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Synergism of Co/Na in BiVO₄ microstructures for visible-light driven degradation of toxic dyes in water†

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In this work, we report a synergism of Co/Na in Co@Na–BiVO₄ microstructures to boost the photocatalytic performance of bismuth vanadate (BiVO₄) catalysts. A co-precipitation method has been employed to synthesize blossom-like BiVO₄ microstructures with incorporation of Co and Na metals, followed by calcination at 350 °C. The structure and morphology of the as-prepared photocatalysts are characterized by XRD, Raman, FTIR, SEM, EDX, AFM, UV-vis/DRS and PL techniques. Dye degradation activities are evaluated by UV-vis spectroscopy, in which methylene blue, Congo red and rhodamine B dyes are chosen for comparative study. The activities of bare BiVO₄, Co–BiVO₄, Na–BiVO₄, and Co@Na–BiVO₄ are compared. To evaluate the ideal conditions, various factors that affect degradation efficiencies have been investigated. The results of this study show that the Co@Na–BiVO₄ photocatalysts exhibit higher activity than bare BiVO₄, Co–BiVO₄ or Na–BiVO₄. The higher efficiencies were attributed to the synergistic role of Co and Na contents. This synergism assists in better charge separation and more electron transportation to the active sites during the photoreaction.

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1. Introduction

Water is the main natural resource covering over 70% of the earth's surface. The accessibility of safe drinking water (0.5%) is crucial not only for humans but also for the survival of other living organisms. Annually, 200 000 tons of toxic dyes are dumped into water bodies.¹ The textile, paper, leather, paint and cosmetics industries are the major contributors of these contaminants (*i.e.* toxic dyes). Such dyes are hazardous, carcinogenic and non-biodegradable effluents which cause damage to human health, plant species, environment and soil even at very low concentrations (*i.e.* less than 1 ppm).²

Common ways to remove the dyes from water are through adsorption and coagulation.³ However, these methods produce secondary pollutants because dyes are only changed from the liquid to the solid phase during adsorption and coagulation.⁴ To resolve this issue, an environment-friendly and cost-effective approach is urgently required that can utilize visible light for the removal of organic dyes from aqueous solutions.⁵

Photocatalysts accelerate the photoreactions and convert photons into chemical energy. Photocatalysts are now widely used in agriculture, medicine, electrical appliances, photo-electrochemical reactions, environmental and energy fields. A number of metal-element-doped semiconductor materials have been employed for visible light induced dye degradation for water purification purposes.⁶

BiVO₄ and TiO₂ are considered the most advantageous photocatalysts because of their photocatalytic activity, stability and non-toxicity. However, TiO₂ only responds to ultraviolet radiations, which restricts its further application.⁷ In this regard, photocatalysts that can efficiently work in the visible range are more desired. Unfortunately some visible light responsive photocatalysts have stability issues; for example, CdS is active under visible light but not stable in an aqueous system due to photocorrosion.⁸ Among the photocatalysts, BiVO₄ has been reported to be a promising candidate.⁹ Various techniques have been introduced for the development of BiVO₄ nanostructures, including the solid-state reaction,¹⁰ hydrolysis of metal alkoxides,¹¹ co-precipitation¹² and hydrothermal synthesis.¹³ Nanostructures obtained by different methods often have different crystal structures and defects that influence the photocatalytic efficiencies. Among the common synthetic protocols, the co-precipitation method was found to deliver higher yields with high purity without using organic solvents.¹⁴ Moreover, this strategy is cost effective and straight forward.

One of the common problems with BiVO₄ is the rapid recombination of photogenerated electrons with holes, which

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was measured to be 19.7 nm. The results showed that intrinsic catalytic activity of the photocatalyst is not a sole factor of particle sizes; however, the rate of dye degradation is mainly due to metal cocatalysts over BiVO₄ surfaces.²⁶

3.2 Raman spectroscopy

The structure, chemical composition and bonding of the as-synthesized materials were further analyzed by Raman spectroscopy as illustrated in Fig. 2(b). The vibration bands observed at 211, 329, 366, 638, 710, and 825 cm⁻¹ were attributed to the

VO₄ tetrahedron. The strong vibrations at 825 cm⁻¹ were allocated to the V–O symmetric stretching mode (A_g). At 710 and 638 cm⁻¹, weak asymmetric stretching bands (A_g and B_g) of V–O were observed. The asymmetric and symmetric bending vibrations of the VO₄ tetrahedron were observed at 327 and 367 cm⁻¹, respectively. In Co@Na–BiVO₄, the intense vibration mode shifted to 828 cm⁻¹ from 826 cm⁻¹. In the presence of Co and Na, a shift was observed due to the decrease in the V–O bond length. Moreover, Raman band intensities and the FWHM also shortens: this behavior corresponds to crystallinity or flaws.^{27,28}



Fig. 3 SEM images of Co@Na–BiVO₄ microstructures (a) 5 μm (b) 2 μm (c) 1 μm and (d) 500 nm, whereas (e) represents the EDX analysis.



3.3 SEM and EDX

The structural and surface morphology of the Co@Na-BiVO₄ photocatalysts were investigated by scanning electron microscopy (SEM). Fig. 3(a-d) shows the typical SEM images of the Co@Na-BiVO₄ photocatalysts. The microstructures are blossom-like due to our new synthesis, rather than the conventional structures.²⁹ The SEM results are in good agreement that Co (in the form of Co₃O₄) and Na (in the form of Na₂O) enhance the surface area of BiVO₄. The novelty of our work is that the blossom-like structures were developed using the time-scaled low temperature co-precipitation method (24 h, 10 °C), which led to an enhancement in the surface area and active sites. An EDX accessory was used to elucidate the elemental composition of the as-synthesized Co@Na-BiVO₄ photocatalysts Fig. 3(e), which confirms the presence of Co and Na contents with BiVO₄. The weights and atomic percentages of elements are tabulated in Table S1.†

3.4 AFM

Atomic force microscopy (AFM) is a characterization technique that provides information about the topography, surface roughness, size distribution, and morphology of materials at a high resolution.³⁰ The Co@Na-BiVO₄ photocatalysts were studied using AFM; the two-dimensional and three-dimensional topographical images are shown in Fig. 4(a-d). The scanning area is 9 × 9 μm, The AFM results revealed the

surface morphology of Co@Na-BiVO₄ particles with an average size of 18.4 nm, as shown in Fig. S1.† The size distribution of particles ranges from 9 to 20.5 nm.

3.5 UV-vis/DRS

To evaluate the optical properties and band gap, UV-vis/DRS results of the as-synthesized photocatalysts were obtained (Fig. 5(a)). Plain BiVO₄ shows maximum absorption at 512 nm, corresponding to its optical band gap $E_g = 2.42$ eV. For the Co@Na-BiVO₄ microstructure, the absorption edge is slightly red-shifted to 525 nm ($E_g = 2.36$ eV), showing an excellent visible light response. The absorption of the Co@Na-BiVO₄ microstructure further extends to 800 nm, which is due to Co d-d transitions³¹ and synergism of metal cocatalysts over BiVO₄.³²

3.6 PL

It is worth mentioning that our photoluminescence results confer the essential information about excitation, trapping and transfer of the charge carriers (e⁻ & h⁺). Higher recombination of e⁻ and h⁺ will result in higher emission intensities of PL signals.³³ In this work, the high PL intensities (Fig. 5(c)) indicate a higher rate of charge recombination. These results indicate the higher charge separation in Co@Na-BiVO₄ as compared to that in bulk BiVO₄. As clearly seen in Fig. 5(c), Co@Na-BiVO₄ intensity is weaker than that of BiVO₄ indicating that recombination of charges is suppressed due to the presence of Co and Na metal oxides.



Fig. 4 AFM images of Co@Na-BiVO₄ (a and b) topographical images, and (c and d) three-dimensional view.





Fig. 5 (a) UV-vis/DRS, (b) energy diagram, (c) PL spectra (both catalysts at the same concentration in ethanol) and (d) FT-IR spectra of the as-synthesized BiVO_4 and Co@Na-BiVO_4 (powders compressed into KBr pellets).

3.7 FT-IR

The FT-IR results of as-synthesized BiVO_4 and Co@Na-BiVO_4 microstructures exhibited the intense and broad absorption bands (Fig. 5(d)), due to V-O vibration at 760 cm^{-1} and 835 cm^{-1} , respectively, whereas Bi-O bending vibration was observed at 680 cm^{-1} . Additional bands are observed at 1390 cm^{-1} and 1470 cm^{-1} , which are characteristic of stretching vibrations of the absorbed atmospheric and adventitious CO_2 of the instrument. The band at 1630 cm^{-1} corresponds to the bending vibration of water due to the moisture content in KBr used in sample preparation for FT-IR analysis. In the FT-IR spectrum of Co@Na-BiVO_4 , Co and Na metal content slightly narrowed the typical absorption band.³⁴

3.8 Photocatalytic degradation studies of MB, CR and RhB

Photocatalytic dye degradation efficiencies are compared and quantified on the basis of the measured absorbance. It is important to select a suitable wavelength at which the dye solution shows the maximum absorbance. Using the Beer-

Lambert law, the amount of dye was deliberated quantitatively with the absorption of light at λ_{max} (specific to each dye).³⁵ The absorbance of dyes was observed to decrease during the photocatalytic reaction, indicating photocatalytic degradation. The efficiencies of photocatalytic degradation of each dye are determined by using the following formula:

$$\% \text{ Degradation efficiency} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C represent the concentrations before and after irradiation, respectively. In this work, MB, CR, and RhB dyes were selected for photocatalytic performances of the synthesized catalysts. For the photoreactions, 5 ppm concentration of each dye was optimized. For MB, CR, and RhB dyes, the maximum absorbance was measured at wavelengths of 664, 498 and 552 nm, respectively (Fig. 6(a)). The absorbance peak of MB at 664 nm is due to its azo groups as well as $\pi-\pi^*$ electronic excitations.³⁶ The UV-vis absorption of CR exhibits two dominant absorption peaks observed at 347 and 498 nm, and a peak observed at 347 nm, attributed to the predominant absorption





Fig. 6 UV-vis spectrophotometry results: (a) lambda max, (b) MB, (c) CR and (d) RhB obtained over Co@Na-BiVO₄ photocatalysts.

of a benzene group.^{37,38} The peak at 498 nm is due to the naphthalene group.³⁹ Similarly, the prime peak for RhB is attributed to the combined effect of four *N*-ethyl groups in the xanthene ring structure.⁴⁰ Based on our UV-vis results (Fig. 6(b and c)), it is confirmed that MB, CR, and RhB were degraded with efficiencies of 88%, 85% and 60%, respectively. Overall, higher photocatalytic degradation activities over Co@Na-BiVO₄ were recorded for MB and CR dyes. The degradation of RhB was found to be less than 60%, due to the stable configuration of the xanthene ring. The blue shift indicates the de-ethylation and organic intermediates produced during the photoreaction.⁴¹ Photocatalytic activities of as-synthesized Co@Na-BiVO₄ were compared with those of Co-BiVO₄, Na-BiVO₄, bulk BiVO₄ and photolysis as well (*i.e.* photoreaction of dyes without any catalyst) as shown in Fig. 7(a-c). The specialty of Co@Na-BiVO₄ is that it gives the highest degradation activity (88%) than previously reported works (see Table S2†). Similarly, 85% efficiency was noted for the CR dye that is almost slightly less than that in the case of MB. BiVO₄ gives 60% activity for CR and direct photolysis exhibits 13% only. Co@Na-BiVO₄ showed 60% degradation efficiency for RhB, whereas BiVO₄ (*i.e.* without Co & Na) exhibits 39% only. It has been observed that Na-BiVO₄ is active and gives 64.6% degradation individually for the CR dye, whereas the Co-BiVO₄ catalyst exhibits 69.1% activity for CR. The catalysts having both Co and Na contents exhibit 85% dye degradation activity that is almost two times higher than that of BiVO₄ or that of individual Co/Na over BiVO₄ surfaces. These results demonstrate that the existence of Co in the form of Co₃O₄ over BiVO₄ is more favorable than the existence of alkali metal oxides (*i.e.* Na₂O), because due to Na and Co, synergism

was established for charge transportation to active sites. Due to synergism, electrons and holes can build equilibrium for migration and transfer from the support to active sites. On the basis of photocatalytic activities, it can be concluded that the presence of Co and Na oxides offers an effective synergism during the photoreaction. Table S1† demonstrates the comparison of the efficiencies of as-synthesized Co@Na-BiVO₄ (the most active) with those of the reported photocatalysts. Fig. 7(d) demonstrates the photocatalytic apparent rate constant *k* for the degradation of MB, CR and RhB dyes using the Co@Na-BiVO₄ catalyst.

3.9 Recyclability of the photocatalyst

The recyclability tests of Co@Na-BiVO₄ microstructures were further investigated (Table S3† and Fig. 8(a-d)). The results of most active photocatalysts demonstrate the highest stability (each run: up to 60 min for each cycle), and only a small loss of 2.6%, 3.4%, 3.1% was observed for MB, CR and RhB, respectively. The slight decrease in efficiency is actually due to the deposition of the photocatalyst particles on the reactor wall, which causes the loss of active sites. Thus, results obtained during recyclability tests assure the stability and continuous use of Co@Na-BiVO₄ for dye degradation and other photocatalytic applications as well.

3.10 Effect of pH

The pH of the dye solution greatly affects the degradation of cationic (MB and RhB) as well as anionic (CR) dyes. The effect of pH was investigated in the range of 4–10 for our selected dyes



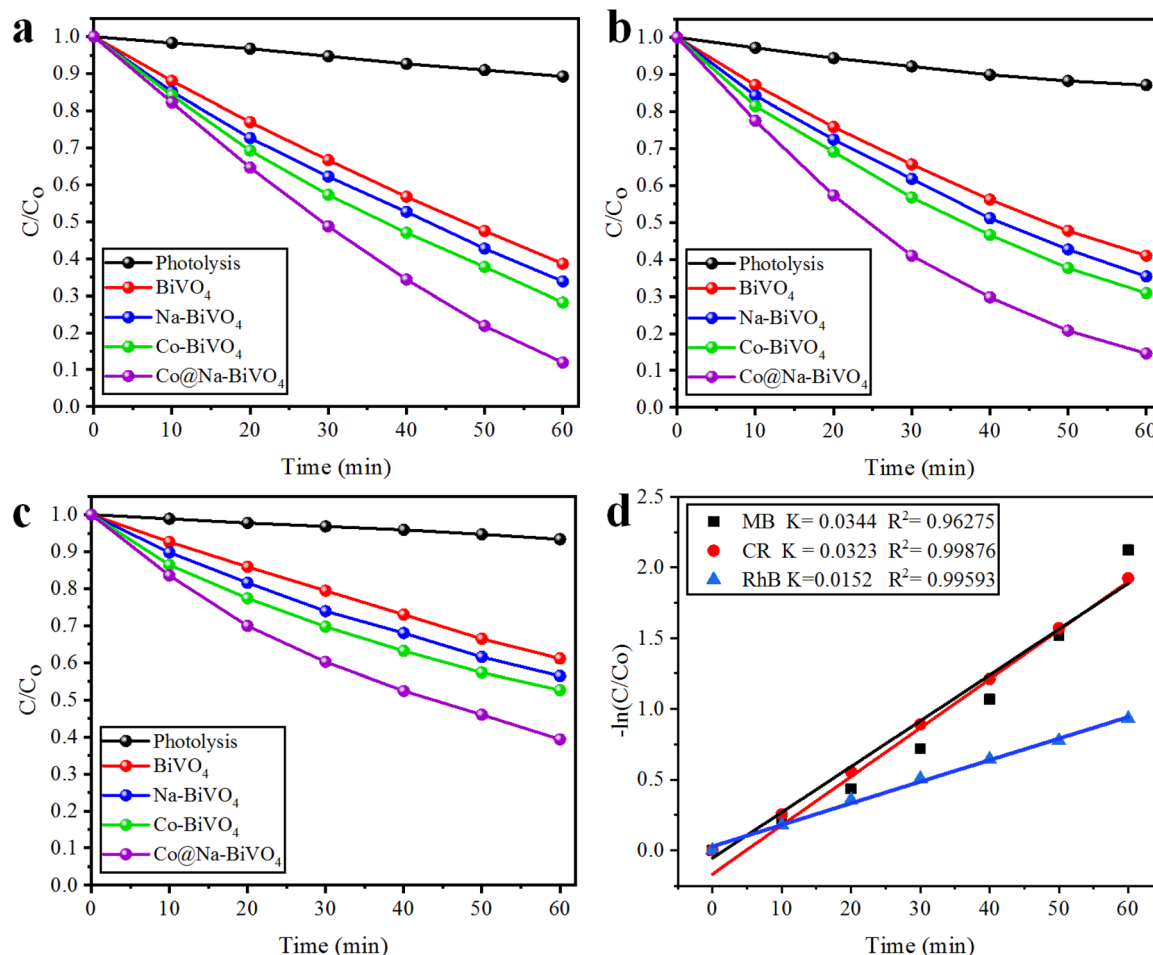


Fig. 7 Comparative degradation activities of dyes with photolysis (degradation via photons), BiVO_4 , Na-BiVO_4 , Co-BiVO_4 and Co@Na-BiVO_4 (a) MB, (b) CR and (c) RhB, whereas (d) represents the kinetic study for MB, CR and RhB obtained over Co@Na-BiVO_4 photocatalysts.

using 10 mg of the Co@Na-BiVO_4 catalyst for each photoreaction. The results for percentage dye removal are illustrated in Fig. 9(a). The results show that degradation of cationic (MB and RhB) dyes is increased under slightly acidic conditions due to their strong affinities with the surface of the catalyst; however, at below pH 5, photocatalytic degradation is inhibited by reducing the number of available electrons. Moreover, anionic (CR) dye degradation is increased at a slightly basic pH, while under highly basic conditions (>9), the formation of hydroxyl radicals hinders the degradation process by reducing the number of available holes.⁴²

3.11 Effect of temperature

The optimized pH for each dye solution was used to evaluate the effect of temperature during the photodegradation reaction. The 20–70 °C temperature range was set using 10 mg of the Co@Na-BiVO_4 catalyst for each photoreaction. The results indicate that 50 °C (± 2) is the optimum temperature that facilitates the effective collisions of photocatalysts and dyes molecules. When the temperature is further increased, the adsorption of dye molecules on the catalyst becomes less which

reduced the photodegradation efficiency.⁴³ In contrast, the results (Fig. 9(b)) illustrate that at low temperature, slower desorption and less collisions between dye molecules inhibits the photoreaction.

3.12 Effect of the photocatalyst dose

The photocatalyst doses have significant effect on the degradation of dyes; the effect of the dose was monitored using 5.0–30 mg Co@Na-BiVO_4 , at an optimized temperature and pH for each dye. The results illustrated in Fig. 9(c) prove that a high photocatalyst dose leads to the generation of more active sites and active species ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$), which results in a higher degradation rate.⁴⁴ However, addition of more than 20 mg of photocatalysts has negative effects on the photocatalytic degradation process. A high dose can initiate the formation of photocatalyst aggregates, which reduces the available surface area, blocks sunlight, and reduces efficiency. In addition to this, a higher photocatalyst dose can cause increased costs, and environmental concerns. Consequently, 20 mg was chosen as the optimal catalyst amount using a 150 mL Pyrex reactor.



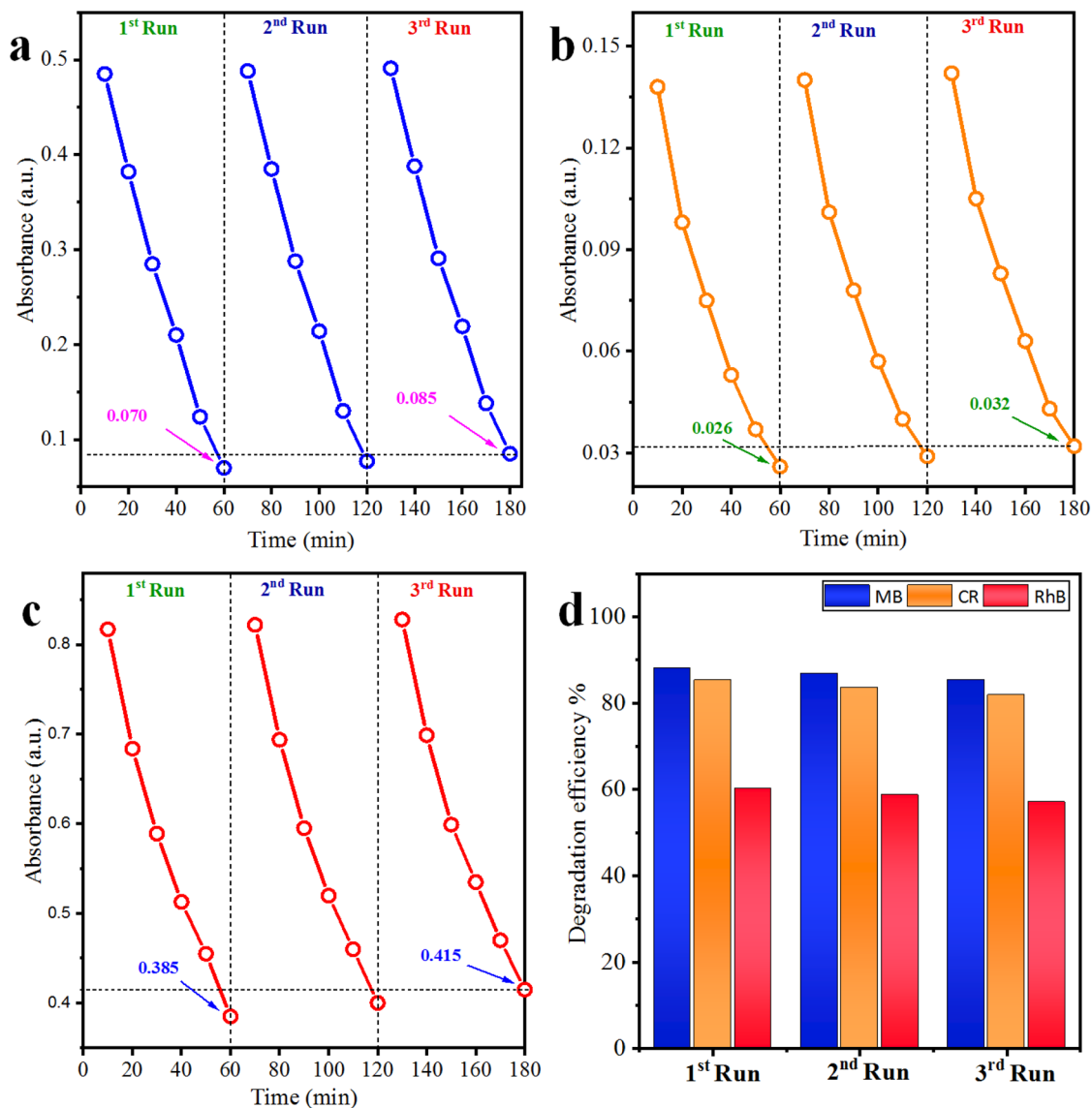


Fig. 8 Recyclability of the Co@Na-BiVO₄ catalyst for (a) MB, (b) CR and (c) RhB, whereas (d) represents the overall % degradation efficiency.

3.13 Role of sacrificial agents

To investigate the role of sacrificial agents, radical quenching experiments were carried out using the Co@Na-BiVO₄ photocatalyst, and MB dye was chosen. Radical scavenging agents used during this study are *p*-benzoquinone (BQ, 0.001 mol L⁻¹ for $\cdot\text{O}_2^-$ radicals), isopropyl alcohol (IPA, 0.01 mol L⁻¹ for $\cdot\text{OH}$), AgNO₃ (0.001 mol L⁻¹ for e⁻) and ethylene diamine tetra acetate (EDTA, 0.01 mol L⁻¹ for h⁺).⁴⁵ The degradation efficiency was considerably suppressed by using BQ, EDTA, and IPA, as illustrated in Fig. 9(d). These results demonstrate that e⁻, $\cdot\text{O}_2^-$ and h⁺ are the major active species. However, the addition of AgNO₃ decreases the activities only a little, which discloses that e⁻ plays a very minor role in dye degradation.

3.14 Mechanism of the photoreaction

Understanding the mechanism is of vital importance in order to understand the overall efficiencies of photocatalysts.⁴⁶ For the

efficiency of any photocatalyst, it is essential to have a band gap less than 3 eV in order to extend light absorption and harvest maximum solar energy.⁴⁷ It has been observed that the synergism between Co and Na enhances the redox sites for dye degradation due to their inherent characteristics during the photoreaction. The mechanism, band energy levels and charge transport (h⁺/e⁻) due to synergism over Co@Na-BiVO₄ photocatalysts are illustrated in Fig. 7 and Scheme 1. The dye degradation results show that bare BiVO₄ catalysts (*i.e.* in the absence of Co/Na) are not capable of transporting the photo induced charges to the active centres. Co₃O₄ is a p-type semiconductor, and when it is assembled with n-type BiVO₄, the Fermi energy of both semiconductor systems aligned and shifted to new energy levels. Fermi level (E_F) of Co₃O₄ lies near to the valence bands. During photoreaction, it gets a new position (raised) that makes the charge transportation more convenient.⁴⁸ The E_F of BiVO₄ present near the conduction band shifted down till equilibrium.





Fig. 9 Effect of (a) pH, (b) temperature and (c) photocatalyst dose on MB, CR, and RhB dyes using the Co@Na-BiVO₄ catalyst, whereas (d) represents the role of major active species.

When the photoreaction starts, electron-hole pairs started to migrate to photocatalyst surfaces where they are actually involved in the photodegradation of dyes. Due to higher CB levels of Co₃O₄ compared to those of BiVO₄, the photogenerated e⁻ of Co₃O₄ preferably transfer to the CB of BiVO₄ support. Electrons are further trapped by Na dopants where these are utilized by dissolved O₂ to generate superoxide anion radicals (⁻O₂),²³ and thus, synergism starts to be established between Co/Na and the BiVO₄ support. Meanwhile, holes (h⁺) migrate

from the valence band of BiVO₄ to the valence band of Co₃O₄, where they react with water molecules to generate [•]OH radicals. These [•]OH radicals are further utilized for dye degradation reactions. Overall higher dye degradation results were obtained in the presence of both Co & Na contents, because Na in the form of Na₂O, when reacted with water produces NaOH (alkali). This NaOH increases the concentration of hydroxyl groups (⁻OH). The hydroxyl groups are further consumed by the holes at the surfaces of BiVO₄ supports.^{49,50} The holes behave as electrophiles that convert -OH groups into radicals ([•]OH). It has been observed that due to the presence of Na contents, a higher concentration of [•]OH is inevitable that is impossible in the case of bare BiVO₄ or Co-BiVO₄. The higher number of [•]OH radicals lead to the increased degradation of dyes that is only possible due to the existence of Na contents. In the presence of synergy, electrons of cobalt oxides migrated to the BiVO₄ system and are trapped by doped Na, whereas holes migrate from BiVO₄ to the Co₃O₄ system. Due to the synergistic effect, photocatalytic performance of BiVO₄ has been increased mainly by (a) higher charge transportation to the active centres, (b) higher absorption of visible light, (c) efficient charge separation and (d) availability of more active sites ([•]OH) due to Na. Without co-



Scheme 1 Photocatalytic reactions involved in dye degradation.





Fig. 10 Synergism and dye degradation on the Co@Na-BiVO₄ photocatalyst.

catalysts (Co and Na), BiVO₄ is not efficient for dye degradation. Overall, as-synthesized Co@Na-BiVO₄ leads to more active sites, which enhances the photocatalytic activity (Fig. 10).

4. Conclusion

Blossom-like BiVO₄ microstructures have been successfully synthesized by the co-precipitation method with an optimized timescale strategy. Co and Na were *in situ* incorporated into BiVO₄ via low temperature chemical reduction followed by calcination. Powdered XRD and EDX analyses confirmed the existence of incorporated Co & Na over the BiVO₄ support. The Raman and FT-IR results revealed the presence of active centers where dye degradation reactions occur. The UV-vis/DRS results revealed an extension in absorption to the visible spectrum, that is, from 512 nm to 530 nm due to Co/Na contents. The PL results indicate the suppressed recombination of photo-induced charges that is due to the synergism and continuous transfer of charges to active sites. Co@Na-BiVO₄ exhibits a higher photocatalytic activity as compared to BiVO₄, Co-BiVO₄ or Na-BiVO₄. Overall, the higher activities are attributed to synergistic charge transfer. Thus, the introduction of Co & Na in this work offers a new approach for photocatalysis applications. Furthermore, the recyclability test assures the structural stability of the as-synthesized catalysts. Although various morphologies of BiVO₄ have been designed for dye degradation, the introduction of Co and Na contents over blossom-like BiVO₄ microstructures delivers higher dye degradation activities.

Conflicts of interest

The authors declare no competing financial interest.

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