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The construction of a wide-spectrum-responsive and high-activity photocatalyst, Bi₂₅CoO₄₀, *via* the creation of large external dipoles[†]

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Currently, a major issue in the field of photocatalysis is the insufficient utilization of solar energy by photocatalysts. Thus, to overcome this problem, herein, a new sillenite photocatalyst, $Bi_{25}CoO_{40}$, was designed to exhibit a nearly full visible-light spectrum response (up to 750 nm) and high activity. In particular, its photocatalytic activity for the degradation of typical wastewater pollutants (e.g., MB and 4-CP) reached up to $3.402 h^{-1}$ for MB under visible-light irradiation and $1.576 h^{-1}$ for 4-CP under full spectrum irradiation. The degradation rates are *ca.* 2–4 times higher than those of well-studied photocatalysts such as P25-TiO₂, Bi_2WO_6 , and $g-C_3N_4$, and are also the best for organic pollutant removal among reported photocatalysts absorbing above 700 nm. Results showed that the remarkable degradation on $Bi_{25}CoO_{40}$ is mainly due to the efficient charge separation resulting from the large external diploe moment between [Co^{III}O₄] and [Bi^VO₄] tetrahedrons. Results further illustrated that the VBM of new photocatalysts is composed of Co 3d–O 2p orbitals and exhibits a potential (*ca.* 2 eV) positive enough to produce oxidative species for the degradation of organic pollutants. The construction of a large external dipole moment without sacrificing the valence band edge potential may provide some design rules for the development of more efficient photocatalysts with a wide-spectrum response.

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1. Introduction

Photocatalytic oxidation is an energy-saving and environmentally friendly technology that can totally convert toxic organic pollutants into CO₂ and H₂O.¹ Since this technology is driven by sunlight, photocatalysts that absorb most of the visible light will be, in principle, highly efficient because visible light occupies a large portion of solar energy (*ca.* 47%).² Accordingly, many narrow band gap photocatalysts have been developed with high activity and an absorption band edge located generally at around 400–600 nm. Photocatalysts such as sulfide,³ nitride,⁴ iron-based photocatalysts⁵ and bismuth-based photocatalysts⁶ have been reported to exhibit superior performances to the commercial photocatalyst-P25 (TiO₂). Thus, currently, photocatalysts that respond to a higher wavelength (above 600 nm) are being researched to achieve the maximum utilization of solar energy. However, the activity of photocatalysts with a narrow bandgap is dramatically reduced, which is probably due to the high e^--h^+ recombination rate derived from their low excitation energy or insufficient band edge, making the production of reactive species difficult.^{7,8} Therefore the development of highly active photocatalysts with an adsorption band edge above 600 nm is still a major challenge in the field of photocatalysis.

Bismuth-based photocatalysts, such as Bi₂WO₆,⁹ BiVO₄,¹⁰ and BiOX (X = Cl, Br, and I),¹¹ are typical photocatalysts with promising activity for environmental remediation. Their high activity originates from the dipole moment-induced promotion of the separation of photogenerated carriers.12 The dipole moment existing inside distorted [BiO₄] or [BiO₅] polyhedrons is created due to the existence of the Bi³⁺ 6s² lone pair. The internal dipole is supposed to solve the issue of the recombination of photogenerated carriers, leading to high activity for wide-spectrum-responsive photocatalysts ($\lambda_{abs} > 600$ nm). However, developed Bi-based photocatalysts with a response at a wavelength larger than 600 nm do not actually exhibit superior activity as expected because they suffer from other problems including multiple defects in their structure, acting as recombination centres (e.g., Pr-doped Bi₂O₃ (ref. 13)), low band edge potential, which is not suitable for producing sufficient oxidation species (e.g., $Bi_{25}MnO_{40}$, V.B. = 1.4 eV (ref. 14) or Vdoped $Bi_{25}FeO_{40}$, VB = 0.8–1.1 eV (ref. 15)), and unstable chemical components that are easily photo-corroded (e.g.,

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BiOI¹⁶). Thus, considering the research gap between actual problems and potential activity advantages, the development of new bismuth-based photocatalysts with a wide spectrum response and high-activity is still of significant interest.

Sillenites are photocatalysts with a wide spectrum response, but their activity is strongly limited by their high rate of carrier recombination. γ -Bi₂O₃, as one of the simplest sillenite photocatalyst, is reported to absorb most of the sunlight ($\lambda_{abs} < 550$ nm) compared to other Bi₂O₃ phases, such as α -Bi₂O₃ (λ_{abs} < 420 nm) and β -Bi₂O₃ (λ_{abs} < 450 nm), and exhibits a positive valence band edge (V.B. = 3.0 eV).^{17,18} Thus, this photocatalyst is regarded as a parent material for studying other sillenites, the structure of which is reported to be $Bi_{12}[(Bi^x{}_{Bi}O_3 \square O_{0.8} (\square O_{Bi}O_4)_{0.2}]O_{16}$.¹⁹ In this structure, the tetrahedral sites are occupied by Bi3+ cations and Bi vacancies (represented as \Box), while the octahedral positions are occupied by Bi³⁺ cations with a 6s² lone pair of electrons. Both O and Bi vacancies exist in the tetrahedral sites to complete the coordination. These vacancies together with the weak driving force for the separation of charge carriers resulting from the narrow bandgap may lead to a high recombination rate of charge carriers, and thus limit the activity of γ -Bi₂O₃.

Regarding the structure difference between γ -Bi₂O₃ and the standard chemical formula of sillenite $(Bi_{12}(Si^{IV}O_4)O_{16})$, complete cation co-substitution of the tetrahedral Bi³⁺ enables the rearrangement of the tetrahedral atoms, which will fill the vacancies, thus decreasing the number of recombination centres. Moreover, a charge difference may form between the co-substituted cation-centred tetrahedrons if co-substitution is performed using paired cations with valence states higher or lower than +4. The formed positive and negative tetrahedrons will cause an external dipole moment in the structure besides the internal dipole moment, resulting from the distortion of the [BiO₄] or [BiO₅] polyhedrons, which may inhibit the rapid recombination of charge carries in narrow-bandgap photocatalysts and significantly enhance their photocatalytic activity. On the other hand, appropriate co-substituted cations will also narrow the bandgap. This effect has been reported in other bismuth salts, such as La/Sr co-doped BiFeO₃ (ref. 20) and Fe/ Mo co-doped BiVO₄.²¹ Although partial substitution has been intensively studied, complete cation co-substitution of Bi-based photocatalysts has been rarely studied, and there is a lack of comprehensive understanding on the relationship between the enhancement of photocatalytic activity and the structural change resulting from complete cation co-substitution.

Herein, Co^{3^+} and Bi^{5^+} were designed to completely cosubstitute for Bi^{3^+} at the tetrahedral sites of γ -Bi₂O₃ to form a newly designed sillenite photocatalyst, $\text{Bi}_{25}\text{CoO}_{40}$ (Bi₂₄(Bi^V, Co^{III})O₄₀). In this design, the 3d orbitals of Co^{3^+} and 6s orbitals of Bi⁵⁺ are proposed to contribute to the band edge and narrow the bandgap, while Bi⁵⁺ and Co³⁺ co-substitution may fill the vacancies in γ -Bi₂O₃, which will create an external dipole moment between the [Co^{III}O₄] and [Bi^VO₄] tetrahedrons and help enhance the separation of photogenerated charge carriers. The crystal structure of Bi₂₅CoO₄₀ has been previously reported by Devalette *et al.*,²² but it has not been studied as a photocatalyst to date. The newly designed sillenite photocatalyst was

prepared via a hydrothermal method, which exhibited both a wide spectrum response (up to 750 nm) and high activity. The formation of Bi25CoO40, which is associated with the structure change resulting from the complete co-substitution method, was examined via physical and spectroscopic methods. The photocatalytic activity of the prepared Bi25CoO40 photocatalyst was evaluated via the degradation of typical pollutants including methylene blue (MB) and 4-chlorophenol (4-CP). In particular, the photocatalytic activity of Bi₂₅CoO₄₀ was not only stable, but also superior to that of well-known photocatalysts, such as g-C₃N₄, P25-TiO₂ and Bi₂WO₆. The relationship between the excellent photocatalytic activity of Bi25CoO40 and complete co-substitution was studied in detail. Furthermore, the effect of the construction of a large external dipole moment without sacrificing the valence band edge potential via the cosubstitution method on the promotion of charge separation and photocatalytic activity was elucidated.

2. Experimental section

All chemicals were of analytic grade and purchased from the National Chemical Company (Shanghai, China) and used as received without further purification. Ultrapure water with a resistivity of 18.20 M Ω was used in all experiments.

2.1 Synthesis of sillenite Bi₂₅CoO₄₀

Bi₂₅CoO₄₀ was prepared *via* a hydrothermal method. In a typical procedure, 2.5 mmol BiCl₃ and 0.1 mmol Co(NO₃)₂·6H₂O were added to a 30 mL ethanol/water mixed solution (1 : 1 volume ratio). Then 10 mL of aqueous 8 mM KOH was added with stirring and a canary coloured suspension was formed. This suspension was stirred for another 30 min at room temperature and then transferred to a 50 mL Teflon-sealed stainless steel autoclave. The autoclave was maintained at 180 °C for 24 h and then cooled to room temperature. After the reaction, the product was washed several times with water and ethanol until pH = 7. The product was finally dried at 60 °C overnight and ball-milled at 1400 rpm for 1 h before use. For comparison, sillenite γ -Bi₂O₃ was prepared in the same manner.

2.2 Characterization of Bi₂₅CoO₄₀

The crystal structure was characterized *via* powder X-ray diffraction (XRD, Bruker D8-ADVANCE X-ray diffractometer German) with a Cu K α monochromator at 40 kV and 40 mA. The morphology was characterized *via* scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, JEM 2100plus, JEOL, Japan). The Brunauer-Emmett-Teller surface area was determined *via* nitrogen absorption-desorption isotherm measurements at 77 K on a nitrogen absorption apparatus (Micromeritics, ASAP2020 MP). The composition of the product was studied *via* X-ray photo-electron spectroscopy (XPS, Axis Supra, Kratos, UK) with Al K α monochromatized radiation ($h\nu = 1486.6$ eV, 225 W) and ICP-AES (PE optima 8000). The XPS spectrum was calibrated using the C 1s peak (284.8 eV) to eliminate the charge effect. The adsorption was recorded using a UV-vis spectrophotometer

(Persee TU-1901, China). Fluorescence spectra were recorded on an FL spectrophotometer (FS5, PL, Edinburgh, UK).

2.3 Evaluation of photocatalytic activity

The photocatalytic activity of the prepared samples was evaluated via the photodegradation of methylene blue (MB, 100 mL, 2 \times 10⁻⁵ M) and 4-chlorophenol (50 mL, 5 ppm) under a 300 W Xe lamp (Perfect Light, Beijing, China) equipped with a 420 nm cut-off filter. The average light intensity was measured to be 90 mW cm⁻². The concentration of the photocatalyst was 0.5 g L⁻¹ in the suspension. Before the reaction, the suspension was ultrasonicated for 10 min for dispersion and then stirred for 30 min in the dark to reach absorption-desorption equilibrium. The saturated adsorption of the organic pollutants in the dark was about 10% in all cases. During the degradation, 4 mL suspension was sampled at certain intervals and centrifuged to remove the contained photocatalyst particles. The concentration of MB solution was analyzed via UV-vis spectroscopy based on its maximum absorption peak (663 nm). The concentration of 4-CP was monitored at 225 nm by high performance liquid chromatography (HPLC, Ultimate 3000 RS) equipped with a C18 reverse phase column.

2.4 Photoelectrochemical test

The photocurrent, open circuit potential (OCP) decay and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical work station (CHI 750E, Chenhua, Shanghai, China). A three-electrode system was employed for the test with the photocatalyst as the working electrode, a platinum net as the counter electrode, and the standard Ag/AgCl electrode (E = 0.210 V vs. NHE) as the reference electrode. During the test, 0.1 M Na₂SO₄ was used as the electrolyte, while a 300 W Xe lamp was used as the light source. The working electrode of Bi₂₅CoO₄₀ was cast on FTO glass *via* the drop-coating method. In particular, 2–3 mg Bi₂₅CoO₄₀ was dispersed in 100 μ L H₂O to form a homogeneous slurry. The slurry was then carefully dropped onto an FTO glass (1 cm × 1.5)

cm) and dried in a vacuum oven overnight to form the $Bi_{25}CoO_{40}/FTO$ electrode. The prepared $Bi_{25}CoO_{40}/FTO$ electrode was finally calcined at 300 °C for 1 h before use. The thickness of the prepared film was estimated to be *ca.* 50–100 μ m.

3. Results and discussion

3.1 The successful formation of $Bi_{25}CoO_{40}$ via paired Co^{3+} and Bi^{5+} cation co-substitution at the tetrahedral sites of sillenite

Fig. 1 shows the XRD patterns of Bi25CoO40 prepared via hydrothermal treatment for different times. In the first stage (0 h), several broad peaks were observed. All these peaks can be assigned to bismuth basic nitrate ($[Bi_6O_{4.5}(OH)_{3.5}]_2(NO_3)_{11}$), as previously reported,23 indicating that no target sillenite was formed at this stage. With an increase in the reaction time from 0 h to 12 h, a peak belonging to the sillenite phase was observed. Notably, the strongest sillenite peak located at ca. 27.5° was split into two, indicating that the formed phase was a mixture. The composition of the mixture is proposed to be sillenite Bi25CoO40 and γ -Bi₂O₃ because the location of the two split peaks is consistent with the standard patterns of Bi25CoO40 (PDF No. 39-0871) and γ-Bi₂O₃ (PDF No. 45-1344), respectively. With a further increase in the reaction time to 24 h, the observed peak splitting disappeared, indicating the successful formation of pure sillenite Bi₂₅CoO₄₀.

We also carried out control experiments without the addition of EtOH and with 100% EtOH as the solvent. The XRD patterns of the prepared samples are shown in the Supporting Information, Fig. S1.† It was found that without the addition of EtOH, XRD peaks belonging to monoclinic α -Bi₂O₃ instead of cubic sillenite Bi₂₅CoO₄₀ were observed. In the case of 100% EtOH, instead of Bi₂₅CoO₄₀, a metallic Bi phase was formed. Thus, the control experiments suggest that both H₂O and EtOH are necessary for the formation of pure sillenite Bi₂₅CoO₄₀ under the used hydrothermal conditions. The existence of H₂O will stabilize the Bi³⁺, which is probably due to the ease of



Fig. 1 (a) XRD patterns of $Bi_{25}CoO_{40}$ prepared *via* hydrothermal treatment for different times. (b) XRD refinement for $Bi_{25}CoO_{40}$ prepared at 180 °C for 24 h with an EtOH/H₂O ratio of 1 : 1.

oxidation of EtOH by Bi^{3^+} cations under conditions. The existence of EtOH will facilitate the formation of $Bi_{25}CoO_{40}$. $C_2H_5O^$ anions will form under basic conditions and coordinate with Bi^{3^+} ,²⁴ which may accelerate the exchange of the tetrahedral Bi^{3^+} with Bi^{5^+} and Co^{3^+} , benefitting the formation of sillenite $Bi_{25}CoO_{40}$.

Fig. 1b shows the XRD refinement of Bi₂₅CoO₄₀ prepared at 180 °C for 24 h with an EtOH/H₂O (V/V) ratio of 1:1. The refinement was performed using the Rietveld method and the parameters are listed in the Supporting Information, Table S1.[†] In Fig. 1b, the circles, red line, orange line and black line represent the raw data, fitting line, background and residuals, respectively. The data shows that the XRD pattern is well fitted with few residuals. R_{wp} and χ^2 , indicators of the fitting goodness, were calculated to be 9.73% and 1.80, respectively, which are comparable to other XRD refinement results for sillenite structures, such as $Bi_{12}FeO_{20}$ ($R_{wp} = 6.48\%$, $\chi^2 = 1.47$)²⁵ and $(Bi,Sm)_{24}V_2O_{40}$ ($R_{wp} = 6.44\%$, $\chi^2 = 1.5$).²⁶ The lattice constant was calculated to be 10.137 Å, which is slightly larger than the theoretical value (10.118 Å). The refinement results further showed that Co occupies the tetrahedral sites of sillenite with a deduced occupation ratio of 0.492, which is close to our ICP result (0.475) and the theoretical ratio (0.5). The rest of the tetrahedral sites were found to be occupied by Bi cations, the valence state of which must be 5+ to maintain charge balance. Therefore, the XRD refinement confirmed that both the Bi⁵⁺ and Co³⁺ cations completely substitute the tetrahedral Bi³⁺ and vacancies in the parent structure, sillenite γ -Bi₂O₃, as we designed.

The existence of Bi^{5+} and Co^{3+} in the sillenite structure was further confirmed by XPS measurement. Fig. 2 shows the full XPS spectrum of $Bi_{25}CoO_{40}$ and narrow scans for Bi 4f, Co 3p, and O 1s, respectively. A peak analysis of the narrow scan spectra was performed to better understand the existence of each species. According to the full XPS spectrum in Fig. 2a, only Bi, Co, O and adventitious C signals can be observed. No K or Cl signals from the KOH or BiCl₃ precursors are observed, indicating that the reaction was complete. According to the Bi 4f XPS scan (Fig. 2b), two pairs of peaks can be observed at around 158.6–163.9 eV and 165.4–160.1 eV, which can be assigned to Bi³⁺ and Bi⁵⁺, respectively.²⁷ In the Co 2p XPS scan (Fig. 2c), one pair of main peaks and one pair of satellites can be observed, which are located at around 794.9–779.4 eV and 804.9–788.8 eV, respectively. The peak splitting between the main peaks and the



Fig. 2 XPS spectra of the prepared $Bi_{25}CoO_{40}$: (a) wide scan, (b) Bi 4f, (c) Co 2p, and (d) O 1s. The dots represent the raw data; the dash line represents the fitting data for each species; and the red line is the whole fitting data.

satellites is *ca.* 9.7 eV. The positions of the main peaks and the peak splitting between the main peaks and the satellites indicate the existence of Co^{3+} in the structure.²⁸ Fig. 2d shows the O 1s XPS scan, which can be fitted into four peaks at 528.6 eV, 529.4 eV, 530.5 eV and 532.4 eV. These peaks can be assigned as Bi–O–Bi, Bi–O–Co, surface O, and surface OH groups, respectively, according to the literature.²⁹ Thus, the Bi, Co and O XPS spectra demonstrate the successful co-substitution of Bi⁵⁺–Co³⁺ at the tetrahedral sites in sillenite, which is consistent with the XRD results.

Fig. 3 shows the morphological characterization of Bi₂₅CoO₄₀. Fig. 3a and b show the SEM images of the prepared Bi₂₅CoO₄₀. Bi₂₅CoO₄₀ exhibits a particle-like structure with a primary particle size of around 20-80 nm. Reported sillenite particles such as γ -Bi₂O₃ (ref. 30) and Bi₂₅FeO₄₀ (ref. 31) always show a particle size larger than 1 µm. In our case, the addition of EtOH clearly inhibited the growth of the primary particles, resulting in a small size. Fig. 3c shows the TEM image of the prepared Bi₂₅CoO₄₀, further confirming its morphology. The TEM image shows that the primary particles easily agglomerated together, forming large secondary particles with a size of ca. 200 nm-1 µm. Notably, the size of the secondary particles shown in the image was reduced by the ball milling method. Without ball milling, the initial secondary particles were larger (2-20 µm), as shown in the Supporting Information, Fig. S2.† The lattice image of the prepared Bi₂₅CoO₄₀ is shown in Fig. 3d,

where the lattice distance is measured to be 0.282 nm, corresponding to the (222) planes of the $Bi_{25}CoO_{40}$ crystals. The BET surface area of $Bi_{25}CoO_{40}$ was also measured, as shown in the Supporting Information, Fig. S3.† The data showed that the prepared sample exhibits a BET surface area of *ca.* 2.3 m² g⁻¹, which is comparable to that of other high-activity Bi-salt phototocatalysts with a similar particle size such as BiPO₄ (3.0 m² g⁻¹ and 150 nm).³²

3.2 Wide-spectrum response and high valence band edge potential of $Bi_{25}CoO_{40}$ resulting from the co-substitution

The band structure of $Bi_{25}CoO_{40}$ is shown in Fig. 4. Fig. 4a and its inset show the UV-DRS spectra of sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 , respectively. The curves show that $Bi_{25}CoO_{40}$ absorbs up to 750 nm, covering most of the UV-visible-light region of the solar spectrum (300–800 nm), while γ -Bi₂O₃ absorbs up to 540 nm. For $Bi_{25}CoO_{40}$, three peaks located at around 350 nm, 450 nm and 700 nm can be observed. The details of these transitions will be discussed in the following paragraph. The bandgap of sillenite $Bi_{25}CoO_{40}$ and γ -Bi₂O₃ was determined using the Tauc plots. Accordingly, the bandgap of sillenite $Bi_{25}CoO_{40}$ was measured to be 1.70 eV, which is much narrower than that of γ -Bi₂O₃ (2.75 eV). Since these two compounds exhibit the same sillenite structure, the narrowing bandgap is probably due to the contribution of the valence orbitals of the substituting Bi^{5+} or Co^{3+} cations.



Fig. 3 SEM (a and b) and TEM (c and d) images of the prepared Bi₂₅CoO₄₀.



Fig. 4 (a) UV-vis spectra of sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . Inset is the Tauc plot of $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . (b) Experimental and calculated band edge positions (*versus* NHE, pH = 0) of sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . (c and d) DFT calculation for $Bi_{25}CoO_{40}$: crystal model (c) and PDOS (d).

It should be noted that the bandgap of Bi₂₅CoO₄₀ was determined according to the first tangent since the transition does not originate from the impurities but due to the transitions between the hybrid orbitals formed by the 3d orbitals of the Co³⁺ cations with O 2p or Bi 6p, as previously reported,³³ which will be detailed in the following discussion on the DFT results. To further confirm that the first tangent does not originate from impurities such as vacancies as previously reported,^{34,35} EPR measurements were carried out, as shown in the Supporting Information, Fig. S4a.† In the EPR spectra, $Bi_{25}CoO_{40}$ shows a one sixth weaker intensity than that of γ -Bi₂O₃, indicating that less oxygen vacancies exist in the Bi₂₅CoO₄₀ lattice. Since the small amount of oxygen vacancies in γ -Bi₂O₃ only show a slight response (around 800 nm) in the UV-DRS spectrum, the much less oxygen vacancies in Bi25CoO40 will lead to a negligible absorbance.

Fig. 4b shows the band edge positions for sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 , which were determined by the measurement of the flat band potential³⁶ and theoretical calculation.³⁷ The Supporting Information, Fig. S4b and c,† shows the Mott–Schottky plots for sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 , respectively, revealing their flat band potentials. The conduction band (C.B.) is suggested to be 0.1–0.3 V above the flat band potentials.³⁶ Referring to previous studies on

Bi₂O₃,^{38,39} here the value was determined to be 0.1 V. The measured flat band potentials for sillenite Bi25CoO40 and y-Bi2O3 were 0.096 V and 0.122 V vs. Ag/AgCl, respectively. Accordingly, the C.B. and valence band (V.B.) of sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 were found to be 0.21 V and 1.91 V, and 0.23 V and 2.98 V, respectively. The theoretical calculation was performed according to a method based on the absolute electronegativity suggested by Xu et al.37 and detailed in the Experimental section of the Supporting Information.[†] The calculation results show that the band edge positions for sillenite Bi₂₅CoO₄₀ and γ-Bi₂O₃ are 0.35 V (C.B.) and 2.05 V (V.B.), and 0.36 V (C.B.) and 3.11 V (V.B.), respectively. The calculation results are similar to our experimental results, indicating the good accuracy of the determination of the band edge positions. The XPS valence band spectrum of Bi25CoO40 was further measured to confirm the measured band edges (shown in the Supporting Information,† Fig. 4d). Again, similar band edge positions were obtained. Notably, the valence band edge positions for sillenite Bi25CoO40 were close to 2 V by all the methods, indicating co-substitution will maintain the rather strong oxidative ability of the new photocatalyst.

The band structure of $Bi_{25}CoO_{40}$ was further studied *via* the DFT method (detailed in the Supporting Information†). Fig. 4c and d show the crystal structure used for the calculation and the

partial density of state (PDOS) of Bi25CoO40. A homogeneous Bi and Co distribution was used to simplify the calculation and also based on our XRD refinement results. Using this model, the valence band maximum (VBM) was calculated to be mainly composed of Co 3d and O 2p, while the conduction band minimum (CBM) was mainly composed of O 2p-Bi 6p. Notably, the 3d orbitals of the Co atoms in the [Co^{III}O₄] tetrahedron contribute mainly to the valence band, and only a little to the conduction band, which is often seen in transition metal-based sillenite (e.g. Bi12TiO20) and other Bi-Co-O systems (e.g. $BiCoO_3$).^{40,41} The 6s and 6p orbitals of the Bi atoms in the [Bi^VO₄] tetrahedron show a slight contribution to the VBM and CBM, indicating the delocalization of their valence shell electrons. The DFT results also explain the three peaks observed in the UV-DRS spectrum of Bi₂₅CoO₄₀. The peak at 350 nm is similar to that observed in γ -Bi₂O₃, which is due to the band transition of the O 2p to Bi 6p orbitals, as previously reported.⁴² The peaks at 450 nm and 700 nm are due to the band transitions from Co 3d-O 2p to the higher energy Bi 6p orbitals (located above 2.0 eV) and to lower-energy hybrid orbitals (located between 1.6-2.0 eV), that is, Bi 6p, O 2p, and a slight contribution from the Co 3d orbitals, respectively. The DFT study indicated that upon light irradiation, e⁻ is excited to the O 2p-Bi 6p orbitals, while h⁺ remains in the Co 3d-O 2p orbitals.

3.3 Remarkable degradation and complete mineralization of MB and 4-CP on wide-spectrum-responsive Bi₂₅CoO₄₀ photocatalyst

Fig. 5 shows the photodegradation of MB and 4-CP on the prepared photocatalysts. The typical model pollutants, MB and 4-CP, were used to evaluate the photocatalytic activity, as previously reported.43,44 Fig. 5a and Supporting Information, Fig. S5[†] show the degradation of MB on the $Bi_{25}CoO_{40}$, γ - Bi_2O_3 , g-C₃N₄ and Bi₂WO₆ photocatalysts. g-C₃N₄ and Bi₂WO₆, which were prepared according to our previously reported methods, were employed for comparison because they are generally regarded as photocatalysts with high visible-light activity.45,46 On sillenite Bi₂₅CoO₄₀, 95% of MB was degraded within 50 min, while within the same time, only ca. 30% of MB was degraded on γ -Bi₂O₃ (Supporting Information, Fig. S5[†]). The kinetic rate constant in the degradation process was calculated to be 3.402 h^{-1} for sillenite Bi₂₅CoO₄₀, which is nearly 14 times that for γ - Bi_2O_3 (0.251 h⁻¹) (Fig. 5a). Remarkable activity enhancement was observed on $Bi_{25}CoO_{40}$ relative to γ - Bi_2O_3 , indicating that the co-substitution of Co^{3+} and Bi^{5+} for tetrahedral Bi^{3+} in γ - Bi_2O_3 may be beneficial to enhance the photocatalytic activity.

On the other hand, MB was degraded quicker on $Bi_{25}CoO_{40}$ than that on g-C₃N₄ and Bi_2WO_6 . Within 50 min irradiation, *ca.* 90% and 52% of MB was degraded on g-C₃N₄ and Bi_2WO_6 ,



Fig. 5 (a) Photodegradation rate of MB on $Bi_{25}COO_{40}$, γ - Bi_2O_3 , g- C_3N_4 and Bi_2WO_6 ($\lambda > 420$ nm). (b) Wavelength-dependent activity of $Bi_{25}COO_{40}$ for the degradation of MB. (c) Stability of $Bi_{25}COO_{40}$ for the photodegradation of MB. (d) Photodegradation curves of 4-CP on $Bi_{25}COO_{40}$ and P25-TiO₂ under full-spectrum irradiation and the concurrent TOC removal on $Bi_{25}COO_{40}$ photocatalyst (Xe lamp, $\lambda > 300$ nm).

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respectively, while more than 95% of MB was degraded on Bi₂₅CoO₄₀ (Supporting Information, Fig. S5[†]). The kinetic rate constant for the degradation of MB on Bi₂₅CoO₄₀ was 3.4 times and 2.2 times higher than that on $g-C_3N_4$ (0.996 h⁻¹) and Bi_2WO_6 (1.576 h⁻¹), respectively (Fig. 5a). The photocatalytic activity of Bi25CoO40 is the best among the reported sillenite photocatalysts with a visible-light response (generally, 4 h is needed for more than 90% degradation of pollutants, as detailed in the Supporting Information, Table S2[†]). Also, our photocatalyst exhibits better activity for pollutant oxidation than other narrow bandgap photocatalysts absorbing above 700 nm, such as Cu-salts and sulfides (Supporting Information, Table S3[†]). For the oxidation of organic pollutants, the activity of Bi₂₅CoO₄₀ is only lower than the newly reported Bi₈(CrO₄)O₁₁ photocatalyst, which contains Cr⁶⁺ in its lattice and has a response slightly below 700 nm.

Fig. 5b and Supporting Information S6[†] show the wavelength-dependent activity of Bi25CoO40 for the degradation of MB. Its activity is presented as series of kinetic rate constants, which were obtained under various wavelength cutoff filters, ranging from 300 nm to 730 nm. In the figure, the kinetic rate constants for the degradation of MB decrease with an increase in the cut-off wavelength. The decreasing tendency is generally the same as the absorption curves of $Bi_{25}CoO_{40}$ (Fig. 4a), indicating the photocatalytic activity originates from the band excitation of Bi25CoO40. Notably, Bi25CoO40 showed apparent activity under the wavelengths larger than 730 nm. In this case, only Bi₂₅CoO₄₀ absorbs light, not MB. This demonstrates again that the activity is due to band excitation, not the excitation of the MB dye. This wavelength-dependent activity suggests that Bi₂₅CoO₄₀ is a promising photocatalyst with a wide-spectrum response above 700 nm.

Next, the stability of $Bi_{25}CoO_{40}$ was tested, as shown in Fig. 5c, which figure shows that its activity for the degradation of MB did not change after 5 cycles, indicating its good stability. According to the DFT results, Bi^{5+} and Co^{3+} contribute little to the CBM, and thus, electron-induced photo-corrosion may barely occur on $Bi_{25}CoO_{40}$ compared that in other photocatalysts containing Bi^{5+} or Co^{3+} , such as $LaCoO_3$ and $NaBiO_3$, which may be responsible for the observed stability.

The oxidative species produced during the photodegradation of MB were also studied (Supporting Information S7†). Research has indicated that hydroxyl radicals (OH⁺), holes (h⁺) and super oxide radicals (O₂⁻⁻) are the typical oxidative species produced on photocatalysts, which initiate the photocatalytic degradation. These species can be trapped by formic acid (FA), *tert*-butyl alcohol (*t*-BuOH) and benzoquinone (BQ), respectively. In our case, the addition of *t*-BuOH and BQ did not influence the activity much, whereas the addition of FA strongly inhibited the activity. This suggests that h⁺, which is produced on Bi₂₅CoO₄₀, may be the main active species involved in the degradation of MB. Simultaneously, e⁻ produced on Bi₂₅CoO₄₀ will form super oxide radicals with O₂, which are supposed to participate in the oxidation process of the fragments derived from the decomposed pollutants.

Encouraged by the superior activity of $Bi_{25}CoO_{40}$, its fullspectrum activity was evaluated to simulate its activity under sunlight, which was compared to the widely used photocatalyst, P25-TiO₂. 4-CP was employed as a general model for colourless and minimally biodegradable pollutants.1 The photodegradation of 4-CP and the concurrent total organic carbon (TOC) removal are shown in Fig. 5d and Supporting Information Fig. S8.[†] The HPLC results (Supporting Information, Fig. S8[†]) and degradation results (Fig. 5d) show that the concentration of 4-CP decreased rapidly after 30 min irradiation; meanwhile, the concentration of intermediates such as benzoquinone (BQ) and hydroquinone (HQ) increased. With an increase in time, the concentration of 4-CP and benzoquinone (HQ) decreased to nearly zero, while the concentration of HQ continued to increase due to the further oxidation of BQ. The accumulated HQ could be further degraded and converted into CO2 and H2O in 4 h according to the TOC results shown in Fig. 5d. For comparison, the photodegradation of 4-CP was also carried out on P25. In this case, the activity of $Bi_{25}CoO_{40}$ (2.28 h⁻¹) was nearly as twice that of P25 (1.05 h⁻¹), indicating its superior activity. In summary, Bi25CoO40 shows superior degradation activity for both MB and 4-CP, indicating that the good activity does not originate from specific pollutants, but due to the nature of the photocatalyst.

3.4 The formation of large external dipoles in Bi₂₅CoO₄₀ and their effect on the enhancement of charge separation and photocatalytic activity

Photocatalytic activity is related to multiple factors, such as particle size, nanostructure, crystal structure, band edge potential, light adsorption, and separation efficiency of photogenerated electrons and holes. In our case, Bi25CoO40 can be regarded as the co-substitution of Bi5+ and Co3+ cations for tetrahedral Bi^{3+} in γ - Bi_2O_3 . The two compounds prepared via a similar method exhibited the same crystal and morphological structure (Supporting Information, Fig. S9^{\dagger}). Besides, γ -Bi₂O₃ exhibited a more positive valence band edge potential than that for $Bi_{25}CoO_{40}$ (Fig. 4). Therefore, γ - Bi_2O_3 is expected to show higher activity than Bi25CoO40. Nevertheless, Bi25CoO40 exhibited much better activity than γ-Bi₂O₃. One reason for this may be that $Bi_{25}CoO_{40}$ absorbs more light than γ -Bi₂O₃. However, this may not be the decisive factor for the observed activity enhancement. Many reported sillenites (Supporting Information, Table S2[†]) also exhibit a narrower bandgap relative to γ -Bi₂O₃, but they do not show obviously activity enhancement. After excluding all the above factors, the most possible reason for the excellent activity of Bi25CoO40 is proposed to be the suppression of the charge carrier recombination rate, which may result from co-substitution, as discussed below.

PEC measurements, such as transient photocurrent, electrochemical impedance measurement, surface photovoltage measurement and OCP decay, are regarded as sensitive indicators for studying the recombination rate.¹ Fig. 6 shows the PEC results for $Bi_{25}COO_{40}$ and γ - Bi_2O_3 to clarify the difference in recombination rate between them. Fig. 6a shows the transient photocurrent of $Bi_{25}COO_{40}$ and γ - Bi_2O_3 under illumination and in the dark. The transient photocurrent signals were recorded at each light on/off interval (40 s). Under irradiation, the transient



Fig. 6 (a) Transient photocurrent for $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 , (b) electrochemical impedance measurement for $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 , (c) Surface P–V spectra for $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 , and (d) open circuit potential (OCP) decay for $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 .

photocurrent of $Bi_{25}COO_{40}$ reached up to 1.1 µA cm⁻², while the current of γ -Bi₂O₃ was reduced to 0.3 µA cm⁻². The higher current indicates a higher separation efficiency of photogenerated carriers in $Bi_{25}COO_{40}$ than that in γ -Bi₂O₃.⁴⁶ These results are also consistent with the LSV results shown in the Supporting Information, Fig. S10.[†]

Fig. 6b shows the electrochemical impedance spectra (EIS) under illumination and in the dark for Bi₂₅CoO₄₀ and γ-Bi₂O₃. A Randles circuit was used to simulate the impedance results, as shown in the inset of Fig. 6b, which has been verified to be effective in many TiO₂-based systems.⁴⁷ The fitting parameters are listed in the Supporting Information, Table S4.[†] In Fig. 6b, both $Bi_{25}CoO_{40}$ and Bi_2O_3 exhibit similar semicircles under illumination and in the dark, but with different radii. In particular, the samples show a smaller radius under illumination relative to that in the dark, indicating a decrease in the charge transfer resistance. This is because illuminating samples will increase the generation of electrons and holes, and further increase the conductivity. The detailed fitting results show that $R_{\rm ct}$, an indicator for the charge transfer in the powder electrode, decreased from 29.3 $k\Omega$ in the dark to 6.12 $k\Omega$ under illumination for $Bi_{25}CoO_{40}$, while for γ - Bi_2O_3 , it decreased from 66 k Ω to 39 k Ω . Clearly, Bi₂₅CoO₄₀ shows a larger R_{ct} change compared to γ -Bi₂O₃, suggesting that the former sample has better charge transfer ability compared to γ -Bi₂O₃ under illumination.

Fig. 6c shows the surface P–V spectra (SPV) for $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . On the one hand, both $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 exhibit a surface photovoltaic response together with their UV-DRS spectrum, indicating that the observed photocatalytic activity is due to band excitation. On the other hand, the SPV response of photocatalysts was reported to result from the separation of the photogenerated electron–hole pairs.⁴⁸ In our case, the SPV of $Bi_{25}CoO_{40}$ is obviously higher than that of γ - Bi_2O_3 , suggesting that $Bi_{25}CoO_{40}$ has a better separation efficiency of photogenerated carriers relative to γ - Bi_2O_3 .

Fig. 6d shows the open circuit potential (OCP) decay curves for $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . The OCP decay has been reported to be capable of determining differences in the photogenerated charge separation process.⁴⁹ In particular, the decay in the OCP is due to the recombination of photogenerated electron–hole pairs, which leads to changes in the flat band potential. The faster the OCP decays, the faster the photogenerated electron–hole pairs decay. During the measurement, $Bi_{25}CoO_{40}$ and Bi_2O_3 were first irradiated under illumination, and then kept in the dark to relax the OCP. As seen in Fig. 6d, the potential change upon UV illumination was ~0.1–0.2 V for both photocatalysts, which is

commonly observed in photocatalysts.⁴⁹ The increase in the OCP under illumination for Bi₂₅CoO₄₀ compared to γ -Bi₂O₃ indicates that Bi₂₅CoO₄₀ excites more electrons than γ -Bi₂O₃. The kinetic constant for the decay process can be fitted by using exponential regression.⁴⁹ Accordingly, the kinetic rate constants for the decay process of Bi₂₅CoO₄₀ and Bi₂O₃ were determined to be 7.80 × 10⁻⁴ s⁻¹ and 1.47 × 10⁻³ s⁻¹, respectively. Bi₂₅CoO₄₀ exhibits a smaller kinetic rate constant compared to γ -Bi₂O₃, suggesting that Bi₂₅CoO₄₀ has a better carrier separation efficiency.

Fig. 7a and b show the PL and PL decay spectra for Bi25CoO40 and y-Bi2O3, respectively. The PL intensity reflects the recombination rate of photogenerated carriers in Bi25CoO40 and y-Bi₂O₃ since they have the same structure and particle size. According to Fig. 7a, it can be found that γ -Bi₂O₃ exhibits a PL peak intensity (ca. 468 nm) four times higher than that for Bi₂₅CoO₄₀, indicating that Bi₂₅CoO₄₀ has a slow recombination rate. The PL decay spectra for $Bi_{25}CoO_{40}$ and $\gamma\text{-}Bi_2O_3,$ as shown in Fig. 7b, supply more direct evidence for the difference in charge separation efficiency because the measurement reflects the lifetime of the photogenerated carriers. The decay curves were fitted according to exponential regression (detailed in the Supporting Information[†]) and plotted as solid lines. As shown in Fig. 7b, the PL peak intensity of Bi₂₅CoO₄₀ decays slower than that of γ -Bi₂O₃. Notably, a hump was observed at 2 ns, which is due to the photomultiplier effect of the instrument, as previously reported.⁵⁰ In particular, Bi₂₅CoO₄₀ and γ-Bi₂O₃ showed a decay time of 2.76 ns and 0.53 ns, respectively. The longer decay time of Bi25CoO40 indicates the longer lifetime of its photogenerated carriers and slow recombination rate.

Thus, the PEC measurement and PL results confirm that the excellent activity in sillenite $Bi_{25}CoO_{40}$ is due to its efficient charge separation. Since the only difference between sillenite $Bi_{25}CoO_{40}$ (a high-activity photocatalyst) and γ - Bi_2O_3 (a low-activity photocatalyst) is the existence of an external dipole moment between the [Co^{III}O4] and [Bi^VO4] tetrahedrons in the former structure, rapid charge separation may result from this, as discussed below.

Fig. 8a details the structural change between sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . In the common sillenite structure, Bi^{3+} occupies an octahedral site with 5 O atoms and a lone pair of

electrons coordinated. The metal cation with a valence state of +4 occupies a tetrahedral site with 4 O atoms coordinated. Each tetrahedron is linked by two octahedrons. In the case of γ -Bi₂O₃, the tetrahedral site is occupied by Bi³⁺ and Bi vacancy with a total of 4 O²⁻ and O vacancies coordinated. For Bi₂₅CoO₄₀, Bi³⁺ and the Bi vacancy are co-substituted by Co³⁺ and Bi⁵⁺ cations, while the O vacancy is occupied by O²⁻ for charge balance. Accordingly, the number of vacancies that act as recombination centres greatly decrease, which may be partially beneficial for charge separation.

More importantly, the structure of $Bi_{25}CoO_{40}$ reveals that the Co^{3+} and Bi^{5+} cations occupy the same tetrahedral sites but possess a lower and higher valence state relative to that in the standard sillenite (+4), respectively. This will form a negative and positive net charge for the Co^{3+} and Bi^{5+} -centred tetrahedron, respectively. The charge difference will cause the formation of an external dipole moment between the paired tetrahedrons. The large external lattice dipole may cause a built-in electric filed and facilitate charge separation, as discussed below.

The electron density difference was calculated via the DFT method to show effect of the above-mentioned external dipole moment on the charge separation. (Detailed in the Experimental section of the Supporting Information[†]). Fig. 8b shows the electron density difference on the (110) planes of sillenite $Bi_{25}CoO_{40}$. The (110) plane is shown because the Co^{3+} and Bi⁵⁺-centred tetrahedrons are both located in this plane and the difference between them is the largest. According to Fig. 8b, it is clear that the valence shell electrons distribute mostly around the Co³⁺-centred tetrahedrons and O²⁻, while the positive charge must distribute around the Bi5+-centred tetrahedrons to maintain the charge balance. Thus, an external dipole moment will form between [Co^{III}O₄] and $[Bi^{V}O_{4}]$, as we supposed. The value of the lattice dipole was calculated to be 30.1 D, which is considerably large compared to that of reported bismuth-salt photocatalysts, such as BiPO₄ (10.5 D) and Bi₈CrO₄O₁₁ (22.23 D).⁵¹ In the previous reports, distortion of the [VO₄] or [TiO₆] polyhedrons formed an internal dipole moment and facilitate charge separation.52,53 In layered photocatalysts such as Bi₂WO₆, the dipole moment



Fig. 7 (a) PL spectra of $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 and (b) PL decay spectra of $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . Excitation wavelength: 350 nm.



Fig. 8 (a) Structure difference between sillenite $Bi_{25}CoO_{40}$ and γ - Bi_2O_3 . (b) Electron density difference on the (110) plane of the $Bi_{25}CoO_{40}$ lattice (2 × 1 × 1), and schematic relationship between the excitation of photogenerated carriers and the dipole moment in sillenite $Bi_{25}CoO_{40}$.

between the [Bi₂O₂] and [WO₄] layers were also reported to facilitate charge separation.54 In our case, when the compound was excited, electrons are transferred from the Co 3d-O 2p orbitals to the Bi 2p–O 2p orbitals, namely, from the [Co^{III}O₄] tetrahedrons to the [Bi^{III}O5] octahedrons (Fig. 8b), according to our PDOS results, as shown in Fig. 4. The formed external dipole moment may help the charge transfer by keeping the holes in the $[CoO_4]$ tetrahedrons and repelling the electrons to the [BiO₅] octahedrons, leading to efficient charge separation. Also, although the Co^{3+} and Bi^{5+} co-substitution in $Bi_{25}CoO_{40}$ did not dramatically decrease the valence band potential, Bi₂₅CoO₄₀ still maintained a rather positive valence band edge potential, which was sufficient to produce oxidative species for degrading organic pollutants. Thus, the highly efficient charge separation induced by the external dipole associated with the positive valence band edge potential may be responsible for the activity observed.

4. Conclusion

In summary, a newly designed sillenite, $Bi_{25}COO_{40}$, was reported for the first time as a wide-spectrum-responsive and highactivity photocatalyst for the degradation of organic pollutants. The photocatalyst exhibited a wavelength response up to 750 nm, and a quick degradation rate for MB and 4-CP. The activity is the best among the reported photocatalysts responsive above 700 nm and also superior to other well-known photocatalysts, such as P25-TiO₂, g-C₃N₄ and Bi₂WO₆. The excellent performance was demonstrated to result from the large external dipole created between the $[Co^{III}O_4]$ and $[Bi^VO_4]$ tetrahedrons associated with a considerably positive valence band edge (*ca.* 2 eV). The development of Bi₂₅CoO₄₀ as a wide-spectrum-responsive and high-activity photocatalyst and the understanding of its high-activity mechanism may give some guide-lines for the design of more efficient photocatalysts with a narrow bandgap in the future.

Conflicts of interest

The authors claim that there are no conflicts to declare.

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