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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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reduces the overall activities. However, this problem could be reduced by generating more active centers in the form of transition metal dopants. Similarly, the BiVO_4 activity can also be enhanced by doping with non-metals, metals, metal cations and non-metal anions or by fusion with another oxide. For combination with BiVO_4 , noble metals such as Pt, Au, Pd and Ag serve as excellent cocatalysts in photocatalysis.¹⁵ But due to high cost, these metals are less common in dye degradation applications, although these metals enhance electron-hole separation (due to electron quenching abilities) and increase light absorption. The separation of charge carriers and their lifetime can also be enhanced by developing composites *via* incorporating suitable dopants. Many composites of metals or metals oxides, such as Au, CeO_2 , WO_3 , CdS, SnO_2 and TiO_2 , still have some drawbacks and their photocatalytic efficiencies are still unsatisfactory.^{16–19} Among the dopants, cobalt (Co) doped^{20,21} and alkali (Na^+ and K^+) doped BiVO_4 nanostructures have been reported for better charge transfer in photocatalysis.^{22,23}

To demonstrate the advantage of an alkali metal oxide (Na_2O) with a transition metal co-catalyst, Co and Na contents were *in situ* employed and incorporated into BiVO_4 . This work was designed to promote the charge transfer from the semiconductor (BiVO_4) to the co-catalyst active sites by shifting the Fermi level. The Co in the form of Co_3O_4 acts as excellent active sites for dye degradation. Another advantage of Co is to enhance the photon absorption surfaces of the semiconductor support. The approach employed in this study exhibits various other advantages like the excellent stability of the synthesized photocatalysts, higher dispersion rather than agglomeration and excellent dye degradation efficiencies. This work demonstrates the extended absorption in visible light that attributes to higher dye degradation efficiencies of various toxic dyes (*e.g.* methylene blue, Congo red and rhodamine B) under solar radiations.

2. Experimental

2.1 Materials used

The following chemicals were used for the synthesis of photocatalysts, bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Sigma Aldrich 98%), ammonium metavanadate (NH_4VO_3 , Sigma Aldrich 98%), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich 98%), sodium hydroxide (NaOH , Sigma Aldrich 98%) and sodium borohydride (NaBH_4 , Sigma Aldrich 98%). To monitor the degradation activities, methylene blue (MB) dye ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, Sigma Aldrich), Congo red (CR) dye ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$), and rhodamine B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, Sigma Aldrich) were used.

2.2 Catalysts preparation

BiVO_4 was synthesized by the co-precipitation method with optimized timescale strategy. Briefly, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution (7 mM) was prepared by dissolving 3.396 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sigma Aldrich, 99%) in 50 mL of 4 M HNO_3 solution. In the next step, NH_4VO_3 solution (7 mM) was prepared by adding

0.819 g of NH_4VO_3 (Sigma Aldrich, 99%) to 50 mL of 2 M NH_4OH solution. To remove the dissolved oxygen, both solutions were purged with high purity argon (Ar) for 30 min. After that, the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution was added dropwise into the NH_4VO_3 solution with vigorous stirring for 12 h while maintaining the pH = 9 at a temperature of 10 °C. The precipitate mixture was then sonicated for 20 min by adjusting the sweep frequency (37 kHz, 300 W). The yellow precipitate was filtered out using high grade filter paper (WHA 1001325, Grade-1). The solid product was washed thoroughly with deionized water and then with absolute ethanol. After that, the product was dried at 94 °C overnight in an oven (Sanyo/MOV-112 Japan).²⁴ For the synthesis of Co@Na- BiVO_4 microstructures, an optimized amount of BiVO_4 (155 mg) powder was transferred into a three-neck, round bottom flask, followed by addition of 50 mL of high purity deionized water (PIAS-GW1-Z) to produce a uniform slurry. After 15 min of purging with argon, Co and Na ions (from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ & NaOH/NaCl) were dispersed and *in situ* incorporated into BiVO_4 by using a chemical method. The amounts of Co and Na metal contents were fixed at 1 : 1 and overall 2% metal contents (2% w/w). To grow the Co@Na- BiVO_4 microstructures, the above mixture solution was under optimized stirring (150 rpm) at approximately 10 °C for 24 h. The final suspension was filtered and dried at 94 °C. The synthesis of Co- BiVO_4 and Na- BiVO_4 are discussed in the ESI.†

2.3 Catalysts characterization

UV-vis/DRS for the as synthesized photocatalysts was obtained over the wavelength range of 265–850 nm on a PerkinElmer (λ -850+/Tungsten-Halogen) spectrophotometer. Powdered XRD analysis was conducted on an advanced XRD system (Bruker D2-phasen) equipped with a LYNXEYE XE-T Detector, 220 V/60 Hz. Using the Scherrer equation, particle sizes were measured having $D \approx 0.9\lambda/(\beta \cos \theta)$; the Cu K α operational X-ray source is ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA). The 2θ range was fixed from 15° to 80° (step: 0.05° and scan rate: 2° min⁻¹), Fourier transform infrared (FT-IR) analysis was performed on a BrukerTensor-27. The SEM results were obtained using an FEI-Nova NanoSEM-450 electron microscope. The elemental composition of Co@Na- BiVO_4 NPs was obtained using a SEM equipped with an energy dispersive X-ray (EDX) accessory. The AFM results were obtained using an Agilent 5500 SPM/AFM. The photoluminescence results were recorded on a spectrometer (LS-45, PerkinElmer). Photocatalytic dye degradation efficiencies were recorded using a UV-vis-spectrophotometer (PerkinElmer/ λ -365).

2.4 Photocatalytic degradation experiments

To investigate comparative efficiencies, degradation experiments of selected dyes (MB, CR and RhB) were performed on a spectrophotometer (PerkinElmer/ λ -365). Dye degradation experiments were performed in a Pyrex reactor of size 6.1 × 4.3 × 4.2 inches (100 mL/silicon septum, ChemGlass AF-0528-06). For photocatalytic experiments, the photoreaction set up was made to elucidate the photolysis reaction of dyes, pure BiVO_4 ,



Na-BiVO₄, Co-BiVO₄ and Co@Na-BiVO₄ microstructures. Photocatalytic activities of all as-synthesized photocatalysts were investigated using direct sunlight. All photoreactions have been carried out on consecutive days under a clear sky to ensure accurate photon absorption. The average photon flux was measured to be $1.388 \times 10^3 \text{ W m}^{-2}$ using a light meter (Extech/LT-300 USA). For each photoreaction, 10 mg of the photocatalyst was optimized, and treated with 50 mL of 5 ppm solution of each dye. Before starting the photoreaction, the analyte solution was stirred in the absence of light for 30 min to soak the dye with photocatalysts. At regular intervals, 3.5 mL reaction mixture was pipetted out and centrifuged to get a clear solution for UV-vis measurements.

3. Results and discussion

The synthesis scheme of all photocatalysts is demonstrated in Fig. 1 (see details in the Experimental section). To remove the impurities and enhance the crystallinity, the as-synthesized photocatalysts were calcined at 350 °C for 3 h.

3.1 XRD

XRD is an excellent tool for the detection or identification of crystal phases in solid-state materials.²⁵ The XRD patterns of the as-synthesized plain BiVO₄, Na-BiVO₄, Co-BiVO₄, and Co@Na-BiVO₄ are shown in Fig. 2(a). The synthesized BiVO₄ is monoclinic in phase (*c.f.* JCPDS#14-0688), with XRD peaks observed at 18.66°, 18.98°, 28.94°, 30.54°, 34.49°, 35.22°, 39.78°, 42.46°, 46.71°, 47.30°, 50.31°, 53.31° and 58.53°, corresponding to (110), (011), (121), (040), (200), (002), (211), (051), (240), (042), (202), (161) and (321) crystallographic planes, respectively.²⁵ No other diffractions were seen, confirming the phase purity of BiVO₄. Co metal exists in the form of cobalt oxide (Co₃O₄, cubic phase), with major diffraction peaks at 36.8 and 65.2° (PDF#43-1003). The ionic radius of Na⁺ (1.02 Å) is almost same as that of the Bi³⁺ ion (1.03 Å), which favors the substitution of Na⁺ on Bi³⁺, while most of the Na exists as sodium oxide Na₂O (cubic), with major peaks observed at 27.7, 32.1 and 46.1°, in accordance with PDF#23-0528. By employing the reported method, the crystallite size

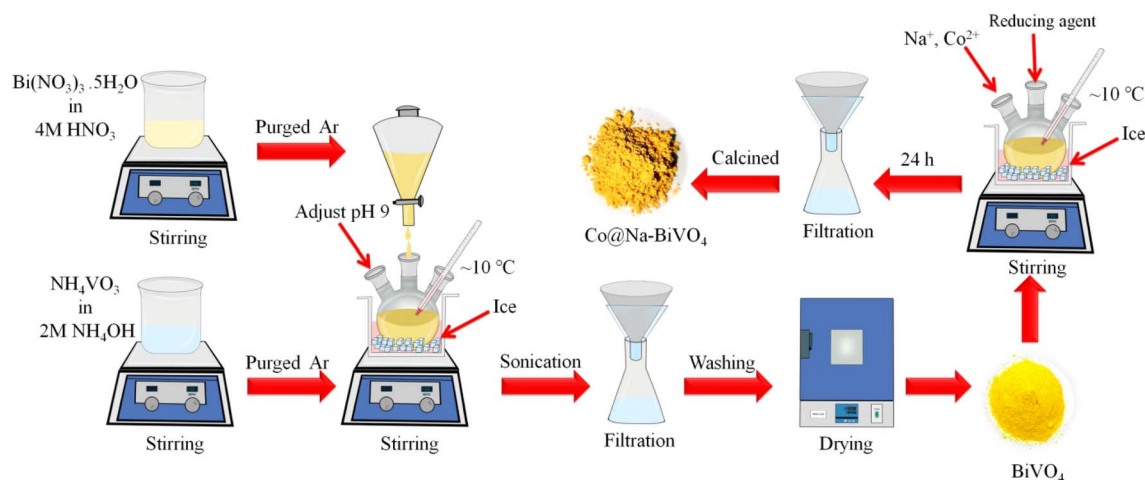


Fig. 1 Scheme employed for the synthesis of BiVO₄ and Co@Na-BiVO₄.

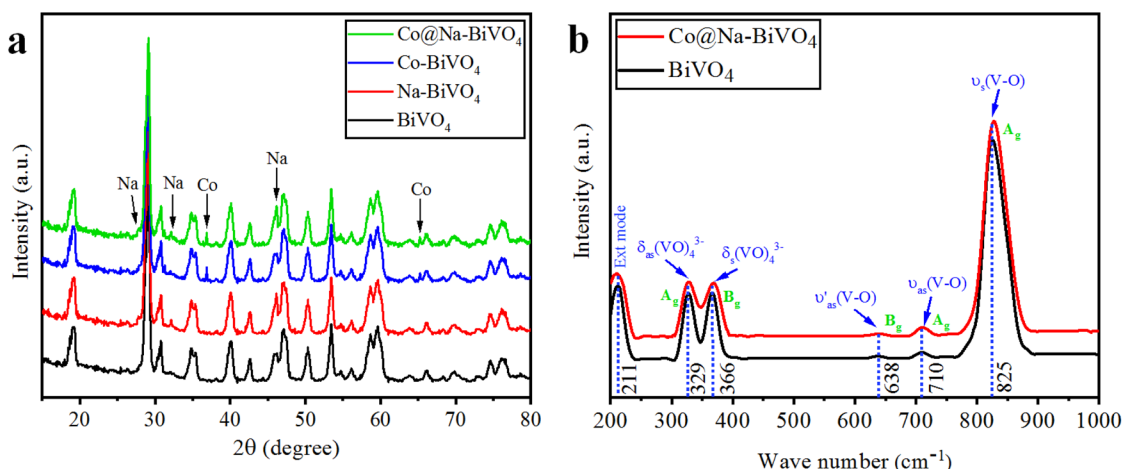


Fig. 2 (a) Powder XRD patterns of BiVO₄, Na-BiVO₄, Co-BiVO₄ and Co@Na-BiVO₄ (b) Raman vibrations of BiVO₄ and Co@Na-BiVO₄ microstructures.

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}

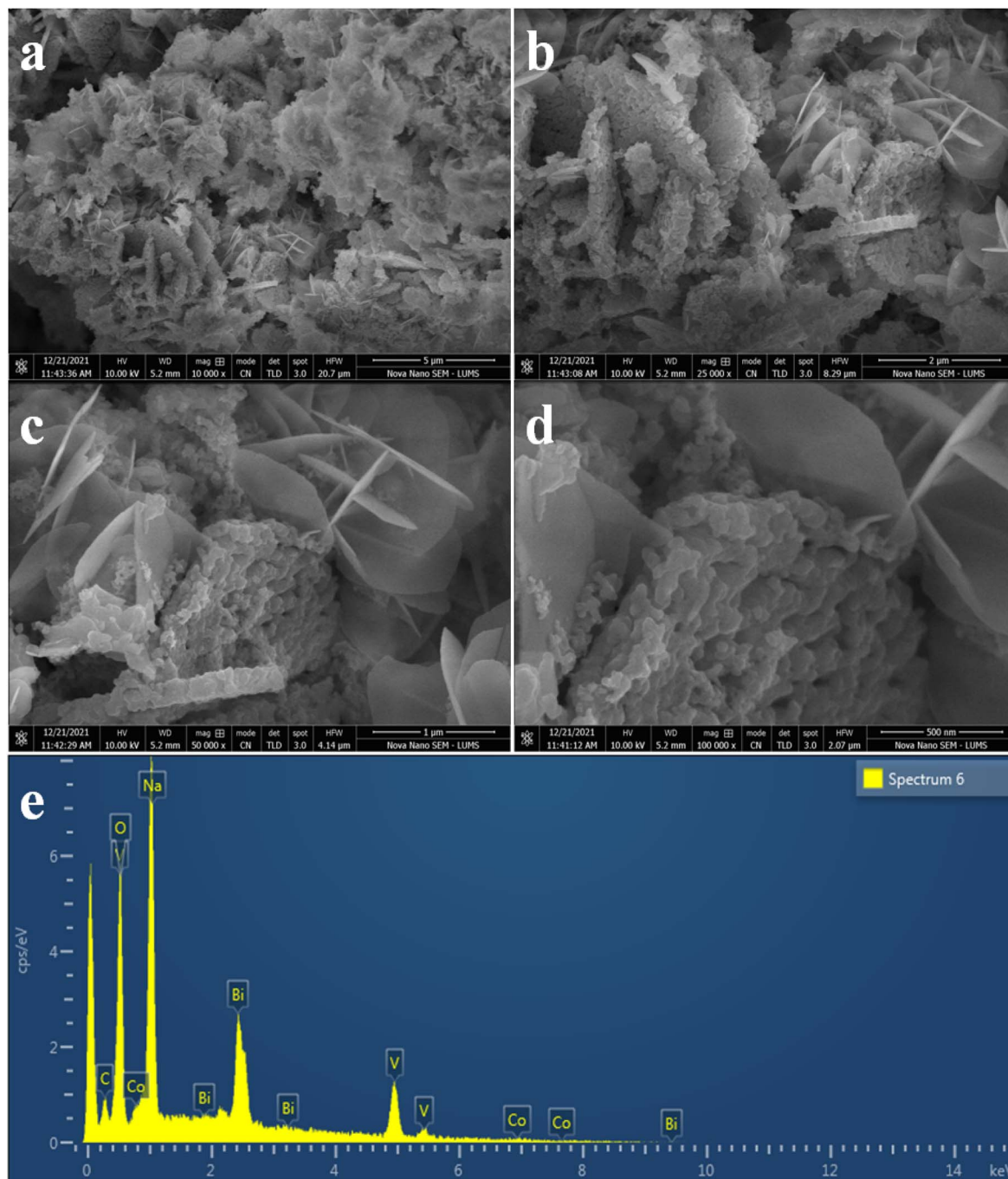


Fig. 3 SEM images of Co@Na–BiVO₄ microstructures (a) 5 μm (b) 2 μm (c) 1 μm and (d) 500 nm, whereas (e) represents the EDX analysis.



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.

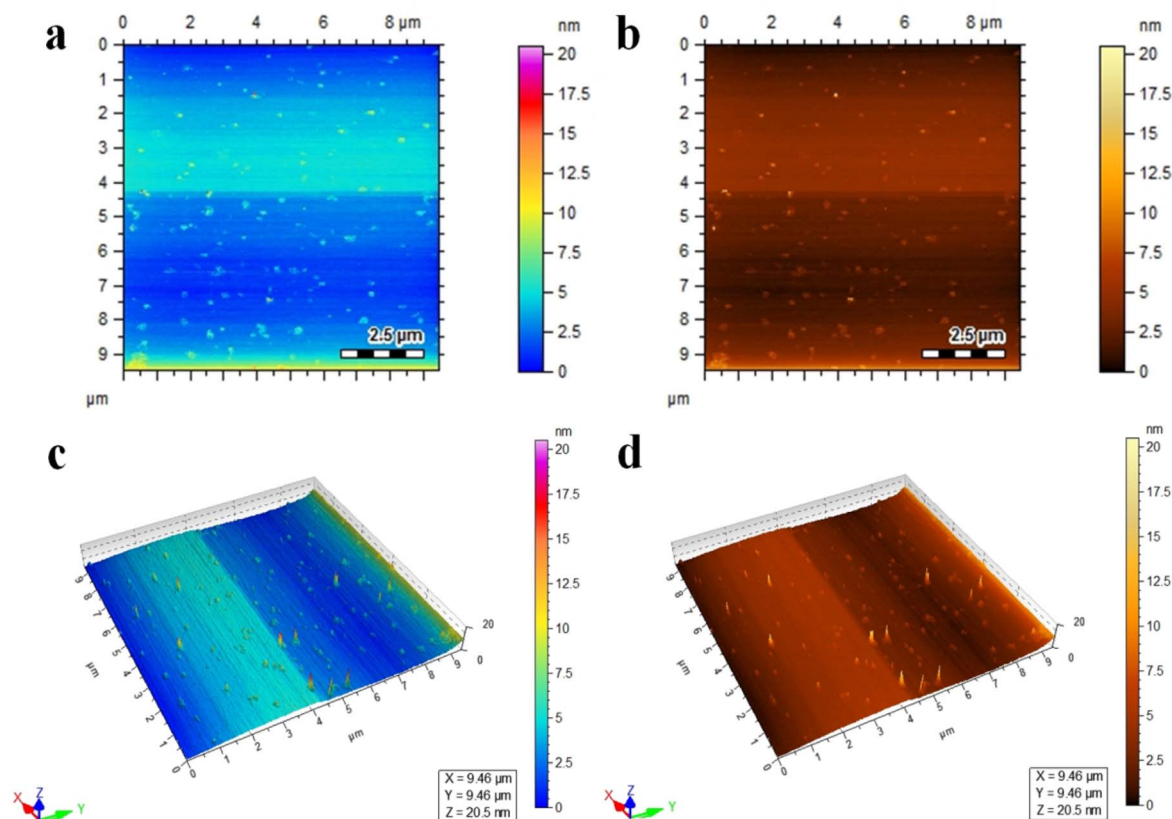
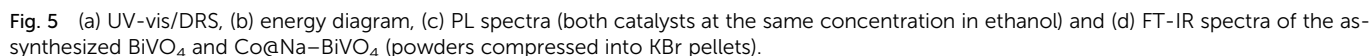
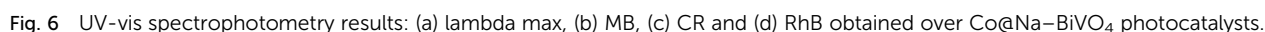


Fig. 4 AFM images of Co@Na-BiVO₄ (a and b) topographical images, and (c and d) three-dimensional view.





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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.

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.

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

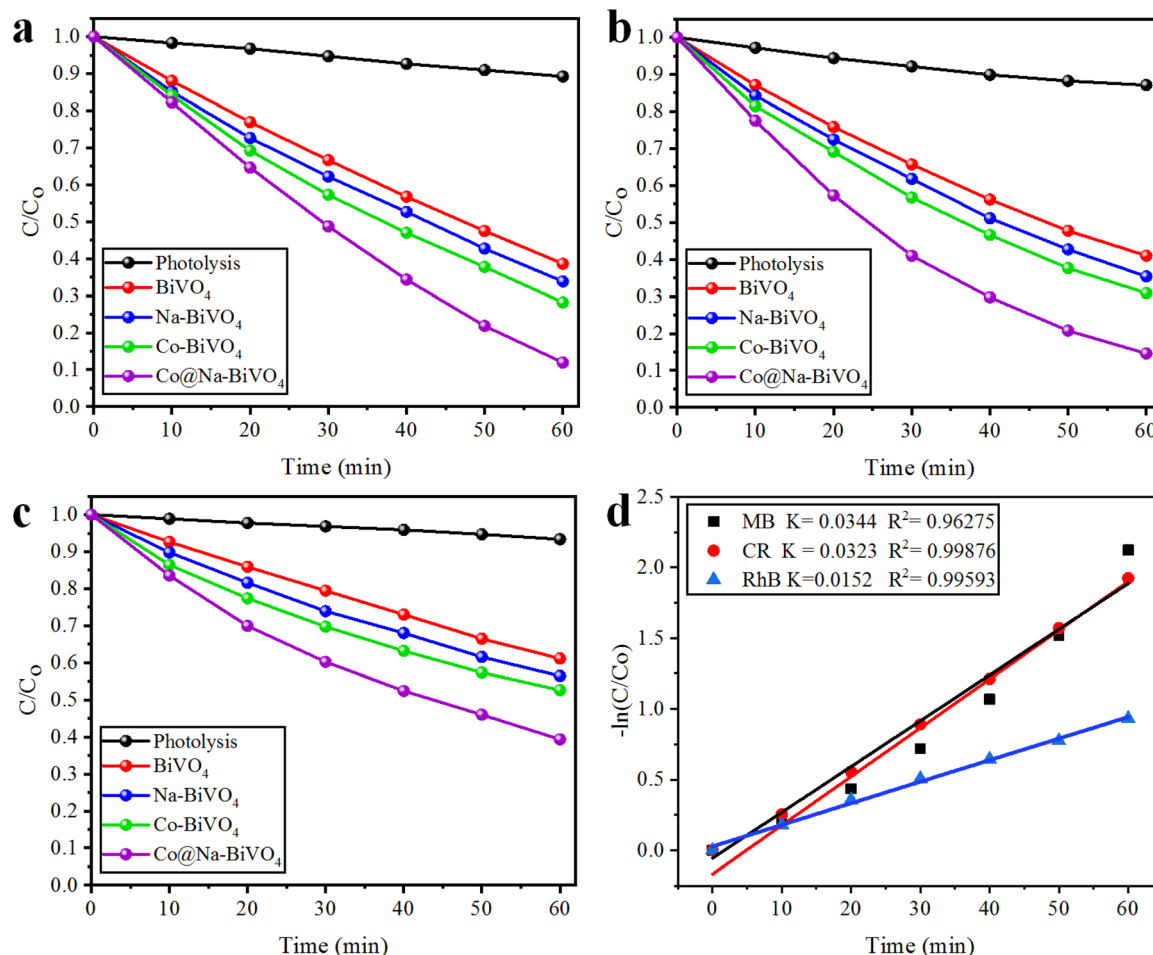


Fig. 7 Comparative degradation activities of dyes with photolysis (degradation via photons), BiVO_4 , Na-BiVO_4 , Co-BiVO_4 and Co@Na-BiVO_4 (a) MB, (b) CR and (c) RhB, whereas (d) represents the kinetic study for MB, CR and RhB obtained over Co@Na-BiVO_4 photocatalysts.

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.



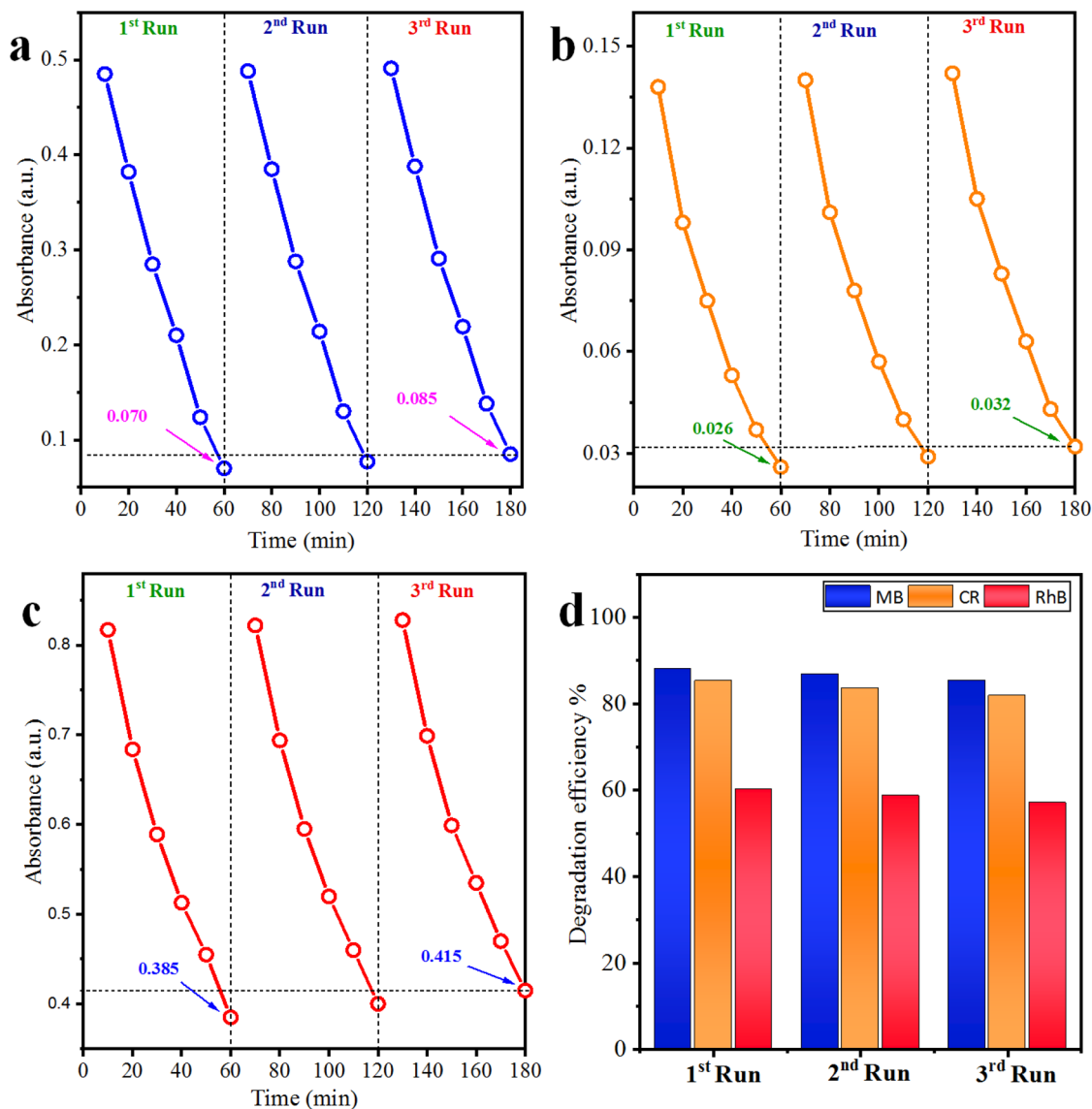


Fig. 8 Recyclability of the Co@Na-BiVO₄ catalyst for (a) MB, (b) CR and (c) RhB, whereas (d) represents the overall % degradation efficiency.

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 [•]O₂⁻ radicals), isopropyl alcohol (IPA, 0.01 mol L⁻¹ for [•]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⁻, [•]O₂⁻ 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.





from the valence band of BiVO_4 to the valence band of Co_3O_4 , where they react with water molecules to generate $\cdot\text{OH}$ radicals. These $\cdot\text{OH}$ 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 Na_2O , 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 BiVO_4 supports.^{49,50} The holes behave as electrophiles that convert ^-OH groups into radicals ($\cdot\text{OH}$). It has been observed that due to the presence of Na contents, a higher concentration of $\cdot\text{OH}$ is inevitable that is impossible in the case of bare BiVO_4 or Co-BiVO_4 . The higher number of $\cdot\text{OH}$ 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 BiVO_4 system and are trapped by doped Na, whereas holes migrate from BiVO_4 to the Co_3O_4 system. Due to the synergistic effect, photocatalytic performance of BiVO_4 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 ($\cdot\text{OH}$) due to Na. Without co-





The authors declare no competing financial interest.

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