Research Article

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MXene- Ti_3C_2 assisted one-step synthesis of carbon-supported $\text{TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ heterostructures for enhanced photocatalytic water decontamination

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Abstract: The strategy to improve the photocatalytic removal efficiencies towards organic pollutants is still a challenge for the novel Sillen–Aurivillius perovskite type $\text{Bi}_4\text{NbO}_8\text{Cl}$. Herein, we report carbon-supported $\text{TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ ($\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$) heterostructures with enhanced charge separation efficiency, which were fabricated via molten-salt flux process. The carbon-supported TiO_2 particles were derived from MXene Ti_3C_2 precursors, and attached on plate-like $\text{Bi}_4\text{NbO}_8\text{Cl}$, acting as electron-traps to achieve suppressed recombination of photo-induced charges. The improved charge separation confers $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ heterostructures superior photocatalytic performance with 53% higher than pristine $\text{Bi}_4\text{NbO}_8\text{Cl}$, towards rhodamine B removal with the help of photo-induced holes. Moreover, the $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ heterostructures can be expanded to deal with other water contaminants, such as methyl orange, ciprofloxacin and 2,4-dichlorophenol with 44, 25 and 13% promotion, respectively, and thus the study offers a series of efficient photocatalysts for water purification.

Keywords: $\text{Bi}_4\text{NbO}_8\text{Cl}$; heterostructures; MXene Ti_3C_2 ; photocatalysis.

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1 Introduction

Visible-light-driven photocatalysis using semiconductors is emerging as a hot topic of research to handle with impending issues related to industrial wastewater [1–5]. In the past decades, plenty of semiconductors have been reported as photocatalyst applied in contaminated water purification [6–8]. Nevertheless, most of them are limited in application for some disadvantages, such as toxicity, low activity or high cost [9]. Bismuth-based semiconductors have been recognized as a new series of visible light-responsive photocatalysts, because of their appropriate band-gap energy, valence band potential and tiny toxicity [10, 11].

Recently, a layered Sillen–Aurivillius perovskite type $\text{Bi}_4\text{NbO}_8\text{Cl}$, previously employed as ferroelectric material, has attracted the interests of researchers who devoted themselves to photocatalytic water decontamination [12–15]. The structure of $\text{Bi}_4\text{NbO}_8\text{Cl}$ is composed of single layer $[\text{NbO}_4]$ perovskite blocks, which are isolated by two layers of $[\text{Bi}_2\text{O}_2]$ blocks [16]. It is worthy to be noted that the hybridization of Bi 6s with O 2p orbitals in this compound is favourable to fast carrier mobility, and internal electric field caused by layered structure is beneficial to better charge separation, thereby improving photocatalytic performance [17]. Mandal et al. synthesized $\text{Bi}_4\text{NbO}_8\text{Cl}$ particles using solid-state reactions, and unveiled an excellent rhodamine B (RhB) degradation efficiency in the acidic medium [18]. Sundaram et al. constructed porous $\text{Bi}_4\text{NbO}_8\text{Cl}$ through solution combustion synthesis, and the nanostructures exhibited mineralization of Congo red by 75.31% in 80 min [19].

In our previous study, the most reactive species involved in the photocatalytic removal of organic dyes by $\text{Bi}_4\text{NbO}_8\text{Cl}$ are photo-induced holes, which are non-selective for organic compounds oxidation [20]. Therefore, it would be more advantageous for the charge separation

leading to holes accumulation, by boosting photo-excited electrons migration in $\text{Bi}_4\text{NbO}_8\text{Cl}$. Besides traditional noble-metal loading, modification by metal-oxide semiconductors seems to be one of the appropriate choices for their preferable stability in the photocatalytic process. Titanium dioxide (TiO_2) is a type of wide band-gap semiconductor with the merits of non-toxicity, low-cost and high chemical stability, which can also be utilized as photocatalysts [21]. Moreover, the conduction band (CB) lie at about -0.30 eV (vs. normal hydrogen electrode, NHE) [22, 23], which is more positive than that of $\text{Bi}_4\text{NbO}_8\text{Cl}$ ($-0.4 \sim -0.5$ eV) [24], resulting in the possibility of acting as electron-traps for improved charge separation efficiency.

Two-dimensional (2D) MXenes have attracted much attention in photo-induced reactions, for their excellent sunlight-harvesting and carrier mobility properties [25–30], for instance, MXene Ti_3C_2 has been expanded rapidly in water-treatment, such as photothermal evaporation, photoinduced antimicrobial, and photocatalytic degradation [31–33]. Besides, benefiting from the layered structures and alternative distribution of Ti and C elements, MXene Ti_3C_2 can be employed as excellent precursor for the synthesis of fine and uniform TiO_2 nanoparticles in the oxidative conditions. The merit of transformation between conductive Ti_3C_2 and semiconductive TiO_2 gives rise to the superiorities in photocatalytic applications. Peng's group synthesized (001)-facet $\text{TiO}_2/\text{Ti}_3\text{C}_2$ in hydrothermal process, and the photocatalytic degradation of methyl orange (MO) was drastically boosted by the synergistic effect of improved charge separation and exposed active facets [34]. Wang et al. obtained mesostructured TiO_2 nanoparticles via direct H_2O_2 treatment, which demonstrated that the MXene Ti_3C_2 was completely oxidized to TiO_2 and 2D-carbon species [35]. Furthermore, small TiO_2 particles modified with disordered graphitic carbon sheets (carbon-supported TiO_2) could be easily obtained by oxidation at high temperatures in air [36–38].

Herein, we synthesized quasi-2D $\text{Bi}_4\text{NbO}_8\text{Cl}$ plates via a flux method in air using NaCl/KCl mixed molten salts, and MXene Ti_3C_2 was simultaneously introduced in this procedure, in order to construct carbon-supported TiO_2 (C- TiO_2) loading on $\text{Bi}_4\text{NbO}_8\text{Cl}$. Based on the feature that photo-induced electrons migrate to edges of $\text{Bi}_4\text{NbO}_8\text{Cl}$ while holes accumulate in plane in the photocatalytic process according to previous report [39], the C- TiO_2 can act as electron-trap to reduce migration distance for electrons. By tailoring the ratio of C- $\text{TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$, the optimal photocatalyst possessed superior degradation efficiency by 53% towards organic dye RhB than that of pristine $\text{Bi}_4\text{NbO}_8\text{Cl}$ photocatalysts, and was also validated effective by other water contaminants, such as MO, ciprofloxacin

(CIP) and 2,4-dichlorophenol (2,4-DCP). Consequently, the mechanism of the MXene Ti_3C_2 derived C- TiO_2 promoted electrons transfer, leading to enhancement of photo-induced holes accumulation for effective oxidation of common water contaminants, was illustrated.

2 Experimental

2.1 Materials

Sodium chloride (NaCl , 99.5%), potassium chloride (KCl , 99.5%), bismuth trioxide (Bi_2O_3 , 99.5%), lithium fluoride (LiF , $\geq 98.0\%$), hydrochloric acid (HCl , $36.0 \sim 38.0\%$) and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd. Bismuth (III) chloride oxide (BiOCl , 98.5%) and niobium pentoxide (Nb_2O_5 , 99.9%) were purchased from Energy Chemical Inc. All the reagents were of analytical grade and used directly without further purification.

2.2 Preparation of MXene Ti_3C_2

MXene Ti_3C_2 was prepared by etching MAX phase Ti_3AlC_2 powders according to our previous reports [40]. Typically, stoichiometric amount of MAX phase Ti_3AlC_2 powders were dispersed in HCl solution with concentration of 6 mol/L, which is placed in a plastic container, and LiF powders were slowly added into the above suspension. Then the plastic container was sealed and the mixture was heated at 50°C for 48 h under continuous stirring. Finally, the MXene Ti_3C_2 powders were obtained by washing with deionized water and centrifuging for several times, and dried in a vacuum oven at 80°C for 10 h.

2.3 Synthesis of C- $\text{TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ (T/BNC-x) heterostructures

C- $\text{TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ samples were prepared by a flux method using Bi_2O_3 , BiOCl , and Nb_2O_5 as raw materials, a mixture of alkali metal chlorides NaCl/KCl was used as flux, and MXene Ti_3C_2 was employed as additive. Typically, the mixed KCl/NaCl ($n(\text{NaCl}) = n(\text{KCl}) = 5$ mmol) salts were grounded with mixture of Bi_2O_3 (130 mg), BiOCl (67 mg), Nb_2O_5 (350 mg) and certain amount of MXene Ti_3C_2 . Afterwards, the mixture was transferred to a porcelain boat and calcined at 750°C for 60 min in a muffle furnace. The products were thoroughly washed with deionized water and ethanol several times, and dried at 80°C for 24 h. In

this process, the value $x\%$ was introduced as the mass fraction of MXene Ti_3C_2 with respect to the mixture (Bi_2O_3 , BiOCl and Nb_2O_5), and the resultant $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ was labeled as $T/\text{BNC-}x$. The value x was set as 0.5, 1.0, 2.0 and 5.0, corresponding to the weight of 27, 55, 109 and 219 mg for the added MXene Ti_3C_2 , respectively.

In addition, pristine $\text{Bi}_4\text{NbO}_8\text{Cl}$ (BNC) was synthesized via the same procedure without the addition of MXene Ti_3C_2 , and different temperatures (650 °C, 700 °C, 750 °C, 800 °C and 850 °C) were set to regulate the morphology and crystallinity of $\text{Bi}_4\text{NbO}_8\text{Cl}$. MXene Ti_3C_2 powders were underwent the same calcination process as that of $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ to obtain carbon-supported TiO_2 , labeled as C-TiO_2 .

2.4 Characterization

X-ray diffraction patterns were recorded on a diffractometer (D8 ADVANCE, BRUKER, Germany) fitted with $\text{Cu K}\alpha$ radiation over the 2θ ranges from 10° to 80°, and the scanning speed was 4° min^{-1} . Scanning (SEM) and transmission electron microscopy were taken on a JSM-7610F field-emission SEM (JEOL, Japan) and a Tecnai G2 F20 S-TWIN microscope (FEI, USA), respectively. X-ray photoelectron spectroscopy (XPS) data were captured on an ESCALAB 250XI (Thermo Fisher, USA) with an $\text{Al K}\alpha$ (1486.6 eV) achromatic X-ray source, and the binding energies were calibrated by adventitious C 1s peak (284.8 eV). UV-vis diffuse reflectance spectra of the photocatalysts and the absorption spectra of degradation products were recorded on a Cary 5000 ultraviolet-visible (UV-vis) spectrophotometer (Agilent, USA) furnished with an integrating sphere. The photoluminescence (PL) spectra were measured with an FLS920 fluorescence spectrometer (Edinburgh, UK) with an excitation wavelength of 365 nm.

2.5 Photocatalytic activity

The photocatalytic activities of the $T/\text{BNC-}x$ samples were evaluated by the decomposition of water-soluble organic compounds. In the experiments, organic compounds RhB, MO, CIP, and 2,4-DCP were used as target pollutants to be decomposed. Typically, as-prepared samples (40 mg) were suspended in 40 mL of 10 mg/L aqueous RhB solution (in other cases, 10 mg/L MO, 5 mg/L CIP and 5 mg/L 2,4-DCP). Before illumination, the suspension was stirred magnetically in a dark chamber for 30 min to ensure adsorption-desorption equilibrium between the pollutant molecules and the photocatalysts. Subsequently, a 300 W Xenon

lamp (Beijing China Education Au-light Co., Ltd, CEL-LAX) equipped with a condensing collector was used as the light source. At scheduled time intervals, 4 mL of the suspension was sampled and filtrated to remove the photocatalyst powders. The concentration of supernatants was measured by a Cary 5000 UV-vis spectrophotometer (Agilent, USA) and the degradation efficiency could be determined by Lambert Beer's law.

2.6 Active species trapping experiments

Isopropanol (IPA), *p*-benzoquinone (BQ), ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) and potassium bromate (KBrO_3) were involved in the system of RhB (10 mg/L) photocatalytic degradation reaction to scavenge the hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$), photo-generated holes (h^+) and electrons (e^-) respectively, in order to elucidate the photocatalysis mechanism. The experiments were similar to the former photocatalytic removal of RhB process except that scavengers were involved in the suspensions before irradiation, and the concentration of IPA, BQ, EDTA-2Na and KBrO_3 was 10.0, 1.0, 1.0 and 10.0 mmol/L, respectively.

2.7 Electrochemical and photoelectrochemical measurements

Electrochemical (EC) and photoelectrochemical (PEC) measurements of the samples were recorded on a CHI 660E electrochemical workstation (Shanghai Chenhua, China), and conducted in the standard three-electrode cell. Fluorine-doped tin oxide glass coated with samples was used as working electrode, a Pt plate as counter electrode and an Ag/AgCl as a reference electrode, respectively, and Na_2SO_4 (0.1 mol/L, Sinopharm Chemical Reagent Co., Ltd) aqueous solution was applied as the electrolyte. The working electrode was prepared as follows: 15 mg of samples were dispersed in the 300 μL of mixture containing 1.0 wt% chitosan and 1.0 wt% acetic acid. Then the above slurry was coated on the Fluorine-doped tin oxide glass with a controlled expose area ($1.0 \times 0.5 \text{ cm}$) and dried under natural conditions. A 300 W Xenon lamp (Beijing China Education Au-light Co., Ltd, CEL-LAX) was employed as the light source. The photocurrent response (PC) was measured by constant potential (+0.5 V) under intermittent illumination (30 s) and the Mott-Schottky measurement was performed at a frequency of 1000 Hz.

Scheme 1: The schematic illustration for the preparation of $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$.

3 Results and discussion

Scheme 1 simply illustrated the preparation of the C-TiO_2 loaded $\text{Bi}_4\text{NbO}_8\text{Cl}$ plate-like heterostructures. By using commercial Bi_2O_3 , BiOCl and Nb_2O_5 nanoparticles as raw materials, NaCl/KCl mixed salts as flux, two-dimensional $\text{Bi}_4\text{NbO}_8\text{Cl}$ could be easily synthesized. When the MXene Ti_3C_2 was utilized as additive blending with the above mixture, the carbon-supported TiO_2 nanoparticles (C-TiO_2) were simultaneously constructed on the surface of plate-like $\text{Bi}_4\text{NbO}_8\text{Cl}$, obtaining $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ heterostructures.

Figure 1a shows the X-ray diffraction patterns of pristine $\text{Bi}_4\text{NbO}_8\text{Cl}$ synthesized by different temperatures. For the samples synthesized at 750 °C or higher temperatures, the diffraction peaks at 12.3°, 23.7°, 26.0°, 29.6°, 32.6°, 33.9°, 41.3°, 46.7° and 56.3° are indexed to the (004), (112), (114), (116), (020), (023), (028), (220) and (316) crystal planes of the Sillen–Aurivillius structured perovskites $\text{Bi}_4\text{NbO}_8\text{Cl}$ (JPCDS No.84-0843), respectively. Moreover, the crystallinity is increased as the temperature rises, which is also

reflected by the values of the full width at half maximum (FWHM), as shown in Table S1 (ESI). However, the patterns of samples synthesized at 650 and 700 °C cannot match $\text{Bi}_4\text{NbO}_8\text{Cl}$, especially as the high-lighted area indicates, which might be caused by incomplete reaction among Bi_2O_3 , BiOCl and Nb_2O_5 powders, especially in the situation for 650 °C.

When MXene Ti_3C_2 powders are introduced in the mixture, as shown in Figure 1b, an obvious peak at 27.45° ascribed to rutile TiO_2 (JPCDS No.21-1276) can be identified in the patterns, and the peak is intensified as the amount of Ti_3C_2 increased. Moreover, the FWHM of main diffraction peak indexed to (116) facet for $\text{Bi}_4\text{NbO}_8\text{Cl}$ becomes larger as the addition of Ti_3C_2 , as shown in Table 1, indicating the crystallinity of $\text{Bi}_4\text{NbO}_8\text{Cl}$ is affected by the growth of rutile particles and endothermic effect of carbon species.

Figure 2a and 2b shows the SEM images of pristine BNC synthesized at 750 °C, and the $\text{Bi}_4\text{NbO}_8\text{Cl}$ possesses the morphology of plate-like shaped particles, which are about 1.5 μm in edge length and dozens of nanometers in thickness. Under the same synthetic conditions, C-TiO_2 can be

Figure 1: X-ray diffraction patterns of (a) pristine $\text{Bi}_4\text{NbO}_8\text{Cl}$ synthesized by different temperatures, (b) T/BNC-x synthesized at 750 °C in the flux.

Table 1: Full width at half maximum (FWHM) of (116) plane of $\text{Bi}_4\text{NbO}_8\text{Cl}$ in the pristine BNC and T/BNC-x.

Samples	BNC	T/BNC-0.5	T/BNC-1	T/BNC-2	T/BNC-5
FWHM	0.196	0.274	0.375	0.411	0.445

obtained by oxidation of MXene Ti_3C_2 [38], and the particles are aggregated with size of several nanometers, as shown in Figure 2c. The lattice fringe in Figure 2d are measured to be 0.325 nm, which is in accordance with the (110) in rutile, and the particle size can be confirmed to be about 10 nm more clearly. As shown in Figure 2e–2g, the morphology and size of the C- $\text{TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ heterostructures are quite similar with those of pristine BNC, while small TiO_2 nanoparticles are observed in the magnified view (Figure 2h). In addition, elemental mapping for the Bi, Nb, Cl, Ti and O elements of T/BNC-1 is conducted, and brighter signals are observed in the circle of the view, implying C- TiO_2 nanoparticles successfully attach on the surface of quasi-2D $\text{Bi}_4\text{NbO}_8\text{Cl}$ plates.

XPS analysis is carried out to determine the chemical states of the elements in the samples, and the existence of the Bi, Nb, O, Cl and Ti are clearly observed by the survey scan (Figure S1, ESI). As shown in Figure 3a, the signals of

Table 2: Conduction band and valence band positions (vs. NHE) for BNC, C- TiO_2 and T/BNC-1.

Samples	Conduction band	Band-gap energy	Valence band
BNC	−1.02 V	2.30 eV	+1.28 V
T/BNC-1	−0.75 V	2.27 eV	+1.52 V
C- TiO_2	−0.20 V	2.49 eV	+2.29 V

BNC with two obvious peaks at 158.50 and 163.85 eV are ascribed to the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ of $[\text{Bi}_2\text{O}_2]$ blocks in $\text{Bi}_4\text{NbO}_8\text{Cl}$, respectively [41]. However, the binding energy of Bi 4f in T/BNC-1 undergoes a blue-shift by 0.2 eV, reaching 158.70 and 164.05 eV for Bi $4f_{7/2}$ and Bi $4f_{5/2}$, indicating the C- TiO_2 nanoparticles acquire electrons from $\text{Bi}_4\text{NbO}_8\text{Cl}$. As for Nb 3d core level in Figure 3b, BNC shows two peaks centered at 206.44 and 209.18 eV for Nb $3d_{5/2}$ and Nb $3d_{3/2}$, while those of T/BNC-1 are shifting to 206.64 and 209.38 eV, respectively. Moreover, there is a doublet peak located at 198.33 and 199.98 eV (Figure 3c) [42], which are assigned to Cl $2p_{3/2}$ and Cl $2p_{1/2}$ in BNC, and corresponding peaks can be found at 198.45 and 200.10 eV for T/BNC-1.

Combining with the above Bi, Nb and Cl XPS spectra, there is an evident electron migration process from

Figure 2: (a, b) SEM images of pristine BNC, (c, d) TEM and HRTEM images of C- TiO_2 , (e, f) SEM images of T/BNC-1, (g, h) TEM images of T/BNC-1 and (i) EDS mapping for Bi, Nb, Cl, Ti and O elements for T/BNC-1.

Figure 3: High-resolution XPS of the samples (a) Bi 4f, (b) Nb 3d, (c) Cl 2p and (d) O 1s.

$\text{Bi}_4\text{NbO}_8\text{Cl}$ to C-TiO_2 , and also confirming efficient interface contact in the heterostructures. As for O 1s spectra in Figure 3d, the deconvoluted peaks are assigned to lattice oxygen in 529.95 eV and surface hydroxyl groups in 531.20 eV for BNC [43], while the values are 530.10 and 531.20 eV for T/BNC-1, respectively. In addition, similar results are obtained in C-TiO_2 , which the peaks of Ti-O located in 530.30 eV and Ti-OH in 531.40 eV [22], while extra C-O peaks in 532.80 eV can be also identified [44], verifying the composition of C-TiO_2 by TiO_2 nanoparticles and residue carbon species in current temperature.

The optical properties of the as-obtained samples are evaluated by UV-vis absorption spectra. As shown in Figure 4a, the absorption edge of pristine BNC is located approximately at 540 nm, while that of T/BNC-1 is slightly red-shifted, and that of C-TiO_2 exhibits obviously intensified absorption in the visible-light region. Meanwhile, the colors of the as-prepared samples become from bright yellow of BNC to dark yellow of T/BNC-5 (Figure S2, ESI), due to the formation of carbon species derived from the MXene Ti_3C_2 precursors. As an indirect band-gap

semiconductor [41], the optical band-gap energy can be calculated by the Tauc equation:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (1)$$

and the plots are shown in Figure 4b.

Mott-Schottky plots (Figure 4c) show that BNC, T/BNC-1 and C-TiO_2 with positive slopes possess n-type feature, while the flat-band potential (E_{fb}) of BNC, T/BNC-1 and C-TiO_2 are measured at -0.38 V, -0.30 V and -0.25 V (vs. Ag/AgCl) according to the intersection of linear potential curve at $C_s^2 = 0$. Generally, the E_{fb} is approximately equal to the Fermi level [45, 46], and thus the equal to the Fermi level values can be calculated to be -0.18 V, -0.10 V and -0.05 V (vs. NHE) for BNC, T/BNC-1 and C-TiO_2 , respectively. By extrapolating the leading edge to the intersection with background counts near the Fermi level, as shown in the Valence band XPS spectra (Figure 4d), the potential of valence band (E_{VB}) with respect to the Fermi level can be determined [47]. Therefore, the E_{VB} values are $+1.28$, $+1.52$ and $+2.29$ V (vs. NHE) for BNC, T/BNC-1 and

Figure 4: (a) UV-vis absorption spectra, (b) Tauc's plots, (c) Mott-Schottky plots and (d) Valence band XPS (VB-XPS) of pristine BNC, C-TiO₂ and T/BNC-1.

C-TiO₂, respectively, while the potential of conduction band (E_{CB}) are obtained according to the optical band-gap energy above, and thus the band structure parameters are listed in Table 2.

The photocatalytic performance of BNC and T/BNC are tested by degradation of RhB as target water contaminants, as shown in Figure 5a. Approximately 77% of the RhB molecules are removed after photocatalytic reaction for 180 min in suspension containing pristine BNC, while the pristine C-TiO₂ shows rather inferior performance due to few actual active TiO₂ components involved. When the pristine $\text{Bi}_4\text{NbO}_8\text{Cl}$ is modified with C-TiO₂ components, the photodegradation efficiency is increased, while the case is deteriorated with further extending the proportion of C-TiO₂ up to 5%. Accordingly, the highest RhB removal is achieved in T/BNC-1 suspension, owning 1.26 times superior than pristine BNC. To further compare the photocatalytic efficiencies of the BNC and T/BNC, the reaction kinetics plots are fitted (Figure S3, ESI) and k is calculated (Figure 5b), where k is the coefficient of the fitted pseudo-first-order kinetic equation,

$$\ln(C_0/C) = kt \quad (2)$$

the calculated k value for T/BNC-1 is $12.67 \times 10^{-3} \text{ min}^{-1}$, which is as 1.53 times as that of BNC ($k = 8.28 \times 10^{-3} \text{ min}^{-1}$).

Additionally, the repeatability and recyclability of the photocatalysts are another important factors to be considered, which are demonstrated to be excellent according to the results shown in Figure S4 (ESI).

To identify the primary reactive species involved in photocatalytic removal of RhB, the effects of different scavengers over T/BNC-1 are tested, and the results are displayed in Figure 5c. The addition of hydroxyl radicals ($\cdot\text{OH}$) scavenger IPA has little effect on RhB degradation, while that of holes (h^+) scavenger EDTA-2Na significantly inhibits the photocatalytic process, indicating h^+ is the main species responsible for the RhB removal over T/BNC-1. Besides, the degradation is slightly affected when superoxide radicals ($\cdot\text{O}_2^-$) scavenger BQ is added, implying $\cdot\text{O}_2^-$ is the minor species in the experiments. Moreover, the photocatalytic degradation process is obviously enhanced when the electron (e^-) scavenger KBrO_3 is added, demonstrating diminished electrons promote accumulation of holes which facilitate the hole-dominant photodegradation further.

T/BNC-1 is also highly active for photocatalytic removal of other water contaminants, such as MO, CIP and 2,4-DCP, suggesting a universal application in industrial wastewater treatment. As shown in Figure 5d, the T/BNC-1 photocatalyst possesses about 1.44, 1.25 and 1.13 times activities of pristine

Figure 5: (a) The photocatalytic degradation of RhB by BNC and T/BNC photocatalysts and (b) corresponding kinetic fitting plots. Conditions: $[\text{RhB}]_0 = 10 \text{ mg/L}$ $[\text{Cat.}] = 1 \text{ g/L}$. (c) Photocatalytic degradation of RhB over T/BNC-1 in presence of different scavengers. Conditions: $[\text{RhB}]_0 = 10 \text{ mg/L}$ $[\text{Cat.}] = 1 \text{ g/L}$. (d) Photocatalytic degradation of different organic pollutants by BNC and T/BNC-1. Conditions: $[\text{MO}]_0 = 10 \text{ mg/L}$ $[\text{CIP}]_0 = 5 \text{ mg/L}$ $[\text{2,4-DCP}]_0 = 5 \text{ mg/L}$ $[\text{Cat.}] = 1 \text{ g/L}$.

BNC for the removal of MO, CIP and 2,4-DCP, respectively, and detailed plots are shown in Figure S5 (ESI).

As rapid charge transfer and efficient charge separation is of significance in improving the photocatalytic performance, and thus PC and electrochemical impedance spectra are employed [48–52]. As shown in Figure 6a, all the T/BNC show higher photocurrent densities as pristine BNC, and the T/BNC-1 exhibits the strongest PCs, which demonstrates the low recombination rate of the photo-generated electrons and holes by Bi modification via appropriate solvothermal process [53–55]. Figure 6b displays the electrochemical impedance spectra spectra of the as-prepared photocatalysts, and the arc radius of T/BNC are smaller than that of BNC, also confirming a faster charge migration in the interface of the photocatalyst. Moreover, Figure 6c shows the PL spectra over the BNC and T/BNC with the excitation wavelength of 365 nm, and a broad emission peak around 484 nm is detected for the pristine BNC, implying an obvious recombination of photo-

induced electron-hole pairs [56]. A distinct decrease in PL intensity is identified, and the lowest intensity of T/BNC-1 means the best charge separation efficiency.

Based on the analysis above, the plausible mechanism for the enhancement of photocatalytic performance by heterostructured $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ towards water decontamination can be illustrated as shown in Figure 7. For the pristine BNC, the Fermi level lies at -0.18 V , and CB potential at -1.02 V and VB at $+1.28 \text{ V}$, while the values are -0.05 V , -0.20 V and $+2.29 \text{ V}$ for the C-TiO_2 (Figure 7a). When the C-TiO_2 and $\text{Bi}_4\text{NbO}_8\text{Cl}$ are coupled to form heterojunction, charges transfer and band bending occur, to achieve equilibrium of Fermi levels (Figure 7b). Upon visible-light illumination (Figure 7c), both the components of $\text{Bi}_4\text{NbO}_8\text{Cl}$ ($E_g = 2.30 \text{ eV}$) and C-TiO_2 ($E_g = 2.49 \text{ eV}$) can be excited to generate electrons and holes, as the visible-light response capability was demonstrated by UV-vis absorption measurement. However, the photocatalytic performance of individual C-TiO_2 is quite limited

Figure 6: (a) Transient PC of different photocatalysts at 0.5 V bias (vs. Ag/AgCl) under Xe lamp illumination, (b) electrochemical impedance spectra Nyquist plots and (c) PL spectra of the pristine BNC, C-TiO₂ and T/BNC-1.

as previously mentioned, therefore the mechanism for the improvement of $\text{Bi}_4\text{NbO}_8\text{Cl}$ after introduction of C-TiO₂ is summarized as follows.

On the one hand, benefiting from the type-II staggered band alignment, the photo-induced electrons in the CB of $\text{Bi}_4\text{NbO}_8\text{Cl}$ can migrate to that of C-TiO₂, leading to an effective charge separation. Moreover, the photo-induced holes in the VB of C-TiO₂ migrate to that of $\text{Bi}_4\text{NbO}_8\text{Cl}$, and thus more holes accumulated in the VB of $\text{Bi}_4\text{NbO}_8\text{Cl}$ to trigger the non-selective oxidation of organic compounds in simulated wastewater. On the other hand, due to the quasi-2D structure, the photo-induced holes in $\text{Bi}_4\text{NbO}_8\text{Cl}$ tend to distribute on the basal {001} planes, according to previous report [39], while photo-generated electrons need migrate long distance to the edge {110} facets. Therefore, the C-TiO₂ loaded on the basal planes can rapidly trap the electrons generated in $\text{Bi}_4\text{NbO}_8\text{Cl}$, accelerating the charge carriers separation. However, the basal $\text{Bi}_4\text{NbO}_8\text{Cl}$ planes for h^+ dominant oxidation were covered when the C-TiO₂ was excessive (T/BNC-2 and T/BNC-5), leading to a declining photocatalytic performance of RhB degradation. As a conclusion,

according to the analysis mentioned above, degradation process of the organics by C-TiO₂/ $\text{Bi}_4\text{NbO}_8\text{Cl}$ are listed as the following involving

4 Conclusion

In summary, heterostructured C-TiO₂/ $\text{Bi}_4\text{NbO}_8\text{Cl}$ was successfully fabricated via one-step molten-salts flux method, and C-TiO₂ particles derived from MXene Ti_3C_2 attached on the plate-like $\text{Bi}_4\text{NbO}_8\text{Cl}$. Benefiting from the efficient interface formation and staggered band alignment, photo-induced electrons in $\text{Bi}_4\text{NbO}_8\text{Cl}$ can fast

Figure 7: Schematic diagram of photocatalytic mechanism of $\text{C-TiO}_2/\text{Bi}_4\text{NbO}_8\text{Cl}$ composites (a) before contact, (b) after contact and (c) upon illumination.

migrate to the CB of C-TiO_2 , while photo-generated holes, which play predominant role in the organic compounds removal, accumulate in the valence band of $\text{Bi}_4\text{NbO}_8\text{Cl}$. Among the prepared photocatalysts, T/BNC-1 exhibits improved photocatalytic performance towards RhB, MO, CIP and 2,4-DCP degradation by 53, 44, 25 and 13%, respectively, due to the rapid electron trapping by C-TiO_2 and adequate exposure of $\text{Bi}_4\text{NbO}_8\text{Cl}$ basal plane where photo-induced holes exists. This work highlights the formation of C-TiO_2 derived from the novel Ti-precursors on $\text{Bi}_4\text{NbO}_8\text{Cl}$, and provide a simple strategy for designing heterostructured materials for water decontamination by photocatalysis.

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References

- [1] P. C. Nagajyothi, S. V. Prabhakar Vattikuti, K. C. Devarayapalli, K. Yoo, J. Shim, and T. V. M. Sreekanth, "Green synthesis: photocatalytic degradation of textile dyes using metal and metal oxide nanoparticles-latest trends and advancements," *Crit. Rev. Env. Sci. Tech.*, pp. 1–107, 2019, <https://doi.org/10.1080/10643389.2019.1705103>.
- [2] J. Brooks, C. Warkentin, D. Saha, E. Keller, and R. Frontier, "Toward a mechanistic understanding of plasmon-mediated photocatalysis," *Nanophotonics*, vol. 7, pp. 1697–1724, 2018, <https://doi.org/10.1515/nanoph-2018-0073>.
- [3] S. Jorfi, S. Pourfadakari, and B. Kakavandi, "A new approach in sono-photocatalytic degradation of recalcitrant textile wastewater using MgO@Zeolite nanostructure under UVA irradiation," *Chem. Eng. J.*, vol. 343, pp. 95–107, 2018, <https://doi.org/10.1016/j.cej.2018.02.067>.
- [4] L. Suhadolnik, A. Pohar, U. Novak, B. Likozar, A. Mihelič, and M. Čeh, "Continuous photocatalytic, electrocatalytic and photo-electrocatalytic degradation of a reactive textile dye for wastewater-treatment processes: batch, microreactor and scaled-up operation," *J. Ind. Eng. Chem.*, vol. 72, pp. 178–188, 2019, <https://doi.org/10.1016/j.jiec.2018.12.017>.
- [5] A. Naldoni, F. Riboni, U. Guler, A. Boltasseva, V. M. Shalae, and A. V. Kildishev, "Solar-powered plasmon-enhanced heterogeneous catalysis," *Nanophotonics*, vol. 5, pp. 112–33, 2016, <https://doi.org/10.1515/nanoph-2016-0018>.
- [6] T. Liu, X. Zhang, F. Zhao, Y. Wang, "Targeting inside charge carriers transfer of photocatalyst: selective deposition of Ag_2O on BiVO_4 with enhanced UV-vis-NIR photocatalytic oxidation activity," *Appl. Catal. B Environ.*, vol. 251, pp. 220–228, 2019, <https://doi.org/10.1016/j.apcatb.2019.03.062>.
- [7] Q. Guo, C. Zhou, Z. Ma, and X. Yang, "Fundamentals of TiO_2 photocatalysis: concepts, mechanisms, and challenges," *Adv. Mater.*, vol. 31, p. 1901997, 2019, <https://doi.org/10.1002/adma.201901997>.
- [8] G. Liao, Y. Gong, L. Zhang, H. Gao, G.-J. Yang, and B. Fang, "Semiconductor polymeric graphitic carbon nitride photocatalysts: the "holy grail" for the photocatalytic hydrogen evolution reaction under visible light," *Energy Environ. Sci.*, vol. 12, pp. 2080–2147, 2019, <https://doi.org/10.1039/c9ee00717b>.
- [9] H. Huang, Y. He, X. Li, et al., " $\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$ as a desirable $[\text{Bi}_2\text{O}_2]^{2+}$ layered photocatalyst: strong intrinsic polarity, rational band structure and {001} active facets co-beneficial for robust photooxidation capability," *J. Mater. Chem. A*, vol. 3, pp. 24547–24556, 2015, <https://doi.org/10.1039/c5ta07655b>.

- [10] B. Sa, Y. L. Li, J. Qi, R. Ahuja, and Z. Sun, "Strain engineering for phosphorene: the potential application as a photocatalyst," *J. Phys. Chem. C*, vol. 118, pp. 26560–26568, 2014, <https://doi.org/10.1021/jp508618t>.
- [11] R. Mohan, "Green bismuth," *Nat. Chem.*, vol. 2, p. 336, 2010, <https://doi.org/10.1038/nchem.609>.
- [12] J. F. Ackerman, "The structures of $\text{Bi}_3\text{PbWO}_8\text{Cl}$ and $\text{Bi}_4\text{NbO}_8\text{Cl}$ and the evolution of the bipox structure series," *J. Solid State Chem.*, vol. 62, pp. 92–104, 1986, [https://doi.org/10.1016/0022-4596\(86\)90220-3](https://doi.org/10.1016/0022-4596(86)90220-3).
- [13] Z. Wei, J. Liu, W. Fang, Z. Qin, Z. Jiang, and W. Shangguan, "Enhanced photocatalytic hydrogen evolution using a novel in situ heterojunction yttrium-doped $\text{Bi}_4\text{NbO}_8\text{Cl}/\text{Nb}_2\text{O}_5$," *Int. J. Hydro. Energy*, vol. 43, pp. 14281–14292, 2018, <https://doi.org/10.1016/j.ijhydene.2018.05.129>.
- [14] H. Fujito, H. Kunioku, D. Kato, et al., "Layered perovskite oxychloride $\text{Bi}_4\text{NbO}_8\text{Cl}$: a stable visible light responsive photocatalyst for water splitting," *J. Am. Chem. Soc.*, vol. 138, pp. 2082–2085, 2016, <https://doi.org/10.1021/jacs.5b11191.s001>.
- [15] X. Lin, T. Huang, F. Huang, W. Wang, and J. Shi, "Photocatalytic activity of a Bi-based oxychloride $\text{Bi}_4\text{NbO}_8\text{Cl}$," *J. Mater. Chem.*, vol. 17, p. 2145, 2007, <https://doi.org/10.1039/b615903f>.
- [16] D. Kato, K. Hongo, R. Maezono, et al., "Valence band engineering of layered bismuth oxyhalides toward stable visible-light water splitting: madelung site potential analysis," *J. Am. Chem. Soc.*, vol. 139, pp. 18725–18731, 2017, <https://doi.org/10.1021/jacs.7b11497>.
- [17] X. Tao, Y. Gao, S. Wang, et al., "Interfacial charge modulation: an efficient strategy for boosting spatial charge separation on semiconductor photocatalysts," *Adv. Energy Mater.*, vol. 9, p. 1803951, 2019, <https://doi.org/10.1002/aenm.201803951>.
- [18] A. Pandey, G. Naresh, and T. K. Mandal, "Sunlight responsive new Sillén–Aurivillius $\text{A}1\text{X}1$ hybrid layered oxyhalides with enhanced photocatalytic activity," *Sol. Energy Mater. Sol. C*, vol. 161, pp. 197–205, 2017, <https://doi.org/10.1016/j.solmat.2016.11.040>.
- [19] S. S. M. Bhat, and N. G. Sundaram, "Photocatalysis of $\text{Bi}_4\text{NbO}_8\text{Cl}$ hierarchical nanostructure for degradation of dye under solar/UV irradiation," *New J. Chem.*, vol. 39, pp. 3956–3963, 2015, <https://doi.org/10.1039/c4nj01814a>.
- [20] X. Qu, M. Liu, H. Zhai, X. Zhao, L. Shi, and F. Du, "Plasmonic Ag-promoted layered perovskite oxyhalide $\text{Bi}_4\text{NbO}_8\text{Cl}$ for enhanced photocatalytic performance towards water decontamination," *J. Alloy Comp.*, vol. 810, p. 151919, 2019, <https://doi.org/10.1016/j.jallcom.2019.151919>.
- [21] K. Qi, S. Liu, and M. Qiu, "Photocatalytic performance of TiO_2 nanocrystals with/without oxygen defects," *Chin. J. Catal.*, vol. 39, pp. 867–865, 2018, [https://doi.org/10.1016/s1872-2067\(17\)62999-1](https://doi.org/10.1016/s1872-2067(17)62999-1).
- [22] H. Huang, Y. Song, N. Li, et al., "One-step in-situ preparation of N-doped TiO_2/C derived from Ti_3C_2 MXene for enhanced visible-light driven photodegradation," *Appl. Catal. B Environ.*, vol. 251, pp. 154–161, 2019, <https://doi.org/10.1016/j.apcatb.2019.03.066>.
- [23] Y. Zhu, M. W. Shah, and C. Wang, "Insight into the role of Ti^{3+} in photocatalytic performance of shuriken-shaped $\text{BiVO}_4/\text{TiO}_{2-x}$ heterojunction," *Appl. Catal. Environ.*, vol. 203, pp. 526–532, 2017, <https://doi.org/10.1016/j.apcatb.2016.10.056>.
- [24] A. Nakada, A. Saeki, M. Higashi, H. Kageyama, and R. Abe, "Two-step synthesis of Sillén–Aurivillius type oxychlorides to enhance their photocatalytic activity for visible-light-induced water splitting," *J. Mater. Chem. A*, vol. 6, pp. 10909–10917, 2018, <https://doi.org/10.1039/c8ta03321h>.
- [25] M. Naguib, M. Kurtoglu, V. Presser, et al., "Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 ," *Adv. Mater.*, vol. 23, pp. 4248–4253, 2011, <https://doi.org/10.1002/adma.201102306>.
- [26] M. Qiu, Z. T. Sun, D. K. Sang, X. G. Han, H. Zhang, and C. M. Niu, "Current progress in black phosphorus materials and their applications in electrochemical energy storage," *Nanoscale*, vol. 9, pp. 13384–13403, 2017, <https://doi.org/10.1039/c7nr03318d>.
- [27] Y. Song, Y. Chen, X. Jiang, et al., "Nonlinear few-layer MXene-assisted all-optical wavelength conversion at telecommunication band," *Adv. Opt. Mater.*, vol. 7, p. 1801777, 2019, <https://doi.org/10.1002/adom.201801777>.
- [28] C. Wang, Y. Wang, X. Jiang, et al., "MXene $\text{Ti}_3\text{C}_2\text{T}_x$: A promising photothermal conversion material and application in all-optical modulation and all-optical information loading," *Adv. Opt. Mater.*, vol. 7, p. 1900060, 2019, <https://doi.org/10.1002/adom.201900060>.
- [29] L. Wu, X. Jiang, J. Zhao, et al., "MXene-based nonlinear optical information converter for all-optical modulator and switcher," *Laser Photon. Rev.*, vol. 12, p. 1800215, 2018, <https://doi.org/10.1002/lpor.201800215>.
- [30] M. Qiu, W. X. Ren, T. Jeong, et al., "Omnipotent phosphorene: a next-generation, two-dimensional nanoplatform for multidisciplinary biomedical applications," *Chem. Soc. Rev.*, vol. 47, pp. 5588–5601, 2018, <https://doi.org/10.1039/c8cs00342d>.
- [31] Z. Xie, Y. P. Peng, L. Yu, et al., "Solar-inspired water purification based on emerging 2D materials: status and challenges," *Solar RRL*, vol. 4, p. 1900400, 2020, <https://doi.org/10.1002/solr.201900400>.
- [32] Z. Xie, Y. Duo, Z. Lin, et al., "The rise of 2D photothermal materials beyond graphene for clean water production," *Adv. Sci.*, vol. 7, p. 1902236, 2020, <https://doi.org/10.1002/advs.201902236>.
- [33] M. Qiu, D. Wang, W. Liang, et al., "Novel concept of the smart NIR-light-controlled drug release of black phosphorus nanostructure for cancer therapy," *Proc. Natl. Acad. Sci. USA*, vol. 115, pp. 501–506, 2018, <https://doi.org/10.1073/pnas.1714421115>.
- [34] C. Peng, X. Yang, Y. Li, H. Yu, H. Wang, and F. Peng, "Hybrids of two-dimensional Ti_3C_2 and TiO_2 exposing {001} facets toward enhanced photocatalytic activity," *ACS Appl. Mater. Interface*, vol. 8, pp. 6051–6060, 2016, <https://doi.org/10.1021/acsami.5b11973>.
- [35] R. Wang, S. Wang, Y. Zhang, D. Jin, X. Tao, and L. Zhang, "Graphene-coupled Ti_3C_2 MXenes-derived TiO_2 mesostructure: promising sodium-ion capacitor anode with fast ion storage and long-term cycling," *J. Mater. Chem. A*, vol. 6, pp. 1017–1027, 2018, <https://doi.org/10.1039/c7ta09153b>.
- [36] H. Ghassemi, W. Harlow, O. Mashtalir, et al., "In situ environmental transmission electron microscopy study of oxidation of two-dimensional Ti_3C_2 and formation of carbon-supported TiO_2 ," *J. Mater. Chem. A*, vol. 2, pp. 14339–14343, 2014, <https://doi.org/10.1039/c4ta02583k>.
- [37] M. Naguib, O. Mashtalir, M. R. Lukatskaya, et al., "One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphitic carbon by oxidation of MXenes," *Chem. Commun.*, vol. 50, pp. 7420–7423, 2014, <https://doi.org/10.1039/c4cc01646g>.

- [38] C. Yang, J. Qin, Z. Xue, M. Ma, X. Zhang, and R. Liu, "Rational design of carbon-doped TiO_2 modified g- C_3N_4 via in-situ heat treatment for drastically improved photocatalytic hydrogen with excellent photostability," *Nano Energy*, vol. 41, pp. 1–9, 2017, <https://doi.org/10.1016/j.nanoen.2017.09.012>.
- [39] C. Hu, H. Huang, F. Chen, Y. Zhang, H. Yu, and T. Ma, "Coupling piezocatalysis and photocatalysis in $\text{Bi}_4\text{NbO}_8\text{X}$ (X=Cl, Br) polar single crystals," *Adv. Funct. Mater.*, vol. 30, p. 1908168, 2019, <https://doi.org/10.1002/adfm.201908168>.
- [40] L. Shi, C. Xu, D. Jiang, et al., "Enhanced interaction in $\text{TiO}_2/\text{BiVO}_4$ heterostructures via MXene Ti_3C_2 -derived 2D-carbon for highly efficient visible-light photocatalysis," *Nanotechnology*, vol. 30, p. 075601, 2019, <https://doi.org/10.1088/1361-6528/aaf313>.
- [41] Y. You, S. Wang, K. Xiao, T. Ma, Y. Zhang, and H. Huang, "Z-Scheme g- $\text{C}_3\text{N}_4/\text{Bi}_4\text{NbO}_8\text{Cl}$ heterojunction for enhanced photocatalytic hydrogen production," *ACS Sustain. Chem. Eng.*, vol. 6, pp. 16219–16227, 2018, <https://doi.org/10.1021/acssuschemeng.8b03075>.
- [42] Y. Shi, X. Xiong, S. Ding, X. Liu, Q. Jiang, and J. Hu, "In-situ topotactic synthesis and photocatalytic activity of plate-like $\text{BiOCl}/2\text{D}$ networks Bi_2S_3 heterostructures," *Appl. Catal. B Environ.*, vol. 220, pp. 570–580, 2018, <https://doi.org/10.1016/j.apcatb.2017.08.074>.
- [43] G. Ni, Y. Li, H. Chen, et al., "The Sol-gel method synthesis of $\text{Bi}_4\text{NbO}_8\text{Cl}$ with (001) facets exposed for high visible-light activity," *J. Mater. Sci. Mater. Electron.*, vol. 30, pp. 7907–15, 2019, <https://doi.org/10.1007/s10854-019-01112-7>.
- [44] W. Yuan, L. Cheng, Y. Zhang, et al., "2D-layered carbon/ TiO_2 hybrids derived from Ti_3C_2 MXenes for photocatalytic hydrogen evolution under visible light irradiation," *Adv. Mater. Interface*, vol. 4, p. 1700577, 2017, <https://doi.org/10.1016/j.ceramint.2020.04.004>.
- [45] N. Tian, Y. Zhang, X. Li, et al., "Precursor-reforming protocol to 3D mesoporous g- C_3N_4 established by ultrathin self-doped nanosheets for superior hydrogen evolution," *Nano Energy*, vol. 38, pp. 72–81, 2017, <https://doi.org/10.1016/j.nanoen.2017.05.038>.
- [46] H. Li, H. Yu, X. Quan, S. Chen, and Y. Zhang, "Uncovering the key role of the fermi level of the electron mediator in a Z-scheme photocatalyst by detecting the charge transfer process of WO_3 -metal-g C_3N_4 (Metal=Cu, Ag, Au)," *ACS Appl. Mater. Interface*, vol. 8, pp. 2111–2119, 2016, <https://doi.org/10.1021/acsami.5b10613>.
- [47] W. Zhao, Y. Feng, H. Huang, et al., "A novel Z-scheme $\text{Ag}_3\text{VO}_4/\text{BiVO}_4$ heterojunction photocatalyst: Study on the excellent photocatalytic performance and photocatalytic mechanism," *Appl. Catal. B Environ.*, vol. 245, pp. 448–458, 2019, <https://doi.org/10.1016/j.apcatb.2019.01.001>.
- [48] C. Liang, C. G. Niu, L. Zhang, et al., "Construction of 2D heterojunction system with enhanced photocatalytic performance: Plasmonic Bi and reduced graphene oxide co-modified $\text{Bi}_5\text{O}_7\text{I}$ with high-speed charge transfer channels," *J. Hazard. Mater.*, vol. 361, pp. 245–258, 2019, <https://doi.org/10.1016/j.jhazmat.2018.08.099>.
- [49] Z. Xie, C. Xing, W. Huang, et al., "Ultrathin 2D nonlayered tellurium nanosheets: facile liquid-phase exfoliation, characterization, and photoresponse with high performance and enhanced stability," *Adv. Funct. Mater.*, vol. 28, p. 1705833, 2018, <https://doi.org/10.1002/adfm.201705833>.
- [50] W. Huang, Z. Xie, T. Fan, et al., "Black-phosphorus-analogue tin monosulfide: an emerging optoelectronic two-dimensional material for high-performance photodetection with improved stability under ambient/harsh conditions," *J. Mater. Chem. C*, vol. 6, pp. 9582–9593, 2018, <https://doi.org/10.1039/c8tc03284j>.
- [51] T. Fan, Z. Xie, W. Huang, Z. Li, and H. Zhang, "Two-dimensional non-layered selenium nanoflakes: facile fabrications and applications for self-powered photo-detector," *Nanotechnology*, vol. 30, p. 114002, 2019, <https://doi.org/10.1088/1361-6528/aafc0f>.
- [52] C. Xing, W. Huang, Z. Xie, et al., "Ultrasmall bismuth quantum dots: facile liquid-phase exfoliation, characterization, and application in high-performance UV-Vis photodetector," *ACS Photonics*, vol. 5, pp. 621–629, 2017, <https://doi.org/10.1021/acsp Photonics.7b01211>.
- [53] H. Huang, X. Ren, Z. Li, et al., "Two-dimensional bismuth nanosheets as prospective photo-detector with tunable optoelectronic performance," *Nanotechnology*, vol. 29, p. 235201, 2018, <https://doi.org/10.1088/1361-6528/aab6ee>.
- [54] W. Huang, C. Xing, Y. Wang, et al., "Facile fabrication and characterization of two-dimensional bismuth(III) sulfide nanosheets for high-performance photodetector applications under ambient conditions," *Nanoscale*, vol. 10, pp. 2404–2412, 2018, <https://doi.org/10.1039/c7nr09046c>.
- [55] Y. Zhang, F. Zhang, L. Wu, et al., "Van der Waals integration of bismuth quantum dots-decorated tellurium nanotubes (Te@Bi) heterojunctions and plasma-enhanced optoelectronic applications," *Small*, vol. 15, p. 1903233, 2019, <https://doi.org/10.1002/sml.201903233>.
- [56] M. Qiu, D. Q. Zhu, X. C. Bao, J. Y. Wang, X. F. Wang, and R. Q. Yang, " WO_3 with surface oxygen vacancies as an anode buffer layer for high performance polymer solar cells," *J. Mater. Chem. A*, vol. 4, pp. 894–900, 2016, <https://doi.org/10.1039/c5ta08898d>.

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