | 0.993        |
| S-V                          | 0.0413      | 0.993        |
| S-VI                         | 0.0413      | 0.993        |

The calculated \( K_1 \), \( K_2 \) and \( R^2 \) values for RhB dye are given in Table 3. Furthermore, the model’s applicability is examined using the \( R^2 \) values of all photocatalyst samples.

Interestingly, the results of kinetic models for the dyes are different. The \( R^2 \) value for MB dye varies from 0.97 to 0.99, and 0.86 to 0.99 for pseudo first and second order kinetic models,
respectively. For RhB dye, $R^2$ varies from 0.91 to 0.99 and 0.96 to 0.99 for first and second order kinetic models, respectively. As a result, the data indicate that photocatalytic degradation of MB dye used a pseudo-first order process, whereas RhB dye used a pseudo-second order mechanism.

The cycling tests were performed to check the stability and reusability of MnV$_2$O$_6$/BiVO$_4$ heterojunction (S-V) for photocatalytic degradation of MB and RhB dyes in solar light. The activity of the heterojunction was retained to a significant extent even after four consecutive cycles (Fig. 11a). The crystallinity and crystal structure of the photocatalyst were retained after four consecutive cyclic runs which is supported by the XRD pattern (Fig. 11b). The absence of leaching on the exterior throughout the photocatalytic response might be responsible for the insignificant drop in photocatalytic execution. These results indicate equitable stability and reusability of the synthesized heterojunction with extensive activity.

4. Conclusions

MnV$_2$O$_6$/BiVO$_4$ heterojunction samples were prepared employing a hydrothermal technique. Among the synthesized samples, MnV$_2$O$_6$/BiVO$_4$ heterojunction sample (S-V) with a ratio of 0.75 : 1.00 (MnV$_2$O$_6$ : BiVO$_4$) showed the best performance under direct sunlight exposure for MB and RhB dye degradation. The active species playing the most significant role in dye photodegradation with MnV$_2$O$_6$/BiVO$_4$ heterojunction was determined by employing isopropl alcohol (IPA), potassium iodide (KI) and benzoquinone (BQ) as scavengers for ‘OH, h$^+$ and ‘O$_2^-$ radicals, respectively. The results revealed that degradation of dyes was significantly suppressed with BQ suggesting that ‘O$_2^-$ played a key role in the photocatalytic degradation process. Furthermore, MnV$_2$O$_6$/BiVO$_4$ heterojunction also successfully reduced 4-NP into 4-AP in a time span of 40 min without the production of any intermediates. This study provides an easy and speedy process for the degradation of toxic contaminants in waste water using direct sunlight.

Conflicts of interest

There are no conflicts to declare.

References

1. D. Shahidi, R. Roy and A. Azzouz, Advances in catalytic oxidation of organic pollutants – Prospects for thorough mineralization by natural clay catalysts, Appl. Catal., B, 2015, 174, 277–292.
2. A. Chatterjee, S. Shamim, A. K. Jana and J. K. Basu, Insights into the competitive adsorption of pollutants on a mesoporous alumina–silica nanosorbent synthesized from coal fly ash and a waste aluminium foil, RSC Adv., 2020, 10, 15514–15522.
3. N. Kaur, J. Kaur, R. Badru, S. Kaushal and P. P. Singh, BGO/AlFu MOF core shell nano-composite based bromide ion-selective electrode, J. Environ. Chem. Eng., 2020, 8, 104375.
4. C. Bradu, M. Magureanu and V. I. Parvulescu, Degradation of the chlorophenoxyacetic herbicide 2,4-D by plasma-ozonation system, J. Hazard. Mater., 2017, 336, 52–56.
5. M. Bilal and H. M. N. Iqbal, Microbial bioremediation as a robust process to mitigate pollutants of environmental concern, Case Studies in Chemical and Environmental Engineering, 2020, 2, 100011.
6. M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, Recent developments in photocatalytic water treatment technology: a review, Water Res., 2010, 44, 2997–3027.
7. M. Ni, M. K. H. Leung, D. Y. C. Leung and K. Sumathy, A review and recent developments in photocatalytic water-splitting using TiO$_2$ for hydrogen production, Renewable Sustainable Energy Rev., 2007, 11, 401–425.
8. M. Muuronen, S. M. Parker, E. Berardo, A. Le, M. A. Zwijnenburg and F. Furche, Mechanism of Photocatalytic Water Oxidation on Small TiO$_2$ Nanoparticles, Chem. Sci., 2017, 8, 2179–2183.
9. F. Lin, Z. Shao, P. Li, Z. Chen, X. Liu, M. Li, B. Zhang, J. Huang, G. Zhu and B. Dong, Low-cost dual cocatalysts BiVO$_4$ for highly efficient visible photocatalytic oxidation, RSC Adv., 2017, 7, 15053.
10. P. R. Paivaa and T. Noel, Application of Metal Oxide Semiconductors in Light-Driven Organic Transformations, Catal. Sci. Technol., 2019, 9, 5186–5232.
11. H. Xu, S. Ouyang, L. Liu, P. Reunchan, N. Umezawaace and J. Ye, Recent advances in TiO$_2$-based photocatalysis, J. Mater. Chem. A, 2014, 2, 12642.
12. X. Shena, H. Shao, Y. Liua and Y. Zhai, Synthesis and photocatalytic performance of ZnO with flower-like structure from zinc oxide ore, J. Mater. Sci. Technol., 2020, 51, 1–7.
13. M. Ganeshbabu, N. Kannan, P. S. Venkatesh, G. Paulraj, K. Jeganathan and D. M. Ali, Synthesis and characterization of BiVO$_4$ nanoparticles for environmental applications, RSC Adv., 2020, 10, 18315.
14. L. Suna, J. Suna, X. Yang, S. Bai, Y. Feng, R. Luo, D. Li and A. Chen, An integrating photoanode consisting of BiVO$_4$, rGO and LDH for photoelectrochemical water splitting, Dalton Trans., 2019, 48, 16091–16098.
15. H. Hirakawa, S. Shiota, Y. Shiraiishi, H. Sakamoto, S. Ichikawa and T. Hirai, Au Nanoparticles Supported on BiVO$_4$: Effective Inorganic Photocatalysts for H$_2$O Production from Water and O$_2$ under Visible Light, ACS Catal., 2016, 6, 4976–4982.
16. X. Xu, M. Du, T. Chen, S. Xiong, T. Wu, D. Zhao and Z. Fan, New insights into Ag-doped BiVO$_4$ microspheres as visible light photocatalysts, RSC Adv., 2016, 6, 98788.
17. J. H. Baek, T. M. Gill, H. Abroshan, S. Park, X. Shi, J. Norskov, H. S. Jung, S. Siahrostami and X. Zheng, Selective and Efficient Gd-Doped BiVO$_4$Photoanode for Two-Electron Water Oxidation to H$_2$O$_2$, ACS Energy Lett., 2019, 4, 720–728.
18. C. Regmi, T. H. Kim, S. K. Ray, T. Yamaguchi and S. W. Lee, Cobalt-doped BiVO$_4$ (Co-BiVO$_4$) as a visible-light-driven photocatalyst for the degradation of malachitegreen and inactivation of harmful microorganisms in wastewater, Res. Chem. Intermed., 2017, 43, 5203–5216.
23 S. Kaushal, P. Kurichh, K. Kaur and P. P. Singh, Novel 3D BiVO4 photocatalytic activity of a g-C3N4/BiVO4 nanocomposite: a first-principles study, Phys. Chem. Chem. Phys., 2015, 17, 10218.

24 M. Nithya, S. Vidhya and K. Praveen, A Novel g-C3N4/MnV2O6 heterojunction photocatalyst for the Removal of imidacloprid and photocatalyst for degradation of organic dyes in waste water, Polyhedron, 2021, 201, 115161.

25 M. Nithya, S. Vidhya and K. Praveen, A Novel g-C3N4/MnV2O6 Heterojunction Photocatalyst for the Removal of Methylene Blue and Indigo Carmine, Chem. Phys. Lett., 2019, 737, 136832.

26 M. Yan, Y. Yan, Y. Wu, W. Shi and Y. Hua, Microwave-assisted synthesis of monoclinic-tetragonal BiVO4 heterojunctions with enhanced visible-light-driven photocatalytic degradation of Tetracycline, RSC Adv., 2015, 5, 90255.

27 F. Guo, W. Shi, X. Lin and G. Che, Hydrothermal synthesis of graphitic carbon nitride–BiVO4 composites with enhanced visible light photocatalytic activities and the mechanism study, J. Phys. Chem. Solids, 2014, 75, 1217–1222.

28 Y. Singh, S. Kaushal and R. S. Sodhi, Biogenic synthesis of silver nanoparticles using cyanobacterium Leptolyngbya sp. WUC 59 cell-free extract and their effects on bacterial growth and seed germination, Nanoscale Adv., 2020, 2, 3972–3982.

29 M. V. Kite, D. J. Sathe, A. N. Kadam, S. S. Chavan and K. M. Garadkar, Highly efficient photodegradation of 4-nitrophenol over the nano-TiO2 obtained from chemical bath deposition technique, Res. Chem. Intermed., 2020, 46, 1255–1282.

30 S. Kaushal, N. Kaur, M. Kaur and P. P. Singh, Dual-responsive pectin/graphene oxide (PC/GO) nano-composite as an efficient adsorbent for Cr(III) ions and photocatalyst for degradation of organic dyes in waste water, J. Photochem. Photobiol., A, 2020, 403, 112841.

31 T. Palaniselvam, L. Shi, G. Mettela, D. H. Anjum, R. Li, K. P. Katuri, P. E. Saikaly and P. Wang, Vastly Enhanced BiVO4 Photocatalytic OER Performance by NiCo2O4 as Cocatalyst, Adv. Mater. Interfaces, 2017, 4, 1700540.

32 S. Long, W. Cai, J. Cai, B. Zhou, X. Chai and Y. Wu, Efficient Photocatalytic Degradation of Phenol over Co3O4/BiVO4 Composite under Visible Light Irradiation, J. Phys. Chem. B, 2006, 110, 20211–20216.

33 Z. Zhang, M. Wang, W. Cui and H. Sui, Synthesis and characterization of a core–shell BiVO4@g-C3N4 photocatalyst with enhanced photocatalytic activity under visible light irradiation, RSC Adv., 2017, 7, 8167–8177.

34 M. Guo, Y. Wang, Q. He, W. Wang, W. Wang, Z. Fu and H. Wang, Enhanced photocatalytic activity of S-doped BiVO4 photocatalysts, RSC Adv., 2015, 5, 58633.

35 X. Lin, L. Yu, L. Yan, H. Li, Y. Yan, C. Liu and H. Zhai, Visible light photocatalytic activity of BiVO4 particles with different Morphologies, Solid State Sci., 2014, 32, 61–66.

36 E. Abroushan, S. Farhadi and A. Zabardasti, Ag3PO4/CoFe2O4 magnetic nanocomposite: synthesis, characterization and applications in catalytic reduction of nitrophenols and sunlight-assisted photocatalytic degradation of organic dye pollutants, RSC Adv., 2017, 7, 18293–18304.

37 A. H. Abbar, A. H. Sulaymon and M. G. Jalhoon, Scale-up of a fixed bed electrochemical reactor consisting of parallel screen electrode used for p-aminophenol production, Electrochem. Acta, 2007, 53, 1671–1679.

38 M. Nasrollahzadeh, S. M. Sajadi, A. R. Vartooni, M. Alizadeh and M. Bagherzadeh, Green synthesis of the Pd nanoparticles supported on reduced graphene oxide using barberry fruit extract and its application as a recyclable and heterogeneous catalyst for the reduction of nitroarenes, J. Colloid Interface Sci., 2016, 466, 360–368.

39 Y. Liu, H. Xu and H. Yu, Synthesis of lignin-derived nitrogen-doped carbon as a novel catalyst for 4-NP reduction evaluation, Sci. Rep., 2020, 10, 20075.

40 K. Yu, S. Yang, C. Liu, H. Li, C. Sun and S. A. Boyd, Degradation of Organic Dyes via Bismuth Silver Oxide Initiated Direct Oxidation Coupled with Sodium Bismuthate Based Visible Light Photocatalysis, Environ. Sci. Technol., 2012, 46, 7318–7326.

41 Y. Ghaffari, N. K. Gupta, J. Bae and K. S. Kim, One-step fabrication of Fe2O3/Mn3O4 nanocomposite for rapid photodegradation of organic dyes at neutral pH, J. Mol. Liq., 2020, 315, 113691.

42 M. Mousavi, A. H. Yangieh and M. Ahitbori, Fabrication of novel magnetically separable nanocomposites using graphitic carbon nitride, silver phosphate and silver chloride and their applications in photocatalytic removal of different pollutants using visible-light irradiation, J. Colloid Interface Sci., 2016, 480, 218–231.

43 S. R. Morrison, Electrochemistry at Semiconductor and Oxidized Metal Electrode, Plenum, New York, 1980.

44 Q. Yuan, L. Chen, M. Xiong, J. He, S. L. Luo, C. T. Au and S. F. Yin, CuO/BiVO4 heterostructures: synthesis and application in simultaneous photocatalytic oxidation of organic dyes and reduction of Cr(VI) under visible light, Chem. Eng. J., 2014, 255, 394–402.
45 M. Han, T. Sun, P. Y. Tan, X. Chen, O. K. Tan and M. S. Tse, m-BiVO₄@γ-Bi₂O₃ core–shell p–n heterogeneous nanostructure for enhanced visible-light photocatalytic performance, *RSC Adv.*, 2013, 3, 24964–24970.

46 Parul, K. Kaur, R. Badru, P. Singh and S. Kaushal, Photodegradation of organic pollutants using heterojunctions: A review, *J. Environ. Chem. Eng.*, 2020, 8, 103666.

47 S. Ma, J. Xue, Y. Zhou and Z. Zhang, Photochemical synthesis of ZnO/Ag₂O heterostructures with enhanced ultraviolet and visible photocatalytic activity, *J. Mater. Chem. A*, 2014, 2, 7272.

48 D. Wang, L. Guo, Y. Zhen, L. Yue, G. Xue and F. Fu, AgBr quantum dots decorated mesoporous BiₓWₒ₆ₓ architectures with enhanced photocatalytic activities for methylene blue, *J. Mater. Chem. A*, 2014, 2, 11716–11727.

49 O. A. Zelekew and D. H. Kuo, A two-oxide nanodiode system made of double-layered p-type AgₓO@n-type TiO₂ for rapid reduction of 4-nitrophenol, *Phys. Chem. Chem. Phys.*, 2016, 18, 4405.

50 F. Y. Tian, D. Hou, W. M. Zhang, X. Q. Qiao and D. S. Li, Synthesis of NiₓP/Ni₁₋ₓP₃ bi-phase nanocomposite for efficient catalytic reduction of 4-nitrophenol based on the unique n-n heterojunction effects, *Dalton Trans.*, 2017, 46, 14107–14113.

51 Y. T. Prabhu, V. N. Rao, M. V. Shankar, B. Sreedhar and U. Pal, Facile hydrothermal synthesis of CuO@ZnO heterojunction nanostructures for enhanced photocatalytic hydrogen evolution, *New J. Chem.*, 2019, 43, 6794–6805.

52 A. S. Kshirsagar and P. K. Khanna, CuSbSe₂/TiO₂: novel type-II heterojunction nano-photocatalyst, *Mater. Chem. Front.*, 2019, 3, 437–449.

53 A. Verma, D. P. Jaihindh and Y. P. Fu, Photocatalytic 4-nitrophenol degradation and oxygen evolution reaction in CuO@g-C₃N₄ composites prepared by deep eutectic solvent assisted chlorine Doping, *Dalton Trans.*, 2019, 48, 8594–8610.

54 A. Verma, S. Kumar, W. K. Chang and Y. P. Fu, Bi-functional Ag-CuₓO@g-C₃N₄ hybrid catalysts for the reduction of 4-nitrophenol and the electrochemical detection of dopamine, *Dalton Trans.*, 2020, 49, 625–637.

55 M. M. Sabzehmeidani, H. Karimi and M. Ghaedi, Enhanced visible light-active CeO₂/CuO/Ag₂CrO₄ ternary heterostructures based on CeO₂/CuO nanofiber heterojunctions for the simultaneous degradation of a binary mixture of dyes, *New J. Chem.*, 2020, 44, 5033–5048.

56 V. Jayaraman, C. Ayappan, B. Palanivel and A. Mani, Bridging and synergistic effect of the pyrochlore like BiₓZr₂O₇ structure with robust CdCuS solid solution for durable photocatalytic removal of the organic pollutants, *RSC Adv.*, 2020, 10, 8880.

57 Q. Wang, B. Li, P. Zhang, W. Zhang, X. Hua and X. Li, 2D black phosphorus and tungsten trioxide heterojunction for enhancing photocatalytic performance in visible light, *RSC Adv.*, 2020, 10, 27538.

58 T. Zeng, D. Shi, Q. Cheng, G. Liao, H. Zhou and Z. Pan, Constructing of novel phosphonate-based MOF/P-TiO₂ Heterojunction Photocatalysts: enhanced photocatalytic performance and mechanistic insight, *Environ. Sci.: Nano*, 2020, 7, 861–879.