Substitution of Ce\(^{\text{III,IV}}\) ions for Bi in BiVO\(_4\) and its enhanced impact on visible light-driven photocatalytic activities

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Bi\(_{1-x}\)Ce\(_x\)VO\(_4\) \((0 \leq x \leq 0.3)\) solid solution photocatalysts were synthesized by substitution of Ce for Bi in the BiVO\(_4\) lattice using the hydrothermal method. X-ray diffraction, Raman spectroscopy and high-resolution transmission electron microscopy revealed that the crystal phase transformed from the monoclinic phase to the tetragonal phase, probably due to the substitution of cerium ions in the Bi\(^{3+}\) positions. UV-vis diffuse reflectance spectroscopy was used to investigate the absorption range and band gap of the photocatalysts. The photocatalytic activities of the prepared samples were examined by studying the degradation of MB and phenol under visible-light irradiation and the best performance was attained for the sample with a cerium content of 20 at% (Bi\(_{0.8}\)Ce\(_{0.2}\)VO\(_4\)). The results of photoluminescence spectroscopy and photocurrent measurement demonstrated that the recombination of photogenerated charges was greatly depressed and the photocatalytic activity was improved by the substitution of Ce for Bi in BiVO\(_4\). Furthermore, the proposed mechanism of the enhanced photocatalytic activity was discussed.

Introduction

The application of semiconductor photocatalysts in water cleaning is regarded as an eco-friendly technology to afford organic pollutant degradation using solar energy. In this case, a number of attempts have been made to pursue the utilization of solar light as efficiently as possible. Bismuth vanadate (BiVO\(_4\)) has recently become a very attractive material as a promising photocatalyst for organic pollutant degradation because of its worthy photoactivity under visible light.\(^1\) As a new type of semiconductor photocatalyst, BiVO\(_4\) possesses three main crystalline phases: monoclinic scheelite-type, tetragonal scheelite-type and tetragonal zircon-type.\(^3\) Among these phases, the monoclinic scheelite-type BiVO\(_4\) exhibits higher photocatalytic activity under visible light due to its relatively narrow band gap (ca. 2.4 eV), whereas the photocatalytic activity of the tetragonal zircon-type BiVO\(_4\) is reported to be negligible.\(^5\,^6\)

The photoactive monoclinic BiVO\(_4\) has been obtained through different synthetic methods in the past ten years.\(^7\) Nevertheless, low separation efficiency of the photogenerated electron–hole pairs is always the main drawback of BiVO\(_4\) for its application, which arouses lots of efforts to improve the visible light photocatalytic activity of BiVO\(_4\) photocatalysts, including heterojunction structure formation,\(^11\) co-catalyst loading\(^14\) and impurity doping.\(^17\) Particularly, the lanthanide ions with the unique 4f electron configuration are regarded as efficient dopants to enhance the photocatalytic activity of BiVO\(_4\). To date, several studies have focused on the lanthanide ion modified monoclinic phase BiVO\(_4\) photocatalysts, such as Ce,\(^19\) Eu,\(^20\) La, Gd, Nd and Sm.\(^21\) These findings confirmed the enhancement in photocatalytic activities and revealed that the lanthanide ions were present as oxides at the surface of BiVO\(_4\). Besides, in a recent paper, Obregón\(^22\) described the enhanced photocatalytic activity of the tetragonal zircon-type BiVO\(_4\) by Er\(^{3+}\) doping. This result showed that the phase of BiVO\(_4\) was transformed to the tetragonal phase after doping a small amount of Er\(^{3+}\) and the photocatalytic performance was improved. And this conclusion was also confirmed by another literature recently.\(^23\) However, the detailed mechanism of the electron–hole pair separation and the enhanced photocatalytic activity derived from the introduction of lanthanide ions have not been entirely understood yet.

This work designed a novel solid solution photocatalyst Bi\(_{1-x}\)Ce\(_x\)VO\(_4\)\(_{1-x}\) to further investigate the influence of lanthanide ions on the electron–hole pair separation and the photocatalytic activity. It is a new challenge to compose photocatalytic materials with a solid solution structure. Within this configuration, the improvement in the separation efficiency of the photogenerated electron–hole pairs might be reached by creating donor and acceptor defects in the crystal lattice. Cerium is one of the most interesting dopants due to its different electronic structure between Ce\(^{3+}\) and Ce\(^{4+}\), leading to...
different chemical states in the crystal lattice. Furthermore, Ce$^{3+}$ and Ce$^{4+}$ possess an ionic radius approximately similar to Bi$^{3+}$, which is conducive for the substitution. In this work, the influence of Ce substituted in the crystal lattice on the crystal phase, optical properties, photogenerated charge separation, photocurrents and photocatalytic degradation of methylene blue and phenol under visible light irradiation were investigated in detail. Moreover, the proposed mechanism of the enhanced photocatalytic activity was discussed.

**Experimental**

**Synthesis of BiVO$_4$ and Bi$_{1-x}$Ce$_x$VO$_4$ photocatalysts**

All chemicals used in this work were of analytical reagent grade (Sinopharm Chemical Reagent Co., Ltd., China) and used without further purification. The solutions were prepared using Milli-Q water. The Bi$_{1-x}$Ce$_x$VO$_4$ photocatalysts were prepared using the hydrothermal method as described below. Proportionate amounts of Bi(NO$_3$)$_3$·5H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O and NH$_4$VO$_4$ were weighed according to the stoichiometric formulation Bi$_{1-x}$Ce$_x$VO$_4$ (x = 0, 0.005, 0.02, 0.05, 0.1, 0.2, 0.3) (abbreviated as BCVO x below). Subsequently, Bi(NO$_3$)$_3$·5H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O were mixed and dissolved in 50 mL of Milli-Q water and 3 mL of nitric acid to form a transparent solution. NH$_4$VO$_4$ was dissolved in 50 mL of Milli-Q water at 70 °C. Afterwards, Bi$^{3+}$ and Ce$^{3+}$ were added dropwise into the NH$_4$VO$_4$ solution and NaOH (0.1 M) was injected constantly to ensure the pH value of the system to be ca. 10. When the two solutions were entirely mixed, 2 mL of H$_2$O$_2$ was added. The dark orange slurry was stirred for 15 min followed by transferring into Teflon-lined stainless steel autoclaves. The sealed reactors were then heated at 180 °C for 4 h. The precipitate was subsequently filtered and washed with Milli-Q water several times to ensure that the residual impurities were removed, and then was dried at 80 °C for 6 h.

**Characterization**

The crystalline phases of BiVO$_4$ (x = 0) and Bi$_{1-x}$Ce$_x$VO$_4$ were determined using X-ray diffraction (XRD) (D/MAX-RB, Rigaku, Japan). The diffraction patterns were recorded in the 20 = 10–70° range with a Cu Kα source (λ = 0.15405) running at 40 kV and 30 mA. The specific surface area of the samples was determined by the Brunauer–Emmett–Teller (BET) method (NOVA 4200e, Quantachrome, USA). The morphology and chemical composition were examined using a scanning electron microscope (SEM) (S-4800, Hitachi, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). The high-resolution transmission electron microscopy (HRTEM) images were recorded on a transmission electron microscope (2010F, JEOL, Japan) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (AXIS ULTRAXLD, Kratos, Japan) using Al Kα radiation. The Raman spectra at room temperature were obtained using a Raman spectrometer (T64000, Horiba LabRam, France), excited by an Ar$^+$ laser (530 nm). All measurements were recorded under the same conditions of 2 s of integration time and 30 accumulations. The UV-vis diffuse reflectance spectra (DRS) of the photocatalysts were recorded at room temperature using a UV-vis spectrophotometer (T9s, Persee, China) equipped with an integrating sphere. BaSO$_4$ was used as the reference. The photoluminescence (PL) spectra were recorded by a fluorescence spectrophotometer (F-4500, Hitachi, Japan) with a Xe lamp as the excitation light source. The electron paramagnetic resonance (EPR) spectra were performed on an EPR spectrometer (EMX Plus, Bruker, Germany). The spectra were obtained using a microwave power of 20 mW, a frequency of 9.85 GHz and a central magnetic field of 3503 G.

**Measurement of photocatalytic activity**

The photocatalytic activities of the BiVO$_4$ and Bi$_{1-x}$Ce$_x$VO$_4$ photocatalysts under visible light were evaluated by degrading 10 mmol L$^{-1}$ methylene blue (MB) with an initial absorbance at 664 nm of 1.062 and 40 mmol L$^{-1}$ phenol with an initial absorbance at 270 nm of 0.671. A 400 W Xe lamp with a UV-cutoff filter (λ > 420 nm) was used as a light source and set about 10 cm apart from the reactor. The experiments were performed at 25 °C using constant temperature circulating water as follows: 40 mg of the photocatalyst was dispersed in 40 mL of MB solution and 40 mL of phenol solution, respectively, followed by stirring for 60 min in the dark to achieve an adsorption–desorption equilibrium before light irradiation. During the irradiation, the reaction samples were collected at 30 min (60 min for phenol degradation) intervals and centrifuged to remove the photocatalyst particles. The ratios ($C/C_0$) of the MB and phenol concentrations were adopted to evaluate the degradation efficiency (i.e., $C_0$ was the initial concentration, where $C$ was the concentration at a certain time) by checking the absorbance spectrum at 664 nm for MB and 270 nm for phenol using a UV-vis spectrophotometer (U-3900H, Hitachi, Japan).

**Photocurrent measurement**

The measurement of the photocurrent was carried out on an electrochemical workstation (5060F, RST, China) in a standard three-electrode system with the samples, an Ag/AgCl electrode (saturated KCl), and a Pt wire used as the working electrode, reference electrode, and counter electrode, respectively. And a 0.5 mol L$^{-1}$ Na$_2$SO$_4$ aqueous solution was introduced as electrolyte. A 100 W incandescent lamp with a 420 nm cut off filter was used as the light source. The preparation of the working electrode is described below: 5 mg samples were dispersed in 2 mL of ethanol and Nafion solution (v/v: 30 : 1), followed by spreading on the bottom middle of an ITO glass in a circle with a diameter of 6 mm. Then the photocurrents of the photocatalysts with the light on and off were measured at 0.8 V.
Results and discussion

Structural analysis

Fig. 1 presents the X-ray diffraction patterns of the BiVO₄ and Biₓ₋ₓCeₓVO₄₋ₓ₋ₓ photocatalysts obtained by hydrothermal synthesis at 180 °C for 24 h. It can be observed that the scheelite-type monoclinic phase was only attained for the unsubstituted sample (JCPDS card no. 14-0688, abbreviated as m-BVO below). As shown in Fig. 1, the low-level substituted photocatalysts were composed of a mixture phase of the monoclinic and tetragonal phases. Even in the BCVO 0.005 sample, an obvious trace of phase transition to the tetragonal phase could be revealed at 2θ of 18.3°, 24.3°, 32.7° and 48.5° which were indexed to the (1 0 1), (2 0 0), (1 1 2) and (3 1 2) planes, respectively, of the zircon-type tetragonal BiVO₄ (JCPDS card no. 14-0133). At the x value increased, the intensity of the tetragonal phase increased whereas the intensity of the monoclinic phase decreased. When the values of x were 0.2 and 0.3, the main peaks of the monoclinic phase could hardly be observed and these samples were almost in the standard tetragonal phase. Meanwhile, no signals of Ce₂O₃ and CeO₂ were found even for the samples with higher cerium content. Different from the XRD results in our previous work on CeO₂/BiVO₄ composites,¹⁹ the monoclinic phase was only attained for the BiVO₄ sample which means that the cerium ions probably substituted for Bi³⁺ in the crystal structure rather than being loaded at the surface as oxide crystal grains.

Raman spectroscopy can provide more structural information and was used to support the transformation from the monoclinic phase to the tetragonal phase as the cerium ion ratio increased. The Raman spectra of the BiVO₄ and Biₓ₋ₓCeₓVO₄₋ₓ₋ₓ photocatalysts are shown in Fig. 2. In the spectra of m-BVO, the strongest mode at 828.4 cm⁻¹ is attributed to the symmetric V–O stretching mode νₛ(V–O) of the monoclinic phase. The doublet peaks observed at about 364.8 cm⁻¹ and 324.9 cm⁻¹ are attributed to the asymmetric bending mode δₐ(VO₄) and the asymmetric bending mode δₐₐ(VO₄), respectively. The external modes (rotation/translation) are observed at 209.5 cm⁻¹ and 124.6 cm⁻¹. However, in the spectra of the Biₓ₋ₓCeₓVO₄₋ₓ₋ₓ samples, the strongest mode that was assigned to the symmetric V–O stretching mode νₛ(V–O) shifted to 851.9 cm⁻¹ and the weak shoulder also had an obvious blue shift. An empirical relationship between the Raman shift and the metal-oxygen bond length has been established for vanadium (ν = 21 349 × exp (−1.9176R), where ν is the Raman shift in cm⁻¹ and R is the V–O bond length in Å), in which the higher frequencies (blue shift) of the Raman stretching band correspond to the shorter bond length in V–O of the tetragonal phase. The Raman spectra of BCVO 0.005 obviously showed a mixture of modes of the tetragonal phase and the monoclinic phase while the νₛ(V–O) mode of the monoclinic phase declined as the x value increased, which was in accordance with the XRD patterns. Additionally, the disappearance of the bending mode δ(VO₄) doublet of the monoclinic phase and the external mode appearance at 248 cm⁻¹ were also evidences of this phase transition. Furthermore, Raman spectroscopy can also be a sensitive method to investigate the doping site in the crystal lattice. The translation and rotation modes of 124.6 cm⁻¹ and 209.5 cm⁻¹ are at a much lower frequency than the internal modes of VO₄, which refer to the motion of the VO₄ as rigid units and are sensitive to the change in the unit mass, because they involve heavier VO₄ units and weaker coupling interactions.²⁸ It can be seen in Fig. 2 that before the disappearance of the external modes, no obvious shift was observed although the mass of Ce is much higher than that of V. These results demonstrated that Ce did not substitute for V in the crystal lattice.

At the same time, it is worthy to note that when increasing the content level of substituted cerium, a slight decrease in the cell parameters and crystal volume, that were refined

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Fig. 1 X-ray diffraction patterns for the BiVO₄ and Biₓ₋ₓCeₓVO₄₋ₓ₋ₓ photocatalysts obtained by hydrothermal synthesis at 180 °C for 24 h: (●) scheelite-type monoclinic phase and (●) zircon-type tetragonal phase.

Fig. 2 Raman spectra for the BiVO₄ and Biₓ₋ₓCeₓVO₄₋ₓ₋ₓ photocatalysts obtained by hydrothermal synthesis at 180 °C for 24 h.
from the X-ray diffraction data of the BiVO$_4$ and Bi$_{1-x}$Ce$_x$VO$_4$ photocatalysts, was observed in Table 1. This phase transition would be achieved by considering the substitution of cerium ions in the Bi$^{3+}$ positions. On this basis, the decrease in the cell parameters and crystal volume was probably attributed to the smaller ionic radius of Ce$^{4+}$ (0.97 Å) and Ce$^{3+}$ (1.143 Å) in comparison to that of Bi$^{3+}$ (1.17 Å) with a coordination number of 8. The substitution of the cerium ions was also reflected in the decline of the Raman band intensity with the increase in the content level, suggesting the weak deformation of the VO$_4$ tetrahedron (Fig. 2). Accordingly, the schematic crystal structures of the monoclinic and tetragonal phases can be built based on the preceding analysis and the refined XRD data of the samples, as it is shown in Fig. 3.

**Morphology characterization**

The phase transition also had a significant effect on the morphology of the as-obtained photocatalysts, as it is shown in Fig. 4. The morphology of the BiVO$_4$ (Fig. 4(A)) shows a buckhorn-like structure as it was in our previous work, and its surface area is 33.46 m$^2$ g$^{-1}$ according to Table 1. However, it is clear that the Bi$_{1-x}$Ce$_x$VO$_4$ photocatalysts in Fig. 4(B)–(G) generally showed nanorod morphologies. From the image of sample BCVO 0.005 in Fig. 4(B), it can be seen that the rod size was larger than that of BiVO$_4$. With the increase in cerium content until 20 at% ($x = 0.2$), the size of the nanorods decreased gradually and the nanorods became less clustered. Whereas, for the sample with the highest cerium content, BCVO 0.3, shown in Fig. 4(G), the dispersed and larger rod-like particles with hundreds of nanometers in width and several micrometers in length came into being. Meanwhile, the surface area in Table 1 also confirmed that when the $x$ values were 0.005, 0.02, 0.05, 0.1 and 0.2, the surface areas of the samples first decreased to 17.42 m$^2$ g$^{-1}$ and then increased to 23.61, 28.38, 33.11 and 42.75 m$^2$ g$^{-1}$, and it decreased again to 11.54 m$^2$ g$^{-1}$ when the $x$ is 0.3. These signify that the presence of cerium in the reaction media may influence the formation of crystalline particles through a characteristic nucleation–dissolution–recrystallization effect in the processing. The substituted Ce induced the crystalline particles to grow into the new morphology and the particle size decreases with the increase in the cerium content.

**Table 1** Surface area, band gap and structural characterization of the BiVO$_4$ and Bi$_{1-x}$Ce$_x$VO$_4$ photocatalysts refined from the XRD data

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Band gap (eV)</th>
<th>Crystal vol (Å³)</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>m-BVO</td>
<td>33.46</td>
<td>2.46</td>
<td>306.85</td>
<td>5.184</td>
</tr>
<tr>
<td>BCVO 0.005</td>
<td>17.42</td>
<td>2.76</td>
<td>344.91</td>
<td>7.306</td>
</tr>
<tr>
<td>BCVO 0.02</td>
<td>23.61</td>
<td>2.74</td>
<td>344.97</td>
<td>7.307</td>
</tr>
<tr>
<td>BCVO 0.05</td>
<td>28.38</td>
<td>2.66</td>
<td>344.65</td>
<td>7.305</td>
</tr>
<tr>
<td>BCVO 0.1</td>
<td>33.11</td>
<td>2.80</td>
<td>344.51</td>
<td>7.303</td>
</tr>
<tr>
<td>BCVO 0.2</td>
<td>42.75</td>
<td>2.81</td>
<td>343.82</td>
<td>7.299</td>
</tr>
<tr>
<td>BCVO 0.3</td>
<td>11.54</td>
<td>2.84</td>
<td>343.35</td>
<td>7.298</td>
</tr>
</tbody>
</table>

**Fig. 3** Schematic crystal structures of the scheelite-type monoclinic and zircon-type tetragonal phases.

However, the larger particle size of the high-level cerium containing sample ($x = 0.3$) might be derived from Ostwald ripening during the process of recrystallization. The homogeneous combination of the Bi$_{1-x}$Ce$_x$VO$_4$ photocatalyst was further confirmed by EDS analysis. Fig. 5 illustrates the image of an individual BCVO 0.2 nanorod which is about 100 nm in width and displays the representative element mapping images. Vanadium was also homogeneous and is not displayed here. It demonstrates an even distribution of the elements in the frame imaging area, reasonably indicating that cerium dissolved into the substrate evenly.

The high-resolution transmission electron microscopy is widely used to characterize the microstructure of nanomaterials. Fig. 6 shows the TEM and HRTEM images of the BiVO$_4$, BCVO 0.1 and BCVO 0.2 photocatalysts. The TEM images (Fig. 6(A)–(C)) clearly confirm that the BiVO$_4$, as well as the Ce-containing samples, had a smooth surface and edged shape, which implied that the cerium species almost anchored into the crystal lattice. As it is shown in Fig. 6(D), the distinct lattice fringes reveal that the BCVO 0.2 nanorod was highly crystallized. The lattice spacing of 0.481 nm in Fig. 6(D) corresponded to the (1 0 1) crystalline plane of the tetragonal phase according to JCPDS card no. 14-0133, whereas lots of defective dots can be observed along the lattice fringes, which reasonably indicated that the substitution of cerium ions in the Bi$^{3+}$ positions could lead to the formation of some lattice defects.

**Chemical state analysis**

The chemical state of the solid solution photocatalysts, especially the effects of unequal-valence substitution on the chemical state, which probably could significantly influence the photocatalytic performance, was further revealed using
XPS analysis. The shift of peak positions was calibrated using the binding energy of C 1s at 284.8 eV before analysis. Fig. 7(A) shows the overall XPS spectra of BCVO 0.2, and only the characteristic peaks of Bi, Ce, V and O were detected. Moreover, the observed peak of C 1s was attributed to the signal from carbon in the instrument. No XPS characteristic peaks of N 1s were detected at around 400 eV although the raw material, ammonium metavanadate, contained the element nitrogen, which indicated that no nitrogen doped into the as-prepared photocatalysts. There were no significant changes in the peak positions of the Bi$^{3+}$ ions and V$^{5+}$ ions after substitution, which were not displayed here. The XPS peaks of Ce 3d are well-known to be complicated because of the hybridization of the Ce 4f orbital with the ligand orbital and fractional occupancy of the valence 4f orbital. Fig. 7(B) illustrates that the Ce 3d spectra were composed of three doublet peaks in the case of the Ce$^{3+}$ species and two doublet peaks in the case of the Ce$^{4+}$ species. The a peaks located at about 881.27 and 885.11 eV in the low binding energy region and at about 899.21 and 904.24 eV in the high binding energy region were assigned to Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$, respectively. These states corresponded to the final states of 3d$^9$4f$^1$ and 3d$^9$4f$^0$ considering the spin–orbit splitting, which indicated the presence of Ce$^{3+}$ in the crystal lattice. The b peaks in Fig. 7(B) at the binding energies of 883.54, 886.49, and 897.78 eV and their spin–orbit splitting peaks at 900.78, 907.02, and 916.59 eV were attributed to Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ of Ce$^{4+}$ as a result of the 3d$^9$4f$^1$, 3d$^9$4f$^2$, and 3d$^9$4f$^0$ final states. Accordingly, from the above results it is quite clear that there is a coexistence of Ce$^{3+}$ and Ce$^{4+}$ in the crystal lattice of the solid solution photocatalysts. Fig. 7(C) shows the XPS peak of the O 1s level in the BiVO$_4$, which is located at 530.02 eV corresponding to the O$^{2-}$ in the crystal lattice. The weak peak for O 1s located at about 531.31 eV was attributed to the O–H bonds of adsorbed water on the sample surface. There are no other peaks in the O 1s XPS spectra of the
BiVO₄ because the binding energy of the metal–oxygen bond is almost located at around 530 eV.³⁶,³⁷ However, the O 1s XPS peak of BCVO 0.2 for the O²⁻ species is much more different after Ce substitution, as it is shown in Fig. 7(D). Three peaks were obtained after the Gaussian–Lorentzian fitting for the O 1s XPS spectra of BCVO 0.2. One of these peaks located at the binding energy of 529.38 eV was assigned to the O–Bi bonds in the crystal lattice. It needs to be noted that this peak
shifted to the low binding energy region by about 0.7 eV in comparison to that of the BiVO₄, which was attributable to the formation of the Ce–O–Bi bonds as a result of the substitution of the Ce ions at the Bi³⁺ positions.38,39 The small peak at 530.76 eV was also attributed to the O–H bonds at the surface of the photocatalyst. And most obviously, a new peak at about 532.41 eV was observed in the spectra for O 1s after Ce substitution. This peak most probably corresponded to the non-stoichiometric O species and interstitial O₂⁻ in the solid solution crystal lattice.30,41

Optical properties
The UV-vis diffuse reflectance spectra of the Bi₁₋ₓCeₓVO₄⁺ₓ⁻дан photocatalysts in comparison with BiVO₄ are shown in Fig. 8. It is clear that the progressive appearance of the tetragonal phase also had a significant effect on the absorption edges of the photocatalysts. As it is shown in Fig. 8, the m-BVO presented an absorption band within the visible range while the Ce-substituted samples showed an absorption band just in the transitional region between the UV and visible range. The newly appeared absorption by the Ce-substituted photocatalysts in the region of λ > 500 nm may be introduced by an f–f transition of cerium species 20 and the absorption improved with the increase in the Ce concentration, which illustrated that the Ce ions in the crystal lattice could have a significant effect on the optical properties of BiVO₄. The optical band gap for the semiconductor photocatalysts was estimated using the following equation:

\[ (A\nu) = a(\nu - E_g)^{n/2} \]

where \( A \) is the absorption coefficient near the absorption edge; \( h \) is the Planck constant with the unit of eV; \( a \) is a constant; \( E_g \) is the absorption band gap energy; BiVO₄ has a direct band gap, and \( n \) is 1 herein.11 The inset in Fig. 8 shows the \((A\nu)^2 \) versus the photon energy \((\nu)\) plots of the m-BVO, BCVO 0.05 and BCVO 0.3 photocatalysts. The band gaps of BCVO 0.05 and BCVO 0.3 were estimated to be about 2.66 and 2.84 eV, respectively, which implied that the adsorption edges of the solid solution samples shifted towards the UV region in comparison to that of m-BVO (2.46 eV). The band gap of the whole Bi₁₋ₓCeₓVO₄⁺ₓ⁻ (0 ≤ x ≤ 0.3) system as a function of the x value was taken into account and is showed in Fig. 9. The crystalline structure changed from the scheelite-type to zircon-type when cerium was introduced, so the band gap variation with composition must be discussed separately according to Vegard’s law.42 The band gap of BCVO 0.005 was 2.76 eV and first sharply decreased to about 2.66 eV at x = 0.05, and then increased non-linearly to 2.84 eV with the increase in the x value. Apparently, these results were in accordance with the so-called bowing effect as reported by Zhou et al.43 However, the situation here was more complex because of the re-transformation of the crystalline structure at x > 0.6.44 Hence, no further comment and bowing fitting was made on this issue. Anyway, the band structure of BiVO₄ changed as the phase transition as well as the composition variation, and the band gaps of all the investigated samples are listed in Table 1.

Photocatalytic properties
The photocatalytic performance of the prepared BiVO₄ and Bi₁₋ₓCeₓVO₄⁺ₓ⁻ samples was first evaluated by examining the photodegradation of MB under visible-light irradiation, as shown in Fig. 10.

All samples were dispersed in MB solution followed by stirring for 60 min in the dark to achieve an adsorption-desorption equilibrium before light irradiation. Fig. 10 shows that the photodegradation rates of MB for the m-BVO, BCVO 0.1 and BCVO 0.02 were about 39%, 36% and 31%, respectively, after 150 min of irradiation, which indicated that only a little portion of MB was degraded by m-BVO and the low Ce
content photocatalysts. This implied that a small amount of cerium substitution probably formed the recombination center for the photogenerated charges because of the short-circuiting mechanism, resulting in the reduced activity of the photocatalysts. As shown in Fig. 10, it is clear that with the subsequent increase in the cerium content, the photocatalytic activity of the Ce-containing samples enhanced obviously. The degradation ratios of MB using BCVO 0.05 and BCVO 0.1 were raised to about 64% and 78%, respectively, after 150 min of irradiation. Especially when the cerium content was 20 at% (BCVO 0.2), a sharp decrease in the MB concentration was observed, and the MB could be entirely degraded within 2 hours under visible-light irradiation. However, the content of cerium sequentially increasing to 30 at% (BCVO 0.3) would lead to the decrease in its photocatalytic performance. A pseudo-first-order kinetic model was used to fit the degradation data. Fig. 11 illustrates the apparent kinetic rate constants of the MB decomposition over the different samples. The rate constant \( k \) was calculated to be \( 1.726 \times 10^{-2} \text{ min}^{-1} \) for the BCVO 0.2, approximately ten-times greater in comparison to that of m-BVO. Generally, a bigger surface area will provide more active reaction sites for both adsorption and degradation. It needs to be noted that BCVO 0.05, BCVO 0.1 and BCVO 0.2 showed much higher photocatalytic activity than that of m-BVO, although they hold approximately the same specific surface areas according to Table 1. These findings clearly demonstrated that the enhanced photocatalytic activity was not mainly derived from the variation of the surface area.

In addition to MB, a typical colorless contaminant, phenol, was also chosen to further evaluate the photocatalytic performance of the samples. There was nearly no adsorption of phenol after 60 min of stirring in the dark and the photodegradation rate of phenol for m-BVO and BCVO 0.2 are shown in Fig. 12. The results indicated that phenol could be hardly degraded under visible-light irradiation without photocatalyst and about 58.6% of phenol was degraded using BCVO 0.2. However, only about 13.4% of phenol could be degraded using m-BVO under the constant experimental conditions. The photocatalytic degradation rate of phenol with BCVO 0.2 is more than four times higher than that of pure BiVO₄. Fig. 13(A) and (B) show the temporal absorption spectral changes of phenol in photodegradation over m-BVO and BCVO 0.2 under visible-light irradiation. Although an obvious absorption peak at 270 nm could be observed after irradiation for 300 min, the absorption peak at 270 nm was much declined for BCVO 0.2 as shown in Fig. 13(B), compared to the m-BVO. These findings further confirmed the enhanced photocatalytic activity of the appropriate Ce-containing solid solution photocatalyst.

**Mechanism of improved photocatalytic activity**

The lower photoactivities reported in the literature for the tetragonal phase BiVO₄ were explained considering the wider
band gap for this phase.\textsuperscript{5,6} Whereas in our case, the solid solution with a relatively wide band gap showed outstanding photocatalytic performance. A possible mechanism can be proposed to illustrate the reasons of the high photocatalytic activity of the solid solution photocatalysts compared to BiVO\textsubscript{4} through the following defect reactions written in the Kröger–Vink notation (eqn (1)–(3)) based on the preceding analysis:

For Ce\textsuperscript{3+}

\[
\text{CeVO}_4 \rightarrow \text{Ce}_{\text{Bi}} + V^\gamma_i + 4O_0 \tag{1}
\]

For Ce\textsuperscript{4+}

\[
\text{Ce}_i(\text{VO}_4)_4 \rightarrow 3\text{Ce}_{\text{Bi}} + 3V^\gamma_i + V^\delta_{\text{Bi}} + 12O_0 + 4O^\delta_i \tag{2}
\]

\[
\text{Ce}_i(\text{VO}_4)_4 \rightarrow 3\text{Ce}_{\text{Bi}} + 4V^\gamma_{\text{Bi}} + 4O^\delta_i + 16O_0 \tag{3}
\]

As shown in eqn (1), Ce\textsuperscript{3+} may occupy the Bi\textsuperscript{3+} positions with the substitution of equal electrical charge. In principle, no charged defects are created in this case. Whereas, there are a number of possible charged defect states (Ce\textsuperscript{3+}, V\textsuperscript{\gamma}_{\text{Bi}}, V\textsuperscript{\delta}_{\text{Bi}} and O\textsuperscript{\delta}_i) in the substituted crystal lattice, which Ce\textsuperscript{4+} ions can introduce according to eqn (2) and (3). The intersitial O\textsuperscript{\delta}_i in the crystal structure of Bi\textsubscript{1-x}Ce\textsubscript{x}VO\textsubscript{4+δ} may exist as O\textsuperscript{2-} species, which was demonstrated by the newly created XPS peak for O 1s after substitution (Fig. 7(D)).

It is commonly accepted that the photodegradation performance in the heterogeneous photocatalytic system comes from the strong oxidizing properties of the active species (hydroxyl radicals (\cdotOH) and superoxide anion radicals (\cdotO\textsubscript{2-})) generated under irradiation. Fig. 14 illustrates the possible mechanism for the enhanced separation efficiency of photogenerated electron–hole pairs and the degradation of MB under visible light irradiation. As shown in the schematic, photo-excited electrons (\cdote) were generated from the valence band into the conduction band of Bi\textsubscript{1-x}Ce\textsubscript{x}VO\textsubscript{4+δ} when the samples were irradiated under visible light. Meanwhile, the corresponding holes (\cdoth) were leaving in the valence band. In the process of transferring to the photocatalyst surface, the photo-excited electrons (\cdote) were trapped by the acceptor defects (Ce\textsuperscript{\gamma}_{\text{Bi}}, V\textsuperscript{\delta}_{\text{Bi}}) and the holes (\cdoth) were trapped by the donor defects (V\textsuperscript{\gamma}_{\text{Bi}}, O\textsuperscript{\delta}_i), which efficiently depress the recombination of the electron–hole pairs. However, excess charged defects in the crystal lattice could form an associated center under Coulomb interaction, which made only a few electron or hole transfers to the surface of the catalyst, resulting in the decline of the photocatalytic activity (the photocatalytic activity of BCVO 0.3 in Fig. 10 and 11). The holes (\cdoth) transferred to the surface could oxidize the H\textsubscript{2}O and O\textsuperscript{-} to hydroxyl radicals (\cdotOH) which played an important role in the photocatalytic oxidation process. Another important active species, the superoxide anion radicals (\cdotO\textsubscript{2-}), were produced by excited electron (\cdote) reduced interstitial O\textsuperscript{2-} species and adsorbed O\textsubscript{2}. In the end, MB can be oxidized and degraded by these active species. The main reactions were concluded as follows:

\[
\text{semiconductor} \rightarrow \text{e}_{\text{CB}}^\cdot + h_{\text{VB}}^+ \\
\text{OH}^- + h_{\text{VB}}^+ \rightarrow \cdot\text{OH} \\
\text{O}_2(\text{O}_2^2) + \text{e}_{\text{CB}} \rightarrow \cdot\text{O}_2 + (2\cdote) \\
\cdot\text{O}_2 + \cdot\text{H} \rightarrow \cdot\text{O}_2\text{H} \\
\cdot\text{OH} + \text{OH}^- \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \cdot\text{O}_3\text{H} \rightarrow \cdot\text{OH} + \text{H}_2\text{O} + \text{O}_2 \\
\text{MB} + \cdot\text{OH} \rightarrow \text{product}
\]

The effective separation of the photogenerated electron–hole pairs was confirmed by PL analysis. Fig. 15 shows the photoluminescence spectra of the BiVO\textsubscript{4} and Bi\textsubscript{1-x}Ce\textsubscript{x}VO\textsubscript{4+δ} samples. The luminescence signal at around 600 nm is actually a characteristic PL peak of BiVO\textsubscript{4}, which corresponded to the
recombination of the hole (h+) formed in the O 2p and the electron (e−) in the V 3d.45 It implied that the lower peak corresponded to the more effective separation of the electron–hole pairs. As shown in Fig. 15, obvious decreases in the PL intensities were observed for the Bi1−xCeIVO4+δ samples with the x value higher than 0.005. When x is 0.2, the PL peak was much more declined in comparison to that of m-BVO and BCVO 0.005. These findings reasonably indicated that the appropriate presence of the charged defects in the solid solution crystal lattice could effectively suppress the recombination of photogenerated electron–hole pairs.

The photocurrent responses of the photocatalysts in an electrolyte under visible light directly correlate with the generation and transfer of the photoinduced charge carriers in the photocatalytic process, which can further confirm the separation of electron–holes pairs.46 Fig. 16 shows the photocurrent responses of m-BVO, BCVO 0.02, BCVO 0.1 and BCVO 0.2 with light on and off. It is clear that the photocurrent responses of BCVO 0.1 and BCVO 0.2 were much higher than that of m-BVO and BCVO 0.02. Compared with the pure BiVO4, BCVO 0.2 exhibited the most enhanced photocurrent response. It implied that a more efficient separation of the photogenerated electron–hole pairs and fast transfer of photoinduced charge carriers occurred in the BCVO 0.2 sample. Additionally, it needs to be noted that all the Ce-containing samples hold residual current with the light off. This is probably attributed to the lattice defects in solid solutions, which could release the trapped electrons or holes under thermal motion.47 Meanwhile, the photocurrent responses of the samples corresponded well to their photocatalytic performance. This reasonably indicated that the Bi1−xCeIVO4+δ photocatalysts exhibited much higher
utilization efficiency of visible light, although they absorbed less visible light in comparison to the m-BVO according to Fig. 8.

To further clarify the reasons of the high photocatalytic activity, the involved active radical species was detected by the spin-trapping electron paramagnetic resonance technique. And DMPO was used to trap the active species produced in the photocatalytic reaction under visible light irradiation. The results are shown in Fig. 17 and there was no signal when all the suspensions were in the dark. In contrast, four characteristic peaks with an intensity ratio of 1 : 2 : 2 : 1 for DMPO-trapped 'OH were observed in the m-BVO and solid solution samples as shown in Fig. 17(A). The signal intensity of the DMPO–OH species produced by m-BVO is weak, suggesting the limited photocactivity of m-BVO. However, the signal intensity of the DMPO–OH species produced by BCVO 0.1 and BCVO 0.2 increased progressively, corresponding to the enhanced photocatalytic performance as confirmed by the degradation of MB and phenol.

DMSO was introduced to quench the signal of the DMPO–OH species in order to detect the EPR signal of the DMPO–O₂⁻ adducts produced by the samples. It can be deduced from Fig. 17(B) that only BCVO 0.2 could generate 'O₂⁻ active species in the dispersion. In addition, methyl radical signals derived from the reactions of the 'OH radical with DMSO were also observed, which are in accordance with the reported studies. Generally, 'O₂⁻ is the product of the reduction of adsorbed O₂ on the catalyst surface and the interstitial O₂²⁻ species in the lattice, as illustrated in Fig. 14. However, there was no obvious signal for DMPO–O₂⁻ produced by m-BVO and BCVO 0.1, although they both create 'OH species. It indicated that the valence band of BCVO 0.2 was raised higher than E(O₂/O₂⁻)¹⁹,⁴⁴ after the appropriate substitution of Ce.

To the best of our knowledge, this work may be the first attempt to create Biₓ₋ₓCeₓVO₄⁺⁺⁺ to improve the photocatalytic activity of BiVO₄. Although the specific process for the formation of the active species was poorly elucidated, there was much reason to believe that the amount of these active species is closely dependent on the separation of the photoexcited electron–hole pairs. And it paves the road for the further investigations of photocatalytic mechanism.

**Conclusion**

In summary, monoclinic phase BiVO₄ and tetragonal phase Biₓ₋ₓCeₓVO₄⁺⁺⁺ photocatalysts have been successfully prepared by homogeneous precipitation with the hydrothermal method. The studies revealed that the introduction of cerium into the BiVO₄ lattice brought an obvious change in the crystal phase and optical properties. The mole ratio of Bi to Ce in Biₓ₋ₓCeₓVO₄⁺⁺⁺ was found to affect the photodegradation of MB and phenol. And the optimum mole ratio was found to be 20% (Bi₀.₈Ce₀.₂VO₄⁺⁺⁺), showing the best photocatalytic performance under visible-light illumination. The PL spectra and the photocurrent responses indicated the lattice defects in the Biₓ₋ₓCeₓVO₄⁺⁺⁺ photocatalysts greatly depressed the recombination of electron–hole pairs. Moreover, both 'OH and 'O₂⁻ were detected using EPR spectroscopy and the possible mechanism for enhanced photocatalytic activity was proposed. Further detailed studies to fully understand the explicit mechanism on improving the photocatalytic performance under visible light are ongoing in our laboratory.

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**References**
