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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Thermodynamic and Dynamic Dual Regulation Bi₂O₂CO₃/Bi₅O₇I Enabling High-flux Photogenerated Charge Migration for Enhanced Visible-light-driven Photocatalysis

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Herein, the essence of high-flux photogenerated charge migration for $Bi_2O_2CO_3/Bi_5O_7I$ heterojunction photocatalysts is revealed from both thermodynamic and dynamic perspectives. The appropriate energy band offset provides the thermodynamic condition of photogenerated electrons and holes migration in the opposite direction, which is derived from the lower valence and conduction band positions of Bi_5O_7I than $Bi_2O_2CO_3$. Meanwhile, the dynamic condition are supplied by the interface electric field generated via the work function difference between Bi_5O_7I and $Bi_2O_2CO_3$, which afford driving force for the above-mentioned reverse migration of photogenerated electrons and holes. Moreover, the Bi-O chemical bond on the interface construct the charge transport bridge between Bi_5O_7I and $Bi_2O_2CO_3$. Benefit from the dual regulation of thermodynamics and dynamics and the charge transport bridge, the photocatalytic activity of $Bi_2O_2CO_3/Bi_5O_7I$ heterojunction photocatalyst has significantly increased at least 23 times under visible light irradition. This finding could be also applied to other fields to tune the optimal charge transport performance of the heterojunctions.

Introduction

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The separation and migration of photogenerated carriers are a key factor determining the photocatalytic performance. ¹⁻³ Semiconductor heterojunction is an effective way to promote the separation of photogenerated charges. ⁴Type II junctions have been widely investigated as an effective strategy for photocatalysis applications due to their interface interaction, allowing the directional electron transport. 5, 6 However, the ambiguity of the effect of interface interaction on photoinduced charge transfer severely limits the further design and development of the heterojunction photocatalyst. Most of the work reported in the literature on heterojunction photocatalysts elaborates the migration direction of photogenerated charges at the interface from the perspective of band position matching. There have also been more or less reports that the interfacial electric field improve the separation effect of photogenerated electron-hole pairs but still lack of in-depth research to quantify the built-in electric field. 7-9 In other words, the adjustment of photogenerated charge by heterojunction has been explained the possibility of this phenomenon from the perspective of thermodynamics. However, the influence of the driving force on the speed of photogenerated charge transfer is lacking to be considered further, that is, the dynamic condition is not used as a measure of the heterojunction material. As we all know, thermodynamics and dynamics are complementary and are two indispensable branches for studying a reaction. Therefore, there is an urgent need to achieve dual regulation of heterojunction photocatalysts from the perspectives of thermodynamics and dynamics.

More importantly, the charge transfer performance of heterojunctions is limited by the migration of random charge accumulation and depletion layer formation of different materials, while a large number of migration channels for interfacial charges are able to effectively reduce this limitation.¹⁰ The 2D-2D heterojunction connected by van der Waals force is widely reported in the literature. ^{11, 12} However, in view of Van der Waals force is an instantaneous induction of electric dipole moment, it decreases rapidly with increasing distance lead to the weak interface interaction force. In contrast, the interface combined with chemical bonds form a much stronger interaction force between the atoms at the contact interface, accompanied by changes in atomic electronic structure. 13, 14 Therefore, the interface connected by chemical bonds provides stable migration bridges for the continuous charge transfer and meanwhile effectively avoid the random accumulation of charges. ^{15, 16} Zhang's group found that the photocatalytic degradation of contaminants can act as carbon source lead to one-unit-cell Bi₂O₂CO₃ layers in-situ grow from the surface of Bi₂O₄ photocatalyst during the progress of photodegradation, and finally forming a heterojunction Bi₂O₄/Bi₂O₂CO₃. ¹⁷ Li' s group constructed Bi2Ti2O7/y-Bi2O3 by in-situ fabrication where the y-Bi2O3 as a support and tertbutyl titanite as

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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titanium source. The co-sharing of Bi-O structure help to fabricate a tightly connected interface. ¹⁸Hou's group reported the synthesis of mesoporous heterostructures In₂O₃-x/In₂S₃ through the in-situ oxidation of In₂S₃ atomic layers by an oxygen plasma-induced strategy.¹⁹ Moreover, they also emphasis on an in-situ phase-induced etching chemical strategy to prepare Ta₃N₅@NaTaON heterojunction with the strong interfacial Ta-O-N bonding connection. ¹⁰Without exception, these heterojunctions are formed by producing another substance in situ on one substance. Inspired by above mentioned, we employed in-situ conversion of Bi₅O₇I to fabricate Bi₅O₇I / Bi₂O₂CO₃ for the following reasons: 1) Insitu conversion is conducive to build an interface contacted with Bi-O bonds between Bi₅O₇I and Bi₂O₂CO₃, which is expected to provide a smooth charge separation pathway; 2) It is easy to realize the controllable preparation of the structure through adjusting the reaction conditions of in-situ conversion; 3) Due to the Bi source control, the interface between Bi5O7I and Bi2O2CO3 is effectively regulated meanwhile forming nanostructure; 4) Carbonate is derived from the oxidation of organic matter during the hydrothermal reaction, which is beneficial to control the thickness and scale of Bi₂O₂CO₃.

Under the guidance of this mentality and based on our previous research on bismuth oxyiodide, Bi₅O₇I (BOI), which has the most photocatalytic potential in bismuth oxyiodide, ²⁰ and Bi₂O₂CO₃ (BOC), which has regular layered structure, is selected to form an interface. This work prepared BOC/BOI type II heterojunction photocatalyst by means of in-situ conversion via a simple one-pot hydrothermal method. The Bi-O chemical bond at the heterojunction interface provides paths for the continuous transmission of photogenerated charges, thereby realizing high-flux photogeneration charge transfer. More importantly, from the perspective of thermodynamics, the possibility of the direction of photogenerated charge transfer is explained by the theory of interfacial band offset. Further from the perspective of dynamics, the interfacial electric field provides the driving force for high-speed migration of photogenerated charges. Thus, the nature of Bi2O2CO3/Bi5O7I achieved efficient separation with minimal recombination was revealed. As a direct envidence, the photocatalytic activity of Bi₂O₂CO₃/ Bi₅O₇I heterojunction has significantly increased at least 23 times under visible light.

Experimental

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Sample preparation

In this paper, different ratios of $Bi_2O_2CO_3/Bi_5O_7I$ (BOC/BOI) heterojunctions were prepared by adjusting the ratio of glycerol as a carbon source. First, BOI is formed at room temperature, then glycerol is oxidized to carbonate in a solvothermal reaction, and BOI is converted in situ to BOC. For $Bi_2O_2CO_3/Bi_5O_7I$ heterojunctions, 0.486 g (1 mmol) of $Bi(NO_3)_3$ ·5 H₂O was dissolved in 40, 25 or 5 ml of deionized water, 10, 25 or 45 ml of glycerol was added with vigorous stirring 30min, followed by addition of 5ml deionized water dissolved with 1mmol KI and 0.24g KOPI. Therefore resulting solution was transferred to a 100 ml polytetrafluoroethylenelined autoclave and heated at 160°C for 6 h. The final product was washed 6 times with deionized water and absolute ethanol and dried at 60 °C. Marked as: BOC/BOI-1, BOC/BOI-2 and BOC/BOI-3 (where 1, 2, 3 respectively represent the ratio of glycerol in the solvent is 0.2, 0.5, 0.9). For the synthesis of Bi₂O₂CO₃, 25 ml of glycerol and 25 ml of water were used as the solvent, no KI was added, and the rest were the same as above.

For the synthesis of Bi_5O_7I , 50 ml of water was used as a solvent, and the rest were the same as above.

Sample characterization

Powder X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker D8 X-ray diffractometer with Cu Ka radiation (λ =0.15418 nm). The morphologies of the samples were survived by SEM on ZEISS Sigma 500, TEM on JEOL JEM-1400 TEM at an accelerating voltage of 100 kV and HRTEM on Tecnai F20 operated at an accelerating voltage of 200 kV. XPS were performed using a Thermo ESCALAB 250 with Al Ka X-ray (hv=1486.6 eV) radiation. UV-Vis diffuse reflection spectra (DRS) were obtained on a spectrophotometer (Shimadzu, UV2550) with BaSO4 as reference. The BET surface area measurements were recorded on an ASAP2020 instrument. The steady-state photoluminescence (PL) spectra was detected by using a Perkline LS55 fluorescence spectrophotometer with λ_{ex} =250 nm. The surface photovoltage (SPV) spectra were recorded with a home-built apparatus, equipped with a lock-in amplifier (SR830, USA) synchronized with a light chopper (SR540, USA). For transient-state surface photovoltage (TS-SPV) responses of the samples, the samples were excited by a radiation pulse of 355 nm with 10 ns width from the second harmonic of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Lab-130-10H, Newport, Co.) and the signals were amplified with a pre-amplier and registered with a 1GHz digital phosphor oscilloscope (DPO 4104B, Tektronix).

Photoelectrochemical measurements were performed on a CHI-660 E (China) electrochemical workstation with a standard three-electrode cell, including counter electrode (Pt wire), reference electrode (saturated calomel electrode) and working electrodes (as-prepared samples covered ITO glass). Na₂SO₄ (0.1 M) was used as electrolyte solution. For the working electrodes, a sample (2 mg) was dispersed in Nafion solution (Naphthol: ethanol=1:9) to obtain a slurry. Then the slurry was coated onto the ITO glass and dried in an oven overnight. Electrochemical impedance spectroscopy spectra were recorded under an AC perturbation signal of 10 mV over the frequency range from 100 KHz to 1 Hz.

Photocatalytic performance evaluation

The photocatalytic activity was estimated by measuring the degradation of Bisphenol A (BPA), 4-chlorophenol (4-CP),

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2,4-dichlorophenol (2,4-DCP) and phenol. In a static photocatalytic system, 50 mg of samples was dispersed in 100 mL of BPA (4-CP, 2,4-DCP and phenol) solution with 10 ppm under $\lambda \ge 420$ nm irradiation. Before the light irradiation, the mixture was stirred for 30 min to reach the adsorption equilibrium in the dark. The temperature of the reactor was maintained at 20°C by continuous circulating water. The continuous flow reaction was conducted in a fixed bed reactor with 50 mg of BOC/BOI-2 photocatalyst loaded in the groove (40 mm \times 20 mm \times 2 mm) and the two opposite sides serve as import and export. A 300 W xenon lamp equip with $\lambda \ge 420$ nm cut-off filter were placed above the reactor as the light source. The 10 mg / L BPA solution was fed by a peristaltic pump with a constant flow rate of 1 ml / min. At given irradiation time intervals, about 2 mL of the solution was taken out to analyse the residual contaminant concentration. The concentration was detected by the HPLC system (Waters Baseline 810) with a Waters 486 tunable UV absorbance detector and a Supelco LC-18-DB column (250mm×4.6mm). Total organic carbon (TOC) analyser (Multi N/C 2100s) was employed for mineralization degree analysis of pollutants.

Theoretical calculations

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All theoretical calculations were performed through the generalized gradient approximation (GGA) within the Perdew–Burke–Emzerhof (PBE) exchange-correlation functional implemented in the CASTEP code. The ultrasoft pseudopential in the Vanderbilt form was used for description of ion-electron interaction. The plane-wave function was set with the cut-off energy of 420 eV. Geometry optimizations were done before single point energy calculation with the self-consistent convergence accuracy of $1 \times 10-5$ eV atom-1. The convergence criterion for the maximal force between atoms is 0.03 eV Å-1. The maximum displacement is $1 \times 10-3$ Å, and the stress is less than 0.05 GPa.

Results and Discussion

Dual regulation of thermodynamic and dynamic for BOC/BOI heterojunction with charge transfer bridges

Firstly, first-principle calculations were conducted to examine the thermodynamic and dynamic conditions for BOC/BOI heterojunction. The DFT calculations show that the inconsistent width of the forbidden band between BOC and BOI (Fig. S1), which means there exits band offset at the interface. ²¹The relative positions of the energy bands of the two semiconductors determine the migration direction of the photogenerated electrons and holes at the interface, that is, the thermodynamic condition. To clear the direction of the interface charge migration determined by the band offset, the energy band alignment structure is extracted by experimental characterization (Fig. S2a, b, c). The CB offset (ΔE_c) produced at the bottom of the CB is +0.12 eV and VB offset (ΔE_v) generated at the bottom of the VB is +0.37 eV (Fig. 1a & Fig. S2d, the specific calculation see support information). ²² The calculation of the energy band step directly indicates





Figure 1 Schematic thermodynamic condition: Δ Ec (Δ Ev) (a), dynamic condition: qV _{barrie} (b) and dual regulation of thermodynamic and dynamic for BOC/BOI heterojunction (c).

that the positions of the VB and the CB of BOC are higher than those of BOI. Therefore, the thermodynamic conditions provided by the energy band offset enable holes to migrate from BOI to BOC and converse for electrons.

According to the work function difference, when BOC and BOI are in contact, the electron would flow from the BOI with low work function (2.4 eV) to the BOC with high work function (2.6 eV) until the Fermi energy level balanced (Fig. S3). ^{18, 23} A depletion layer and an accumulation layer of electrons are respectively formed at BOI and BOC meanwhile, and an energy barrier (qV_{barrier}) about 0.2 eV is generated, thereby forming band bend and interfacial electric field (IEF) directed from the BOI to the BOC (Fig. 1b). 24-26 It is well known that the electric field influences the migration of interface charges. Electric field force accelerates the forward electric field movement of positive charges and the reverse electric field movement of negative charges. Fortunately, the direction of the IEF at the BOC/BOI interface is the same (opposite) to the direction of movement of the photogenerated holes (electrons) determined by the above thermodynamic condition. In fact, for BOC/BOI, it can be predicted that the dynamic result must accelerate the direction photogenerated charge that determined of by thermodynamics. This is because the direction of the IEF must be from a material with a small work function to a large work function. According to the above DFT calculation, it is known that the work function of BOI is smaller than BOC. The thermodynamic conditions provided by the energy band position allow photogenerated holes to be transferred from BOI to BOC. It cannot be neglected that the IEF directed from BOI to BOC provides a driving force for the transfer motion of photogenerated charges to achieve a dynamic acceleration process. The photogenerated holes of BOI arrive the VB of BOC and then migrate to the surface of BOC. The motion

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Figure 2 (a) Schematic illustration of the preparation of BOC/BOI-2. (b) TEM (c) HRTEM, (d) AFM image (e) and the corresponding height profile of BOC/BOI-2.

direction of photogenerated electrons is opposite. In this process, thanks to the kinetic acceleration process offered by IEF, the photogenerated electron-hole pairs are effectively separated. Eventually, photogenerated holes and electrons arrived at the surfaces of BOC and BOI participate in oxidation and reduction reactions, respectively. At this point, the thermodynamic condition indicates the possibility of directional migration of photogenerated charges at the interface, and the dynamic condition demonstrates this movement is an accelerated process. As a result, BOC / BOI achieves both thermodynamic and dynamic regulation--qV_{barrier} + ΔE_v (ΔE_c) (Fig. 1c).

The interface effect plays an important role during the photogenerated charge transfer process. 27-30 Because the interface with no tight connection is not support to the charge transmission at the interface. Providing efficient transport pathways has been applied to maximize the efficiency of photogenerated charge utilization. 19,31 Compared with pure material, the partial projected density of states (PDOS) are higher coincidence for heterojunction (Fig. S4), which shows their electronic states highly hybrid and means more likely of charge transfer at the interface. ³² To reveal the presence of Bi-O chemical bonds between BOC and BOI, the static charge changes of the interface atoms were analysed firstly. Compared to pure substances, the Bi static charge at the interface is significantly changed, which indicates that charge transfer after the formation of heterojunction, resulting in strong Bi-O electron coupling (see Fig. S5 & Table S1 for specific analysis). Moreover, taking the charge density map containing Bi1-O1 as an example (Fig. S6), the electron density at the interface is strong around the O1 of the BOI, but weak for the Bi1 of the BOC, which make clear close electronic coupling between BOI and BOI. Then, after avoiding the error of the atomic static charge value inherent and express the net change in the spatial distribution of charge, the differential charge density difference also suggested that Bi-O has obvious electron accumulation and

depletion at the interface (Fig. S7). The bond levels further illustrate the electron coupling originates from the presence of Bi-O bonds at interface (see Table S2 for specific analysis). These theoretical results confirm the constructing carrier migration channels of Bi-O bond is a candidate for weak recombination effect.

In-situ conversion to prepare BOC/BOI heterojunction

Motivated by these theoretical calculations, we synthesized BOC/BOI heterojunction by one-pot in-situ conversion. XRD, FT-IR, XPS were employed to prove heterojunctions successfully obtained by in-situ conversion (see Fig. S8 for specific analysis). Fig. 2a displays the in-situ conversion process of BOC on BOI by replacement reaction. Firstly, thick board BOI produced at room temperature (Fig. S9a and Fig. S10a), then CO_3^{2-} favorably bind with the surface of BOI under the electrostatic force during the hydrothermal reaction, next BOI surface begin to transform into BOC piece meanwhile eroded into block itself. Enough CO₃²⁻ continue to corrode the surface of the BOI to nanorods, and BOC become thinner into two-dimensional (2D) nanosheets in subsequent reactions. Finally, a nano heterojunction BOC/BOI-2 with large contact area was obtained (Fig. S9c and Fig. S10c). However, too little carbon source causes the reaction to stay in step 3, forming a micron-sized heterojunction (Fig. S9b and Fig. S10b) while excessive carbon source resulting serious agglomeration (Fig. S9d and Fig. S10d). The Fig. 2b illustration shows the two-phase boundary of BOC/BOI-2 and a large contact area benefiting from the flakes and the small size of the nanorods. Further, the lattice fringes of 0.273 nm and 0.283 nm correspond to the (0 10 0) crystal plane of BOC and (0 0 4) of BOI, respectively (Fig. 2c). AFM shows that the thickness of these sheets is ~5 nm (Fig. 2d-e), which directly confirm that BOC is a 2D sheet. Furthermore, electron paramagnetic resonance (EPR) has been performed on the prepared samples (Fig. 3a), which is a sensitive and direct technique for monitoring the behavior of material surface defects. The peaks at $g = \sim 2.1^{-33,34}$ and $g = \sim 2.0^{-35}$

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represent bismuth defects and oxygen defects, respectively. Interestingly, compared to other synthetic samples,



Figure 3 (a) ESR spectra, (b) UV–vis diffuse reflection spectra, (c) N2 adsorption–desorption isotherms of as-prepared samples. High resolution XPS spectra of (d) C 1s, (e) O 1s (f) Bi 4f.

BOC/BOI-2 has the least bismuth defects and the EPR signal of BOC/BOI-2 oxygen deficiency was hardly detected. Because of the less defects of BOC/BOI-2, the more regular of lattice, the local state proportion caused by defects in the lattice is reduced. On the contrary, the degree of delocalization is increased, and the degree of commonality is increased. 36, 37 The results of energy band broadening, reducing the band gap, and red-shifting the absorbed light are obtained by BOC/BOI-2 (Fig. 3b). Note that the specific surface area of nano heterojunction BOC/BOI-2 (up to 126.93 m² g⁻¹) is significantly larger than that of BOI (4.62 m² g⁻¹) and BOC (27.51 m² g⁻¹), which provide efficient diffusion and transportation in degradation (Fig. 3c). Moreover, 2D with high specific surface area helps to form a large contact area at the interface, thereby making it possible for the interface to dominate. Although BOC/BOI heterojunctions can be prepared with different proportions of carbon source dosing, there is an optimal amount of carbon source dosing to make the prepared heterojunction a neat morphology and larger contact interface. Considering that the morphology affects the transfer of charges on the semiconductor, the large contact interface determines the amount of separated photogenerated charges, obviously BOC/BOI-2 has more advantages.

The realization of BOC/BOI-2 allow to apply XPS testify DFT about Bi-O bonds at interface. Geherally, other \$\$ binding energy is negatively correlated with the surface electron density.³⁸ The 288.3 eV and 285.7 eV characterizing C = O and C - O in BOC increase to 288.7 eV and 285.9 eV, ³⁹ which attributed to the strong interaction between BOC and BOI affecting the electrons of C in CO_3^{2-} (Fig. 3d). The binding energy of 530.7 eV in BOI belongs to Bi-O, which shifted down to 530.6 eV after forming a heterojunction, ⁴⁰ because Bi electron of BOC at the interface transfer to O atom of BOI to form strong Bi-O chemical bonds (Fig. 3e). Meanwhile, higher binding energies of 166.7 and 161.5 eV appeared in BOC (Fig. 3f), which is also consistent with its strongest Bi defect signal shown in Fig. 3a. As mentioned earlier, theoretical calculations show that strong Bi-O chemical bonds tightly connect BOC and BOI to form a strong interaction interface. Experimental characterization confirms that among the BOC/BOI heterojunctions prepared by different carbon source dosing ratios, the interface owned by BOC/BOI-2 is closest to the result of theoretical settlement.

Dual regulation and charge transfer bridges promote photogenerated charge separation



Figure 4 (a) Electrochemical impedance spectroscopy (EIS) (b) photoluminescence spectra (PL) at 250 nm excitation wavelength, (c) Photocurrent under $\lambda \ge 420$ nm, (d) surface photovoltage irradiation (e) normalized open-circuit potential (OCP) attenuation curves after turning off the $\lambda \ge 420$ nm irradiation for samples prepared (f) the apparent reaction rate constants for BPA under visible light ($\lambda \ge 420$ nm) irradiation.

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Next, the effect of dual regulation and bridges at the interface on photogenerated charge separation were explored. The charge transfer resistance of the photocatalyst is simulated by using the equivalent circuit R(C(R(QR))) (CR) of Fig. 4a according to the electrochemical impedance spectroscopy (EIS). The analog charge transfer resistance of BOC/BOI-2 $(724.9 \ \Omega \ cm^{-2})$ is far less than that of the BOI $(1032 \ \Omega \ cm^{-2})$ and BOC (2913 Ω cm⁻²), exhibiting that the lots bridges reduce the charge transfer resistance between the BOC and BOI. The BOC/BOI-2 quenches the steady-state photoluminescence (PL) intensity of BOI and BOC by 76.3% and 67.2%, respectively (Fig. 4b), meaning the decrease of the recombination of photogenerated electron-hole pairs. The excellent separation effect promotes extensive photogenerated charges to reach the surface of the photocatalyst, which proved by strongest photocurrent density (Fig. 4c) and SPV signal (Fig. 4d) of BOC/BOI-2. Subsequently, the charge recombination efficiencies of BOC/BOI-2 were quantitatively measured with the open circuit potential (OCP) transients. Fig. 4e compares the attenuation curve of OCP after turning off the light among asprepared samples without externally applied bias. The average recombination constant is estimated by normalizing the OCP signal and fitting the data to a first-order dynamic model (Equation 1): ^{41, 42}

$$\frac{E_t - E_{ph}}{E_{da} - E_{ph}} = 1 - \exp^{-kt} \tag{1}$$

Where E_t is the OCP over time, E_{da} is the static OCP value in the dark, E_{ph} is the steady OCP value under visible light illumination, and k is the pseudo first order recombination rate constant. The OCP decay dynamics reflect charge recombination and show how the heterojunction alters recombination. The fitted k of BOC/BOI-2 (2.06×10⁻⁴ s⁻¹) is reduced by 90% and 96% compared to BOI $(2.01 \times 10^{-3} \text{ s}^{-1})$ and BOC $(3.16 \times 10^{-3} \text{ s}^{-1})$, respectively. The OCP decay is markedly retarded significant for BOC/BOI-2 due to lots of channel at the interface avoids the random accumulation and the recombination of photogenerated charges. These results powerfully suggest constructing dual regulation and generous bridges at the interface is a promising approach to improve photogenerated charge transfer by inhibiting the recombination.

The photoactivity is highly correlated with the charge separation efficiency, and the ameliorative photogenerated charge transfer endowed BOC/BOI-2 with visible photoactivity for degradation. The apparent rate constants of BOC/BOI-2 with outstanding activity are 23, 17, 15, 60 times that of BOI, BOC/BOI-1, BOC/BOI-3 and BOC (Fig. 4f & Moreover, BOC/BOI-2 shows S11). remarkable photodegradation BPA activity under visible light compared to some other reported photocatalysts as presented in Table S5. Then, the results in Fig. S12 demonstrate the universality of BOC/BOI-2 for photodegradation of organic pollutants. Next, the TOC removal results show that BOC/BOI-2 has acceptable salinity for different pollutants due to its nice oxidizing ability (Fig. S13). In addition, the excellent



photodegradation under λ≥420 nm irradiation

recycling performance of BOC/BOI-2 heterojunction has been shown in Fig. S14. Moreover, the EPR shows that $\cdot O_2^{-1}$ is the main active species, while hole has little effect on it, and OH radical has no effect (Fig. S15).

In order to approximate the effect of photocatalysis applied to the purification of actual water treatment project, besides static tests, continuous flow experiments for BOC/BOI-2 photocatalytic degradation was carried. Phenol which is more difficult to degrade was employed as a probe to flow through the reaction system at 1ml/min. After continuous operation for 45 hours, the removal rate of phenol retains about 70% (Fig. S16), which not only shows that BOC/BOI-2 has efficient photodegradation activity and once again proves that the excellent stability for BOC/BOI-2.

To fully understand the process of BPA oxidative degradation by photogenerated active species in the BOC/BOI-2 system under $\lambda \ge 420$ nm irradiation, the main degradation intermediates identified with UPLC/MS/MS further the possible degradation path was analysed. A total of 10 intermediate products were inferred during BOC/BOI-2 photodegradation BPA. The molecular structure and MS/MS fragmentation information of the oxidation products are displayed in Fig. S17. Based on these degradation intermediates, the possible degradation pathway of BPA is proposed in Fig. 5. Due to the two-electron donating hydroxyl group increased the electron density of each benzene ring, the C-C bond connecting the two benzene rings in BPA is more vulnerable.⁴³ The β -cleavage of the isopropyl group between the two phenyl groups is generated, forming phenol (m/z=93),

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Figure 6 (a) The Time-resolved fluorescence spectrum (b) The lifetime of photogenerated holes detected by time-resolved SPV of the as-prepared samples.

4-isopropylphenol (m/z=133) and 1-(4-hydroxyphenyl)-2propanol (m/z=151). Phenol is generally oxidized to hydroquinone (m/z=109) further oxidized to p-benzoquinone (m/z=107) that cannot be detected as not easily ionized.⁴⁴ Meanwhile the active oxygen component further oxidizes 4isopropylphenol to 4-hydroxycetophenone (m/z=135). Then, the intermediate products were subsequently attacked yielding small organic acids such as maleic acid (m/z=115), glycolic acid (m/z=75) acetic acid (m/z=59) and 2gydroxypropionic acid (m/z=89), which were eventually mineralized.

Dual regulation and charge transfer bridges extend photogenerated charge lifetime

Inspired by the better photogenerated charge transfer and remarkable photodegradation achieved via the dual regulation and charge transfer bridges at the interface, the carrier lifetime was investigated. First, the lifetime of the photogenerated charge in the excited state was quantified by the time-responsive PL spectrum (Fig. 6a & Table S3). Compared with BOI and BOC with decay lifetimes of 0.58 ns and 0.68 ns, respectively, the decay lifetime of the BOC/BOI-2 is as long as 2.93 ns. The longer excited states of photogenerated charges means that they are more likely to migrate to the surface to participate in photocatalytic reactions. Therefore, the lifetime of the photogenerated holes at the photocatalyst surface was tested next. The timeresolved SPV shows that SPV of BOC/BOI-2 is higher than other samples (Fig. S18), which agree on the SPV results. It should be emphasized that the peaks 1 and 2 representing the two successive transfer processes of photogenerated charges can be clearly observed for hybrids (Fig. 6b). Peak 1 is attributed to the photogenerated holes generated by BOI reaching its surface, and peak 2 is the photogenerated holes that migrate to the BOC through the bridge under the action of the dual drivers at the interface. BOC/BOI-2 has the longest decay time (see Table S4 for detailed analysis), means that the photogenerated holes reaching the surface have a longer survival time. 45-47 The above charge lifetime proves that, on the one hand, the dual regulation at the BOC/BOI-2 interface enables the photogenerated charge to be separated quickly and efficiently, thereby having a longer carrier lifetime. On the other hand, the extensive charge channels built on the large contact area give high-flux photogenerated

charges access to the surface of the photocatalyst_{withereby} obtaining excellent photodegradation activity (FPE) ST99:588G

Conclusions

Through the interfacial band offset and the IEF, the dual regulation of the thermodynamic and dynamic conditions of the heterojunction is achieved, which promotes the high-speed directional migration of photogenerated charges. And BOC/BOI heterojunction photocatalyst was constructed with Bi-O chemical bonds as interface charge transfer bridge for high-flux charge migrate. The visible photocatalytic activity of BOC/BOI heterojunction has increased above 23 times. This strategy is applicable to the interface structure photocatalysts for high performances.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partly supported by the National Natural Science Foundation of China (No. 51978098, 21872077, 21673126, 21761142017, 21621003) and Collaborative Innovation Center for Regional Environmental Quality.

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Conclusions

The conclusions section should come in this section at the end of the article, before the acknowledgements.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partly supported by the National Natural Science Foundation of China (No. 51978098, 21872077, 21673126, 21761142017, 21621003) and Collaborative Innovation Centre for Regional Environmental Quality.

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View Article Online DOI: 10.1039/D0TA02588G

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Dual regulation of thermodynamic and dynamic of Bi₂O₂CO₃/Bi₅O₇I heterojunction enabling visible-light-driven high-flux photogenerated charge migration.

