An Innovative Anion Regulation Strategy for Energy Bands of Semiconductors: A Case from Bi$_2$O$_3$ to Bi$_2$O(OH)$_2$SO$_4$

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How to develop a new, efficient photo catalyst is still a big challenge to us. A suitable band gap is the key for light absorption of semiconductor. Herein, an innovative anion intercalation strategy is, for the first time, developed to regulate the energy band of semiconductor. Typically, we introduce a layered sulfate compound (Bi$_2$O(OH)$_2$SO$_4$) as a new photo catalyst, which has not been known before. Both partial density of states (PDOS) and total density of states (TDOS) have demonstrated that compared with Bi$_2$O$_3$ (2.85 eV), the band gap of Bi$_2$O(OH)$_2$SO$_4$ has been widened to 4.18 eV by the intercalation of sulfate anion. Moreover, the band gap width of oxyacid salt compound is mainly predominated by the number of the outmost charged PO$_4^{3-}$ anion that benefits the photogenerated charge separation. Besides BiPO$_4$ and Ag$_3$PO$_4$, the other oxyacid salts containing nonmetals have also been reported to have higher activities than titania, including Bi$_2$O$_3$Cl, Bi$_2$O$_2$CO$_3$, and Cu$_2$(OH)PO$_4$, and so on. In these cases, the characteristic layered structure of (Bi$_2$O$_2$)$_2$Cl is believed to produce an internal electric field that is favorable for the efficient separation and transfer of photogenerated electrons and holes. Furthermore, Bi-based semiconductors are also found to possess the hybridized energy band structures on account of the lone pair electrons of bismuth, which can effectively inhibit the recombination of photogenerated electrons and holes. Since the first report by Fujishima and Honda, photo catalysis has been researched extensively, which only utilizes abundant solar energy. Up to now, a variety of semiconductors photo catalysts have been developed including oxides, sulfides, oxysalts and polymers and many efforts have been made to explore beneficial structure and suitable compositions. Regrettably, the practical applications are limited by the low quantum efficiency, light utilization efficiency and photo activity. Thus, it is still a big challenge to develop the efficient, inexpensive photo catalysts, which would greatly promote the applications of this technology in practices.

Recently, nonmetal oxyacid salts have attracted significant attentions from researchers. Ye et al. have reported that Ag$_3$PO$_4$ has an outstanding photo oxidation activity, and they have further suggested that the new oxyacid salts photo catalysts could be potentially developed through combining $p$-block nonmetal elements (e.g., B, P, S, etc.) with binary oxide (e.g., Bi$_2$O$_3$, Cu$_2$O, etc.). This prediction can be demonstrated by an efficient BiPO$_4$ photo catalyst. Zhu et al. have revealed that it is the inductive effect of large dipole resultant from negatively-charged PO$_4^{3-}$ anion that benefits the photogenerated charge separation. Besides BiPO$_4$ and Ag$_3$PO$_4$, the other oxyacid salts containing nonmetals have also been reported to have higher activities than titania, including Bi$_2$O$_3$Cl, Bi$_2$O$_2$CO$_3$, and Cu$_2$(OH)PO$_4$, and so on. In these cases, the characteristic layered structure of (Bi$_2$O$_2$)$_2$Cl is believed to produce an internal electric field that is favorable for the efficient separation and transfer of photogenerated electrons and holes. Furthermore, Bi-based semiconductors are also found to possess the hybridized energy band structures on account of the lone pair electrons of bismuth, which can effectively inhibit the recombination of photogenerated electrons and holes. First, the highly-positive valence band has not only endowed the photogenerated holes with a strong oxidizing ability, leading to the complete mineralization of organic pollutants without forming intermediate chemicals; Second, the abundant OH groups on crystal surfaces facilitate the formation of the reactive hydroxyl radicals ($\cdot OH$) = 2.38 eV). The complete mineralization is beneficial to maintain a clean surface and stable activity of photo catalyst. Furthermore, it has been reported that sulfate anion-modification of TiO$_2$ can increase the decolonization rate due to the intrinsic attribution of sulfate anion: i) its strong bonding ability with H$_2$O...
favors for the formation of ·OH; ii) its high negative charge favors to
draw holes to the interface by electrostatic force, leading to an
efficient separation of photogenerated charges. Meanwhile, the
layered Bi₂O₂[BO₂(OH)] has been developed as an efficient photo
catalyst and its photo activity is 2.5 times higher than commercial
rutile TiO₂ for the degradation of methylene blue (MB). On base of
the reports above, we could expect that the Bi₂O₂SO₄ compound,
simultaneously containing Bi, OH and SO₄²⁻, may be a
new, inexpensive, promising photo catalyst. Among nonmetal oxy-
acid semiconductors, nevertheless, the Bi₂O(OH)₂SO₄ compound as
a photo catalyst has not been reported to date.

Herein, we introduce the hydroxyl-containing layered sulfate
compound (Bi₂O(OH)₂SO₄) as a new photo catalyst. First, the
Bi₂O(OH)₂SO₄ compound is prepared by a simple water-bath
method. Secondly, theory simulation method is employed to analyze
its crystal, electronic and energy band structures. Finally, we have
mainly revealed the essential correlation of its activity with energy
band and crystal structures. The innovative contribution of the study
includes: i) The layered sulfate compound (Bi₂O(OH)₂SO₄) is found
to have a high photo catalytic activity, which has been unknown
before; ii) Compared with Bi₂O₃, the intercalation of sulfate anions
have adjusted the energy band structure of Bi₂O(OH)₂SO₄; and as a
general strategy, it can also suitable for Bi₂O₂[BO₂(OH)], Bi₂O₂CO₃,
Bi₂O₂(NO₃(OH)), etc. iii) The regulation strategy of energy band
provides us a novel idea to find new photo catalysts, namely, various
new photo catalysts can be developed by grouping anions with the
existing oxides or sulfides photo catalysts.

Results
Crystal structures of Bi₂O(OH)₂SO₄. Figure 1(a) presents the
crystal structure model of Bi₂O(OH)₂SO₄. It has a monoclinic
space group (P2₁/c) with the unit cell parameters of a =
7.692(3)Å, b = 13.87(1)Å, c = 5.688(2)Å and β = 109.01(3)°. It
consists of sulfate anions groups and [Bi₂O(OH)₂⁺]n double chains,
with a featured layered structure. According to crystallographic data,
the polycations double chains (Figure 1(b)) are constructed by four-
member ring (Bi₁(1)-OH(1)-Bi₂(2)-O) and six-member ring (Bi₁(1)-
OH(2)-Bi(2)-O-Bi(1)-O). It is observed that each hydroxyl (OH)
should connect two Bi atoms, and each O atom connects three Bi
atoms. The coordination spheres of both Bi₁ and Bi₂ are
completed by the redundant O atoms of SO₄²⁻ anion. It is
noteworthy that the distance of between OH(1) and O(4) is
calculated to be 2.77(1) Å (Figure 1(c)), indicating that a hydrogen
bond can form between them, which favors to stabilize the whole
structure. These hydroxyl groups are verified by infrared spectra (IR)
(Figure S1, seeing electronic supporting information (ESI)). In
particular, the [Bi₂O(OH)₂⁺]n polycations double chains can only
extend along the [001] direction, as known from the net structure of
[Bi₂O₂]²⁺ in Aurivillius-phase (e.g., Bi₂MoO₆, Bi₂WO₆, Bi₂SiO₅) or
Sillen-phase (e.g., BiOX, X = Cl, Br, and I). This interesting

Figure 1 | (a) Crystal structure of Bi₂O(OH)₂SO₄; (b) The projection figure of [Bi₂O(OH)₂⁺]n polycations along a axis; (c) Environment of OH(1)-
O(4) hydrogen bond.
characteristic results from the involvement of negative hydroxyl groups.

The Bi$_2$O(OH)$_2$SO$_4$ sample was prepared by a water-bath method. Figure S2 (Seeing ESI) shows the X-ray diffraction (XRD) patterns of the-prepared sample. All the diffraction peaks are well in agreement with the standard card (JCPDS 761102). No impurities peaks, e.g., Bi(OH)$_3$ or Bi$_2$O$_3$ or Bi, are observed, which confirms the formation of phase-pure Bi$_2$O(OH)$_2$SO$_4$. Figure S3 (Seeing ESI) presents the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the as-prepared sample. It is obvious that the Bi$_2$O(OH)$_2$SO$_4$ flowers form, which are self-assembled by the nanorods of (1–1.5) $\mu$m x 0.5 $\mu$m. Its single crystalline nature has been revealed by the electron diffraction pattern (ED). Furthermore, Bi$_2$O(OH)$_2$SO$_4$ has a small solubility product value of $1.8 \times 10^{-31}$, meaning a good stability in an aqueous media. The pH value of supernatant is 1–2 after preparation, indicating that Bi$_2$O(OH)$_2$SO$_4$ is also stable under acidic condition.

**Optical property and band gap of Bi$_2$O(OH)$_2$SO$_4$.** Figure 2 and Figure S4 (Seeing ESI) show the ultraviolet-visible diffusion reflectance spectra (UV-DRS) of Bi$_2$O(OH)$_2$SO$_4$. In the absorption edge region of semiconductor, the square of absorption coefficient is linear with direct optical transition energy, whereas the square root of absorption coefficient linear with indirect optical transition energy$^{30}$. As observed from the inset of Figure 2, the plots of absorbency$^{2}$ ((zhv)$^2$) and absorbency$^{1/2}$ ((zhv)$^{1/2}$) vs. photon energy (hv) in the absorption edge region are different: the plot of (zhv)$^2$ vs. hv is nearly linear, while the plot of (zhv)$^{1/2}$ vs. hv deviates from the fitted straight line. Hence, we could hold that the absorption edge of Bi$_2$O(OH)$_2$SO$_4$ is caused by direct optical transition. The optical band gap of Bi$_2$O(OH)$_2$SO$_4$ can be determined by Equation (1) as follows.

$$ahv = A(hv-E_g)^{n/2}$$  \hspace{1cm} (1)

where $n$ is dependent on the optical transition type of a semiconductor ($n=1$, direct absorption; $n=4$, indirect absorption)$^{31}$, $a$, $v$, $A$ and $E_g$ represent absorption coefficient, photon frequency, proportionality constant and band gap, respectively. From the plot of (zhv)$^2$ vs. hv, the direct band gap of Bi$_2$O(OH)$_2$SO$_4$ is determined to be 4.18 eV, corresponding to an optical absorption edge of 302 nm (Figure S4). It is obvious that Bi$_2$O(OH)$_2$SO$_4$ has a wider band gap than Bi$_2$O$_3$ (Figure 3). Moreover, we have calculated the positions of conduction band ($E_{CB}$) and valence bands ($E_{VB}$) using Equations (2) and (3) as follows, respectively$^{32}$.

$$E_{CB} = \chi - E_e - 0.5E_g$$  \hspace{1cm} (2)

$$E_{VB} = \chi - E_e + 0.5E_g$$  \hspace{1cm} (3)

Where $\chi$ is the geometric mean of Mulliken’s electronegativities of constituent atoms, $E_e$ is the energy of free electrons at the hydrogen scale (~4.5 eV), and $E_g$ is the band gap. The $\chi$ value is calculated to be 6.80 eV, $E_{VB}$ and $E_{CB}$ are determined to be 4.39 and 0.21 eV, respectively. The highly positive valence band suggests that Bi$_2$O(OH)$_2$SO$_4$ may have a high oxidation ability, which favors for the complete oxidation of organic dye.

**Effect of sulfate anion and electronic structure.** The Ab initio density functional theory (DFT) calculations have been carried out to insight the electronic structures of Bi$_2$O(OH)$_2$SO$_4$. Figure 4(a) shows its band structure calculated by the CASTEP package. Both valence band maximum (VBM) and conduction band minimum...
(CBM) at the G point further confirm the direct band gap property of Bi$_2$O(OH)$_2$SO$_4$, in good agreement with the feature of the measured absorption spectrum. Meanwhile, the indirect transition from G point to B point is also allowed, in that the indirect band gap and the direct band gap at G point are fairly close energetically. The direct band gap between VBM and CBM is 3.88 eV, with an expected diminution that is frequently pointed out as a common feature of DFT calculations. For Bi-based semiconductors, it is always found that the Bi 6s and O 2p orbits could form a preferable hybridized valence band (VB). Accordingly, a reasonable dispersed energy can be observed in Figure 4(a), which would favor the transportation of the photogenerated electrons and holes, thus improving the photo catalytic activity.

The total density of states (DOS) and the partial DOS (Figure 4(b)) are employed to explore the electronic properties of Bi$_2$O(OH)$_2$SO$_4$. Several characteristics can be concluded as follows: (i) the VB upper of Bi$_2$O(OH)$_2$SO$_4$ is found to be not only composed of O 2p orbital, but also a little of Bi 6s and 6p orbits; while the CB bottom is dominantly composed of the Bi 6p orbital, rather than O 2p orbital. This characteristics are similar to CaBiO$_2$Cl, Bi$_2$O$_2$[BO$_2$(OH)]$_3$, and so on; (ii) In SO$_4^{2-}$ group, a significant hybridization can be observed among S 3s, 3p and O 2p orbits located at $-23$ eV and $-19$ eV, respectively. The hybridization in VB favors for the formation of stable chemical bonds between oxygen and sulfur; (iii) At the energies higher than $-5$ eV, the H 1s and S 3s, 3p orbits contribute little to the VB top or CB bottom; (iv) The contribution of electronic state distribution of O (bonding to S) orbit to VB top seems much larger than that of O (bonding to Bi) orbit; (v) A large orbit hybridization occurs between H 1s orbits and O (bonding to Bi and S) orbits; (vi) For Bi$_2$O(OH)$_2$SO$_4$, the charge transfer upon photo exciting occurs from the hybrid orbits of both O 2p and Bi 6s to the empty Bi 6p orbit. It is noted that the electronic structure can provide an important

**Figure 4** | (a) Electronic state structures of energy band and (b) Total and partial density of state (TDOS and PDOS) of Bi$_2$O(OH)$_2$SO$_4$: The vertical dash line represents the valence band maximum (VBM).
insight into the physicochemical behavior of materials. In fact, O (in SO$_4^{2-}$) 2p orbit predominantly constitutes the VB top, but the contribution of H to band edge is negligible, suggesting that the addition of sulfate anion can adjust the band structure, thus resulting in a higher positive VB of Bi$_2$O(OH)SO$_4$ than that of Bi$_2$O$_3$ ($E_{VB} = 2.85$ eV)$^{37}$. Moreover, a large hybridization between H 1s and O 2p (in SO$_4^{2-}$)不失本性 exists the existence of hydrogen bonds (OH(I) to O(4)), which benefits to stabilize the Bi$_2$O(OH)$_2$SO$_4$ structure.

To further understand the role of SO$_4^{2-}$ anion in the energy band structure of Bi$_2$O(OH)$_2$SO$_4$, we have compared four typical Bi-based oxyacid compounds with the similar layered structure. Table 1 lists the $E_{VB}$ and $E_{CB}$ values of four Bi-based oxyacid compounds, which are calculated by Eq. (3) and (4) above. Among the four compounds, all the central atoms (B, C, N, and S) in the anions locate in p block, and their numbers of the outmost electrons (NOE) increase in order. Their CBM values are positive, meaning that they cannot be used to directly acquire H$_2$ by water splitting. It is obviously observed from Figure 5 that both band gap and VBM value are positively correlated (in SO$_4^{2-}$) with the similar layered structure. Table 1 list the $E_{VB}$ and $E_{CB}$ values of four Bi-based oxyacid compounds, which are calculated by Eq. (3) and (4) above. Among the four compounds, all the central atoms (B, C, N, and S) in the anions locate in p block, and their numbers of the outmost electrons (NOE) increase in order.

| Chemicals | $\gamma$ (eV) | $E_g$ (eV) | $E_{VB}$ (eV) | $E_{CB}$ (eV) | NOE |
|-----------|---------------|------------|---------------|---------------|-----|
| Bi$_2$O$_3[OH]BO_2$ | 6.34 | 3.0$^{23}$ | 3.26 | 0.41 | 3 |
| Bi$_2$O$_2$CO$_3$ | 6.54 | 3.10$^{17}$ | 3.59 | 0.49 | 4 |
| Bi$_2$O$_2[OH]NO_3$ | 6.80 | 3.54$^{48}$ | 4.07 | 0.53 | 5 |
| Bi$_2$O(OH)$_2$SO$_4$ | 6.80 | 4.18 | 4.39 | 0.21 | 6 |

*Notes: $\gamma$, Geometric mean of Mulliken’s electronegativities; $E_g$, Band gap; VBM, Valence band maximum; CBM, Conduction band minimum; NOE, Number of outmost electron.

Photo catalytic properties. Rhodamine B (RhB) is chosen as a probe molecule to evaluate the photo catalytic performances of the samples. Figure 6(a) shows the degradation curves of RhB over the Bi$_2$O(OH)$_2$SO$_4$ and commercial rutile TiO$_2$. After 50 min, 71% of RhB can be degraded by Bi$_2$O(OH)$_2$SO$_4$, while only 31% of RhB is degraded by commercial rutile TiO$_2$, demonstrating a high photo oxidizing ability of Bi$_2$O(OH)$_2$SO$_4$. In Figure 6, the apparent reaction rate constants ($k_a$) are determined to be 0.024 min$^{-1}$ and 0.0076 min$^{-1}$ for Bi$_2$O(OH)$_2$SO$_4$ and commercial rutile TiO$_2$, respectively; and the degradation rate of RhB over Bi$_2$O(OH)$_2$SO$_4$ is 2.16 times faster than that of the latter. To increase light response performance in future.

Photo electrochemical properties. Electrochemical impedance spectroscopy (EIS) is measured to investigate the electron transfer (Figure 7). Under UV illumination, the semicircle radius of Bi$_2$O(OH)$_2$SO$_4$ electrode is obviously smaller than that under darkness. Also, its semicircle radius is significantly smaller than
that of commercial rutile TiO\textsubscript{2} under UV illumination or darkness. A smaller semicircle radius in Nyquist plot means a smaller electric resistance of electrode, which favor for electron transfer, thus leading to an efficient charge separation\textsuperscript{44}. Therefore, we hold that the intrinsic layer structure of Bi\textsubscript{2}O(OH)\textsubscript{2}SO\textsubscript{4} favors for the transfer and separation of electron-hole pairs, leading to an improved photo catalytic properties.

The photo catalytic activity of material can be directly reflected by the transient photocurrent generated under light illumination\textsuperscript{45}. As shown in Figure 8, the photocurrent of Bi\textsubscript{2}O(OH)\textsubscript{2}SO\textsubscript{4} electrode can continuously generate while light-on, and its photocurrent density is greatly larger than that of commercial rutile TiO\textsubscript{2}. The unique layer structure may favor for the separation and transfer of charges. The result is in accord with the order of photo catalytic activity, because...
the generation of photogenerated carriers is a critical step of photo catalytic reactions. The result demonstrates an excellent photo catalytic performances of Bi₂O(OH)₂SO₄. Besides, an incident photon-to-electron conversion efficiency (IPCE) measurement was performed. However, a very small efficiency or almost no photon-to-electron conversion can be observed in wavelength range of 200–800 nm in our experiment (Figure S11 of ESI). It is because the light intensity is fairly weak at light wavelengths shorter than 300 nm for the Xe lamp.

Discussion
The BET area of Bi₂O(OH)₂SO₄ is determined to be 9.8 m² g⁻¹, which is only one fifth of that (50 m² g⁻¹) of commercial rutile TiO₂. Its high degradation activity seems closely relative to the characteristic layer structure that may favor for the separation and transfer of charges. Herein, we hold that two main factors play an important role in the photo catalytic oxidation of RhB dye: (i) the separation and transfer efficiencies of photogenerated electrons and holes; (ii) the number of the formed ‘OH radicals.

First, the [Bi₂O(OH)²⁺]n double chains extend along the [001] direction, and they independently interleave with the slab of SO₄²⁻ to form an unique layered structure. The layered structure would lead to an internal electric field perpendicular to the cationic [Bi₂O(OH)²⁺]n slab and anionic SO₄²⁻ slab, similar to BiOCl. This internal electric field, different somewhat from BiOCl, is also parallel to anionic SO₄²⁻ slab, which result from the intervened arrangement of [Bi₂O(OH)²⁺]n double chains. Strikingly, a strong electrostatic force can be produced by the large negatively charged SO₄²⁻ anions than Cl⁻ anions. Therefore, its unique layered structure may be mainly responsible for the efficient separation of photogenerated electrons and holes. Summarily, the photo catalytic activity of Bi₂O(OH)₂SO₄ can be significantly improved by the efficient separation and transfer of charges, as confirmed by the EIS and photocurrent results above.

Second, Bi₂O(OH)₂SO₄ has a more positive E_vb (4.39 eV) due to the intercalation of anionic sulfate, compared with Bi₂O₃ (2.85 eV), TiO₂ (2.7 eV) and E’ (‘OH/OH⁻) = 2.38 eV. As a result, the highly positive holes generated over Bi₂O(OH)₂SO₄ are thermodynamically favorable to react with H₂O and/or OH⁻ to produce more ‘OH radicals. Thus, the ‘OH radicals and/or highly positive holes result in the mineralization of organic dyes. Meanwhile, the intercalated SO₄²⁻, with a highly negative electrostatic force, has a strong bonding ability with H₂O molecules, and also favors to draw the holes to the surface. As a result, the photo catalytic performance of Bi₂O(OH)₂SO₄ can be improved effectively.

Third, we hold that a synergetic effect between OH⁻ and SO₄²⁻ play an important role in the improved performance of Bi₂O(OH)₂SO₄. The OH⁻ anions are necessary to capture the photogenerated holes to form hydroxyl radicals, while the negatively charged SO₄²⁻ groups would prefer to attract the positive holes and repel the negative electrons. The other researchers have also reported that under light excitation, the OH⁻ anions in crystal structure are easy to form hydroxyl radicals. Therefore, more reactive ‘OH can be produced over Bi₂O(OH)₂SO₄ due to the co-presence of both OH⁻ and SO₄²⁻, leading to a significantly improved photo catalytic performances.

To conclude, the layered Bi₂O(OH)₂SO₄ compound has been developed as a new, wide band-gap photo catalyst. The co-presence of both hydroxyl and sulfate anion, as well as its unique layered structure mainly endow Bi₂O(OH)₂SO₄ with a high photo catalytic properties. The PDOS and TDOS results reveal that the intercalated SO₄²⁻ is mainly responsible for the wide band gap and highly positive VB. The study would provide an important strategy to develop new photo catalysts by grouping anions with the existing oxides or sulfides photo catalysts.

Methods
Sample preparation. All the reagents were analytical grade, purchased from Shanghai chemical company in China and used without further purification. Bi(NO₃)₃·5H₂O was synthesized by a simple water bath method. Typically, 1 mmol Bi(NO₃)₃·5H₂O was added into 30 mL distilled water at room temperature under stirring, until the Bi(III) ions dissolve completely. Then, 1 mmol Na₂SO₄ was added to the system above. The mixture was heated at 60 °C for 6 h in water bath. After reaction, the pH value of supernatant is determined to be about 1–2. The resultant precipitate was washed with distilled water and absolute ethanol for several times, respectively. Finally the sample was dried at 60 °C for 6 h.

Sample characterizations. The crystal structures of the samples were determined by X-ray powder poly crystalline diffractometer (Rigaku D/max-2550VB), using graphite monochromatized Cu Kα radiation (λ = 0.154 nm), operating at 40 kV and 50 mA. The XRD patterns were obtained in the range of 20–80° (2θ) at a scanning rate of 7° min⁻¹. The samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 kV. The samples were coated with 5-nm-thick gold layer before observations. The fine surface structures of the samples were determined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) equipped with an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. UV-vis diffuse reflectance spectra (UV-DRS) of the samples were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO₄ was used as a reflectance standard in a UV-vis diffuse reflectance spectrometer (UV-1800, Shimadzu, Japan).

Sample reaction. The samples were exposed to UV light for 60 min. All the experiments were performed in aqueous solution (100 mL) containing 5 mg/L RhB dye and 1 mL of 10 M H₂SO₄. The reaction mixtures were not stirred, and the UV light intensity at the samples was measured to be 1.2 W m⁻² at a distance of 30 cm. The reaction was carried out in a water bath at 60 °C. At regular intervals, a 1 mL aliquot was withdrawn and centrifuged for 2 min at 16000 rpm. Then, 0.5 mL of saturated NaOH solution was added to the supernatant. The absorbance at 554 nm was measured at a CEM UV-1800 UV-vis spectrophotometer.

Figure 8 | Transient photocurrent responses of Bi₂O(OH)₂SO₄ (Blue curve) and commercial rutile TiO₂ (Red curve) under UV light irradiation (λ = 254 nm) in 0.1 M Na₂SO₄ aqueous solution.
reflectance experiment. Nitrogen sorption isotherms were performed at 77 K and < 10^-5 bar on a Micromeritics ASAP2010 gas adsorption analyzer. Each sample was degassed at 150 °C for 5 h before measurements. Surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

**Measurements of photocurrents and EIS.** An electrochemical system (CHI-660B, China) was employed to measure the photocurrents and electrochemical impedance spectroscopy (EIS). Electrochemical impedance spectroscopy (EIS) was performed from 0.1 Hz to 100 kHz at an open circuit potential of 0.3 V and an alternating current (AC) voltage amplitude of 5 mV. The data were analyzed by ZSimWin software. Photocurrent measurements were carried out in a conventional three-electrode system, in which indium-tin oxide (ITO) glass was used as the current collector to fabricate photo electrode, and 0.1 M Na2SO4 was used as the electrolyte solution. TiO2/ITO and Bi2O(OH)2SO4/ITO photo electrode were prepared by a dip-coating method. The photo electrode was implemented as the photo anode in a photoelectrochemical cell (PEC). IPCE measurement of Bi2O(OH)2SO4 under air mass (AM) 1.5 illumination coupled with a series of band-pass filters.

**Evaluation of photo catalytic activity.** The photo catalytic activity of the sample was evaluated by the degradation of rhodamine B (RhB) aqueous solution under UV light (λ < 420 nm), using a 300 W Xe arc lamp (CEL-HXF 300) equipped with an ultraviolet cutoff filter as a light source. The photo reaction system was placed in a sealed black box with the top opened, and was maintained a distance of 15 cm from the light source. The photo catalysts (100 mg) were dispersed in 200 mL of 10 mg/L RhB aqueous solution before the lamp was turned on. Before lamp was turned on, the suspension was continuously stirred for 30 min in the dark to ensure the establishment of an adsorption–desorption equilibrium between the catalysts and RhB. During degradation, 3 mL of solution was collected at an interval of irradiation by pipette, and subsequently centrifuged to remove the photo catalysts. UV–vis spectra were recorded on a SpectraMax 7200 spectrophotometer to determine the concentration of RhB. The photo catalytic activity is characterized by an apparent first-order rate constant (kapp), which can be calculated using Equation (4) as follows:

\[
\text{ln} (C_0/C) = k_{\text{app}} \times t, \quad \text{or} \quad C = C_0 \times e^{-k_{\text{app}} \times t}
\]

Where C0 is the initial concentration of RhB solution, and C is the concentration of RhB at t min irradiation.

**Theoretical calculations.** The simulations of band structures, total and partial densities of states (DOS) were calculated by density functional theory (DFT) as implemented in the CASTEP. The calculations were carried out using the generalized gradient approximation (GGA) level, and Perdew–Burke–Ernzerhof (PBE) formalism for combination of exchange and correlation function. The cut-off energy is chosen as 380 eV, and a density of (3 × 2 × 1) Monkhorst-Pack K-point was adopted to sample the Brillouin zone.

1. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972).
2. Xu, X. X., Random, C., Efstathiou, P. & Irvine, J. S. T. A red metallic oxide photo catalytic collector to fabricate photo electrode, and 0.1 M Na 2SO4 was used as the electrolyte solution. TiO2/ITO and Bi2O(OH)2SO4/ITO photo electrode were prepared by a dip-coating method. The photo electrode was implemented as the photo anode in a photoelectrochemical cell (PEC). IPCE measurement of Bi2O(OH)2SO4 under air mass (AM) 1.5 illumination coupled with a series of band-pass filters.
3. Zhou, Y. X., Shi, H. X., Chen, M. D. & Teng, F. Splitting growth of novel CuO straw sheaves and their improved photo catalytic activity due to exposed active (110) facets and crystallinity. CrystEngComm. 16, 2417–2423 (2014).
4. Xiao, F. X., Miao, J. W. & Liu, B. Layer-by-layer self-assembly of Cds quantum dots/graphene nanosheets hybrid films for photoelectrochemical and photo catalytic applications. J. Am. Chem. Soc. 136, 1559–1564 (2014).
5. Linford, M. R., Auch, M. & Mohwald, H. Nonmonotonous effect of ionic strength on surfactant dye extraction during dye–polyelectrolyte multilayer formation. J. Am. Chem. Soc. 120, 178–182 (1998).
6. Zhao, Y. X., Shi, H. X., Chen, M. D. & Teng, F. Splitting growth of novel CuO straw sheaves and their improved photo catalytic activity due to exposed active (110) facets and crystallinity. CrystEngComm. 16, 2417–2423 (2014).
7. Xu, X. X., Random, C., Efstathiou, P. & Irvine, J. S. T. A red metallic oxide photo catalytic collector to fabricate photo electrode, and 0.1 M Na 2SO4 was used as the electrolyte solution. TiO2/ITO and Bi2O(OH)2SO4/ITO photo electrode were prepared by a dip-coating method. The photo electrode was implemented as the photo anode in a photoelectrochemical cell (PEC). IPCE measurement of Bi2O(OH)2SO4 under air mass (AM) 1.5 illumination coupled with a series of band-pass filters.
8. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972).
9. Xu, X. X., Random, C., Efstathiou, P. & Irvine, J. S. T. A red metallic oxide photo catalytic collector to fabricate photo electrode, and 0.1 M Na 2SO4 was used as the electrolyte solution. TiO2/ITO and Bi2O(OH)2SO4/ITO photo electrode were prepared by a dip-coating method. The photo electrode was implemented as the photo anode in a photoelectrochemical cell (PEC). IPCE measurement of Bi2O(OH)2SO4 under air mass (AM) 1.5 illumination coupled with a series of band-pass filters.
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Author contributions
H.T. performed the experiment and wrote the main text. F.T. designed the experiment, revised the paper and provided the financial support; J.X. performed UV-DRS characterization, prepared Figure 2 and wrote this part; S.L. performed the EIS test, prepared Figure 6 and wrote this part. N.L. prepared the Figure 5; Y.Z. performed the calculation and prepared the Figure 3; M.C. made the SEM and HRTEM characterization and revised the paper. All authors discussed the results and commented on the manuscript. All authors have reviewed the manuscript.

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