Improved photoelectric properties of BiOBr nanoplates by co-modifying SnO₂ and Ag to promote photoelectrons trapped by adsorbed O₂

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ABSTRACT It is highly desired to improve the photoelectric property of nanosized BiOBr by promoting the photogenerated charge transfer and separation. Herein, SnO₂ and Ag co-modified BiOBr nanocomposites (Ag-SO-BOB) have been prepared through a simple one-pot hydrothermal method. Surface photovoltage response of BiOBr nanoplates has 4.1-time enhancement after being modified with SnO₂ nanoparticles. Transient-state surface photovoltage (TS-SPV) and the atmosphere-controlled steady-state surface photovoltage spectroscopy (AC-SPS) confirmed that this exceptional enhancement of the photovoltage response can be ascribed to the coupled SnO₂ acting as platform for accepting the photoelectrons from BiOBr so as to prolong the lifetime and enhance charge separation. Remarkably, the surface photovoltage response can be further enhanced by synchronously introducing Ag nanoparticles, which is up to 15.4-times enhancement compared with bulk BiOBr nanoplates. The enhancement can be attributed to the improved O₂ adsorption by introducing Ag to further enhance charge separation. Finally, the synergistic effect of SnO₂ and Ag co-modification enhances the surface photovoltage response due to the enhanced charge separation and promoted O₂ adsorption, which is also confirmed through photoelectrochemistry and photocatalytic experiment.

Keywords: Ag-SnO₂-BiOBr, photoelectron trapping, O₂ adsorption, charge separation, surface photovoltage response

INTRODUCTION

During the rapid development of information technology, optoelectronic devices play significant roles in aerospace, military industry, nuclear energy and other important fields [1,2]. Surface photovoltage (SPV) response is the

most important property for photoelectric materials on fabricating photoelectric devices. Generally, surface photovoltage spectra (SPS) is used to monitor the surface potential of a semiconductor while generating electron-hole pairs with a light source [3,4]. SPS signals are driven by the build-in electric field and the carrier diffusion, respectively. For nanoscaled materials, the build-in electric field can be ignored due to the nano-size effect. It is acceptable that the SPS signals are based on the diffused photoelectrons trapped by the adsorbed O₂ for nanomaterials in aerobic environment [5]. Thus, improving the trapping of photoelectrons by adsorbed O₂ is effective to enhance the SPV responses, which involves the effective modulating of the thermodynamic energy and lifetime of photoelectrons, and the promoted adsorption of O₂.

Bismuth based materials are potential semiconductors for photoelectric response owing to the visible light response, abundant resource, environmental friendliness and controllable structures [6–8]. Interestingly, the special Bi 6s orbital contributes to both the conduction band (CB) and valence band (VB) for most bismuth based materials, resulting in the broken symmetry to drive the charge separation [9]. BiOBr (BOB) is a typical bismuth-contained oxide with the advantages of narrow band gap, simple preparation, controllable structure and so on [10,11]. In particular, its unique two-dimensional layered structure of [Bi₂O₂] ion unit and double halogen ions arrange alternately, which is beneficial to the separation and transfer of the photogenerated electrons and holes [12]. However, the positive CB bottom potential of BOB leads to the fast electron-hole

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recombination, due to the short lifetime and low thermodynamic energy of photoelectrons to be trapped by O_2 . The fast charge recombination is adverse to SPV response. Therefore, it is crucial to prolong the lifetime, and maintain the thermodynamic energy of photoelectrons to improve the photoelectric property of BOB.

In our previous work, the lifetime and thermodynamic energy of photoelectrons of narrow bandgap semiconductors such as Bi_2O_3 , $BiFeO_3$ and $BiVO_4$ can be effectively improved by modification with wide bandgap semiconductors like TiO_2 and SnO_2 for accepting the photoelectrons to prolong the lifetime and enhance the charge separation [13,14]. In addition, the wide bandgap electron acceptors often possess more negative CB potential with enough energy of photoelectrons for thermodynamically trapping by O_2 . Hence, it is expected to enhance the charge separation, prolong the carrier lifetime and maintain the thermodynamic energy of photoelectrons of BOB by modifying with wide bandgap semiconductor. As it is confirmed previously, SnO_2 with suitable CB potential and high mobility is suitable for modifying bismuth based oxides [15]. However, photocatalytic system of SnO_2 /BOB is hindered by interfacial charge transfer between the mismatched SnO_2 and BOB and O_2 adsorption.

Noble metals like Ag are excellent electron transporters with large dielectric constant and strong electronic conductivity [16]. Quan *et al.* [17] demonstrated that Ag can effectively promote the photoinduced charge transfer and enhance the electron-hole pair separation of C_3N_4 . Besides, Ag modification is beneficial to O_2 adsorption [18–20]. Introducing Ag in SnO_2 -BOB system may be effective to enhance the SPV responses.

Herein, Ag- SnO_2 -BOB nanocomposites have been synthesized by a simple one-pot hydrothermal method. SnO_2 nanoparticles are well dispersed on the BiOBr nanoplates, forming close nanojunctions favoring the charge transfer and separation to prolong the lifetime. Consequently, Ag is introduced to further enhance the photoelectrons separation and improve the O_2 adsorption, which results in the obviously enhanced photoelectric responses for 15.4- and 3.8-time higher than those of BOB and SnO_2 -BOB, respectively. This work, with fundamental study for enhancing the photoelectric property of BiOBr based materials, is significant to the design of high activity photoelectric response devices.

EXPERIMENTAL SECTION

Material synthesis

All the reagents were of analytical grade and used as-

received without further purification. Deionized water was used throughout the reaction.

Synthesis of BiOBr nanoplate

BOB nanoplate was synthesized through a one-pot hydrothermal method. In a typical synthesis, 1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 25 mL of distilled water to prepare solution A. 1 mmol of KBr was dissolved in 50 mL of distilled water to prepare solution B. Then, solution A was slowly added into solution B under continuous stirring at room temperature ($\sim 25^\circ C$) to form a suspended solution. The solution was stirred for 30 min. Then the solution was divided into three equal parts and transferred to a 50 mL of Teflon-lined stainless autoclave, respectively. After cooling down to room temperature, the precipitate was collected and washed using deionized water and ethanol several times and then transferred to a vacuum drying oven at $80^\circ C$ for 12 h. The samples are denoted as BOB-T/H (T=140, 160 and $180^\circ C$; H=10, 12 and 14 h).

Synthesis of SnO_2 /BiOBr nanocomposites

Similarly, $Bi(NO_3)_3 \cdot 5H_2O$ (1 mmol) and different molar ratio (1.0, 1.5 and 2.0%) of $Na_2SnO_3 \cdot 3H_2O$ was dissolved in 25 mL of distilled water to prepare solution A. 1 mmol of KBr was dissolved in 50 mL of distilled water to prepare solution B. Then, solution A was slowly added into solution B under continuous stirring at room temperature ($\sim 25^\circ C$) to form a suspended solution. The solution was stirred for 30 min. Then it was divided into three equal parts and transferred to a 50 mL Teflon-lined stainless autoclave, respectively. The autoclave was hydrothermally treated at $160^\circ C$ for 12 h under autogenous pressure. After cooling down to room temperature, the precipitate was collected and washed using deionized water and ethanol several times and then transferred to a vacuum drying oven to dry at $80^\circ C$ for 12 h. Thus, XSO-BOB-160/12 nanocomposites were obtained, in which X is the theoretical molar percentage of SO to BOB ($SO=SnO_2$; X=1, 1.5 and 2). For comparison, 0.5SO/BOB-160/12 was prepared by using the previous reported wet chemical method, including the preparation of SO nanoparticles [21].

Synthesis of Ag- SnO_2 -BiOBr nanocomposites

In a typical synthesis, 1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ and 0.0015 mmol of $Na_2SnO_3 \cdot 3H_2O$ were dissolved in 25 mL of distilled water to prepare solution A. 1 mmol of KBr were dissolved in 50 mL of distilled water to prepare solution B. Then, solution A was slowly added into

solution B under continuous stirring at room temperature ($\sim 25^{\circ}\text{C}$) to form a suspended solution. The mixed solution was stirred for 10 min, and then different molar percentage (0.1%, 0.5% and 1.0%) of AgNO_3 was added into the solution with continuous stirring for 20 min. Then the solution was divided into three equal parts and transferred to a 50 mL of Teflon-lined stainless autoclave, respectively. The autoclave was hydrothermally treated at 160°C for 12 h under autogenous pressure. After cooling to room temperature, the precipitate was collected and washed using deionized water and ethanol several times and then transferred to a vacuum drying oven at 80°C for 12 h to obtain YAg-XSnO-BOB-T/H (Y=0.1, 0.5 and 1; X=1.5; T= 160°C ; H=12 h).

Characterizations

The crystal structure was analyzed by a X-ray powder diffraction (XRD) diffractometer (Bruker D8 Advance) by using Cu K α radiation ($\lambda=1.5406\text{ \AA}$, 40 kV, 40 mA). The size and morphology of the final products were investigated by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, JEM-2100). UV-vis absorption spectra were determined by a UV-vis spectrophotometer (Shimadzu UV-2550, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) were tested using a Kratos-AXIS ULTRA DLD apparatus with Al(Mono) X-ray source, and the binding energies were calibrated with respect to the signal for adventitious carbon (binding energy= 284.6 eV).

Photochemical cell measurements were performed in a sealed quartz cell, by using three-electrode configuration including a saturated KCl Ag/AgCl reference electrode, a working electrode and a Pt foil counter electrode, and the electrolyte using 0.5 mol L^{-1} NaClO_4 ethanol solution. The samples were illuminated with a 150W Xenon lamp and the whole process bubbles through oxygen-free nitrogen gas in the dark. The preparation of sample films was described in detail elsewhere [22].

To evaluate the amount of hydroxyl radicals, firstly, 0.05 g sample was dispersed into 50 mL coumarin aqueous solution (0.01 mol L^{-1}) in a breaker. Prior to irradiation, the reactor was magnetically stirred for 10 min to achieve an adsorption-desorption equilibrium. After irradiation for 1 h, the sample was centrifuged and a certain amount was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin at 390 nm excitation wavelength through a spectrofluorometer (Perkin-Elmer LS 55).

The surface photovoltage (SPV) responses of different samples were measured by a home-built surface photo-

voltage spectroscopy with an atmosphere controlling system equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). The powder sample was sandwiched between two indium-tin-oxide (ITO) glass electrodes kept in an atmosphere-controlled sealed container. A monochromatic light was obtained from 500 W Xenon lamp (CHF XQ500W, Global Xenon lamp power) through a double prism monochromator (SBP300).

The transient-state surface photovoltage (TS-SPV) can obtain the dynamic information of lifetime and attenuation of carriers. Pulse time can be controlled to nanoseconds level. Different from SS-SPS, a layer of mica was put between ITO and the sample, with thickness about $10\text{ }\mu\text{m}$. The samples were excited by the laser source with a radiation pulse of 355 nm with 10 ns width from a second harmonic Nd:YAG laser (Lab-130-10H, Newport, Co.). The intensity of pulsed laser was measured by a high energy pyroelectric sensor (PE50BF-DIF-C, Ophir Photonics Group). The photovoltage signals generated by the sample were amplified with a preamplifier and collected by a 1 GHz digital phosphor oscilloscope (DPO 4104B, Tektronix).

Temperature-programmed desorption (TPD) for desorption O_2 was performed in a conventional apparatus by Chemisorption Analyzer, tp 5080 Chemisorb equipped with a thermal conductivity detector (TCD). About 50 mg samples were preheated to 300°C to remove the moisture for 1 h and then cooled down to room temperature under an ultra-high-pure He flow of 30 mL min^{-1} . The highly pure O_2 gas was introduced in a constant temperature of 30°C under flow rate of 30 mL min^{-1} for 60 min. The excess weakly physically adsorbed O_2 was removed by exposure to ultra-high-pure He flow at 30°C for 60 min. Then the temperature was increased to 550°C with the heating rate of $10^{\circ}\text{C min}^{-1}$ under pure He. The desorbed O_2 was analyzed by Chemisorption Analyzer, tp 5080 Chemisorb.

In typical CO oxidation experiment, 0.1 g sample was put into a Pyrex glass cylindrical reactor with a diameter of 7.0 cm and effective volume of 670 mL. The initial gas contained 1,000 ppm of CO, 20% O_2 , and 80% N_2 . The samples were irradiated by a 300 W Xenon arc lamp for 4 h, and then measured with a gas chromatograph (GC-7920, AuLight, Beijing) equipped with a TCD detector.

RESULTS AND DISCUSSION

Effect of SnO_2 introduction

In this work, BOB nanoplates were prepared *via* the one-step hydrothermal method. Fig. S1a shows the UV-vis

Figure 1 HRTEM image (a) of 1.5SO-BOB-160/12 and fine XPS of Sn element (b) of BOB-160/12 and 1.5SO-BOB-160/12.

diffuse reflectance spectra (UV-DRS) of different samples. The optical properties are unchanged for the BOB-T/H samples prepared in different conditions. The steady-state surface photovoltage spectra (SS-SPS) in Fig. S1b show that BOB-160/12 has the highest SPS response. Thus, BOB-160/12 is chosen as the fundamental sample for the following study. In addition, SEM images in Fig. S1c show the plate-like structure of BOB-160/12 with the size of about 2–6 μm . TEM and HRTEM images in Fig. S2 indicate that the obtained BOB-160/12 is plate-like in accordance with the SEM images. The lattice fringes of (001) plane with the inter-planar distance of 0.26 nm are attributed to tetragonal BiOBr. This is further proved by XRD analysis in Fig. S3a, from which we can see that the typical diffraction peaks at $2\theta=10\text{--}60^\circ$ can be well indexed to the tetragonal PbFCl-type BOB (JCPDS File No.09-0393) [23]. The intensity of (001) plane is significantly higher than other crystal surfaces, indicating the crystal is dominated by (001) surface. No peaks of any other phases or impurities are found in the XRD pattern.

SnO_2 (SO) with different amounts is coupled with BOB-160/12 with one-pot hydrothermal method. UV-DRS (Fig. S3b) shows that the optical properties are unchanged after SO coupling. It can be found that SO coupling does not influence the phase of BOB-160/12. HRTEM image in Fig. 1a shows that SO nanoparticle grows on the BOB to form a close heterogeneous junction. The lattice fringes of (001) plane with the inter-planar distance of 0.26 nm and the spacing of the (110) lattice plane with 0.35 nm are observed which can be attributed to the tetragonal PbFCl-type BOB and the rutile SnO_2 , respectively. The high resolution XPS spectra in Fig. 1b further prove the successfully coupling of SO, by observing the two symmetric peaks located at 486.9 and 495.3 eV which are respectively attributed to the $3d_{3/2}$ and $3d_{5/2}$ of Sn^{4+} [24]. Therefore, SO coupled BOB

nanoplates have been successfully prepared and 1.5SO-BOB-160/12 are the optimized one.

SPS technique, with its very high sensitivity, is an established contactless and nondestructive technique for semiconductor by means of measuring the surface photovoltage response through SPS which investigates the photophysics of excited states generated by adsorption in the aggregate state like O_2 [25,26]. SPS signal is produced by the capture of photoelectrons by adsorbed O_2 . However, SPS signal will also be produced when it is driven by the interfacial electric field in a heterogeneous junction. Thus, it is very hard to judge the real attribution of the SPS signal for heterojunctions. In order to reveal the bulk SPS responses, atmosphere controlled surface photovoltage spectroscopy (AC-SPS) was usually utilized because there is no photoelectron capture in N_2 atmosphere. As the AC-SPS shown in Fig. S1d, the BOB-160/12 displays SPV responses in O_2 , air and N_2 atmosphere. This indicates two different SPS mechanism in BOB-160/12. One is the photoelectrons trapped by the adsorbed O_2 on BOB and the other is the photogenerated holes trapped by Br in BOB due to the lone pair electrons in Br [27]. However, the enhanced SPV response in O_2 demonstrates that O_2 trapping dominates the SPS signal. Thus, to effectively enhance the separation of photoelectrons and to promote the surface O_2 adsorption are advisable strategies to enhance the photoelectric properties of BOB.

SPS responses of different samples are obviously enhanced, since SO can act as appropriate platform for accepting the photoelectrons from BOB to prolong their lifetime and enhance the charge separation. To verify this, SO coupled BOB-160/12 (1.5SO/BOB-160/12) was prepared by a two-step wet chemical method. The SPS response (Fig. S4) indicates that the SPS signal intensity of 1.5SO/BOB-160/12 sample is about 1.5-time higher

Figure 2 SS-SPS (a) and FS spectra related to the amount of produced $\cdot\text{OH}$ (b) of BOB-160/12, XSO-BOB-160/12 samples. Inset of (a) is TS-SPV responses of BOB-160/12 and 1.5SO-BOB-160/12 samples.

after SO coupling than BOB-160/12, demonstrating the positive effect of SO coupling to the SPV response. However, the poor interfacial quality of SO and BOB leads to the weak charge separation and little SPS enhancement for 1.5SO-BOB-160/12. A one-pot hydrothermal method is available to *in-situ* prepare close junction of SO and BOB. The SPS signal intensity of optimized 1.5SO-BOB-160/12 sample is 4.1-time higher than that of BOB-160/12. After coupling with the SO platform, the lifetime of the photoelectrons is prolonged, as it is shown from the time-resolved surface photovoltage (TR-SPV) (inset of Fig. 2a). This is also confirmed by the produced hydroxyl radicals ($\cdot\text{OH}$) in Fig. 2b, consistent with SPS response in Fig. 2a.

Effect of Ag modification

In order to further promote the SS-SPS response of the prepared XSO-BOB-160/12 nanocomposites, Ag is introduced into such system. As shown in Fig. S5a, the XRD pattern of 0.5Ag-1.5SO-BOB-160/12, 0.5Ag-BOB-160/12 and 1.5SO-BOB-160/12 are consistent with BOB-160/12 without any obvious changes. No characteristic diffraction peak of Ag in the composite can be observed, due to the tiny amount. From the UV-DRS in Fig. S5b, there is almost no change of the optical absorption after different amounts of Ag modification for both BOB-160/12 and XSO-BOB-160/12. The results showed that Ag modification does not change the structure and optical absorption of the BOB. The metallic Ag (0) has been confirmed by XPS as shown in Fig. S5c. XPS in Fig. S6 indicates the successful preparation of Ag-SnO₂-BiOBr composite without any impurities. TEM and HRTEM images in Fig. S7 display that Ag nanoparticles are well dispersed on BOB nanoplate with size about 2–10 nm.

Figure 3 TEM (a, b) and HRTEM (c) image of 0.5Ag-1.5SO-BOB-160/12 sample.

TEM and HRTEM images of 0.5Ag-1.5SO-BOB-160/12 in Fig. 3 show a close triple heterojunction of SnO₂, Ag and BiOBr, where the small Ag nanoparticles with size ca. 2–10 nm lies on SnO₂ and BOB. The lattice fringes of (001) plane of BOB with the inter-planar distance of 0.26 nm, the spacing of the (110) lattice plane of SnO₂ with 0.35 nm and the (111) lattice plane of Ag with 0.24 nm, are respectively observed in the HRTEM image, further verifying the successful preparation of Ag-SnO₂-BOB heterojunctions. UV-DRS in Fig. S8a further displays that there is almost no change of the optical absorption after different amounts of Ag modification to the XSO-BOB-160/12.

As shown in Fig. S8b, it is clear that appropriate amount of Ag modification can effectively enhance the SS-SPS response of the 1.5SO-BOB-160/12. The optimized 0.5Ag-1.5SO-BOB-160/12 displays the highest SPS response which can be attributed to the enhanced charge separation, confirmed by the produced $\cdot\text{OH}$ radical and

AC-SPS in Fig. S8c and d, respectively. The photoelectric properties of BOB-160/12 can be gradually improved by co-modifying with SO and Ag due to the synergistic effect of them. As shown in Fig. S9, the SPS signal of 0.5Ag-1.5SO-BOB-160/12 has about 1.3, 3.8 and 15.4-time enhancement compared with 0.5Ag/BOB, 1.5SO/BOB, and bulk BOB, respectively. From TS-SPV responses in Fig. 4a and Fig. S10, the positive signal indicates the capture of photoelectrons by O_2 and the lifetime of photoelectrons is obviously prolonged after introducing Ag. The prolonged lifetime of photoelectrons results in the enhanced charge separation due to the increased concentration of $\cdot OH$ radicals in Fig. 4b.

The photoelectric property of BOB is greatly enhanced *via* co-modifying with SO and Ag due to their synergistic effect for prolonging the lifetime of photoelectrons, enhancing the charge separation and improving O_2 adsorption. This is confirmed by electrochemical impedance spectra (EIS) in Fig. 5a (light) and Fig. S11a (dark). Generally speaking, the smaller radius is, the lower is the interfacial resistances [28,29]. The smaller

radius of 0.5Ag-1.5SO BOB-160/12 suggests the positive effect for improving the interfacial charge separation through Ag modification. This is further demonstrated by the photocurrents of different samples (Fig. 5b and Fig. S11b). As shown in Fig. S12, the 0.5Ag-1.5SO-BOB-160/12 shows the smallest slope of the Mott-Schottky plots, which suggests the most enhanced charge separation. In addition, the time-dependent transient photocurrent densities indicate that all the BOB based samples are stable (Fig. S13).

The improved O_2 adsorption after Ag modification is confirmed by O_2 -TPD (Fig. S14a). Chemical adsorption of O_2 at about 400°C becomes stronger after modifying with SO and Ag, in particular Ag. The improved O_2 adsorption favors the trapping of photoelectrons, leading to the enhanced SPS signals and charge separation. This is further confirmed by using a model reaction of photocatalytic CO oxidation [30]. In Fig. S14b, the photocatalytic activity of BOB-160/12 for CO oxidation is greatly enhanced after modifying with SO and Ag, especially, the co-modified one. This experiment demon-

Figure 4 TS-SPV responses (a), FS spectra related to the amount of produced $\cdot OH$ (b) of BOB-160/12, 1.5SO-BOB-160/12, 0.5Ag-BOB-160/12 and 0.5Ag-1.5SO-BOB-160/12 samples.

Figure 5 EIS Nyquist plots (a), $J-V$ curves (b) of BOB-160/12, 1.5SO-BOB-160/12, 0.5Ag-BOB-160/12 and 0.5Ag-1.5SO-BOB-160/12 samples.

strates the improved O_2 adsorption and charge separation.

Mechanism

The introduction of SO and Ag synergistically promotes the separation of photogenerated charges of BOB, leading to the highly improved SPV response. It is assumed that the SPV enhancement is attributed to the prolonged lifetime of photoelectrons and then enhanced charge separation of BOB through transferring photoelectrons to SO platform. To clarify this assumption, the photocurrent action spectra of BOB-160/12, 1.5SO-BOB-160/12, 0.5Ag-BOB-160/12 and 0.5Ag-1.5SO-BOB-160/12 with different wavelength have been obtained (Fig. S15).

A weak photocurrent is observed at 440 nm, resulting from the photo-excited BOB (2.8 eV) to Ag with low Fermi level. Noticeably, the photocurrents for all the three catalysts are obviously increased below 440 nm, which corresponds to the minimum energy difference between the VBM of BOB and CBM of SO (~410 nm), and the interfacial electrons transferring between BOB and Ag. Due to the synergistic effect of photoelectrons transferring and separation, the 0.5Ag-1.5SO-BOB-160/12 sample exhibits the largest photocurrent density, also due to the superior O_2 adsorption of Ag.

A possible mechanism is depicted in Fig. 6. Fig. 6a shows that the electron-hole pairs of BOB are separated under excitation. However, most of them are recombined due to the poor O_2 adsorption and sluggish charge separation. When only SO is coupled, the photoelectrons with high level energy will transfer to the CB of SO from the CB of BOB. In particular, the coupled SO acts as an appropriate platform to maintain the enough thermodynamic energy and prolong the lifetime of the photoelectrons. However, the O_2 adsorption of SO is weak, as shown in Fig. 6b. Although the O_2 adsorption capacity is promoted, the thermodynamic energy and lifetime of photoelectrons are insufficiently utilized when only Ag is coupled as shown in Fig. 6c. Therefore, the synergistic effect of SO and Ag enhances the SPV response. As is shown in Fig. 6d and e, in such a triple junction of Ag-SO-BOB, SO acts as a platform to prolong the lifetime, enhance the charge separation and maintain the thermodynamic energy of photoelectrons, and meanwhile Ag as O_2 adsorber to improve the O_2 adsorption to trap the photoelectrons leads to the high SPV response.

CONCLUSIONS

In summary, Ag-SnO₂-BOB nanocomposites were prepared via the one-pot hydrothermal method which

Figure 6 The mechanism of charge diffusion and trapping by adsorbed O_2 in different samples (a–d) and charge transfer and separation (e).

displays superior photoelectric properties with high SPV response about 15.4, 3.8, 1.3-time higher than that of bulk BOB-160/12, 1.5SO-BOB-160/12 and 0.5Ag-BOB-160/12, respectively. The exceptional SPV response is attributed to the synergistic effect of SnO₂ and Ag co-modification. According to SPS, TS-SPV and other characterizations, SO coupling leads to long lifetime and maintains the thermodynamic energy of the photoelectrons owing to its suitable CB. On the other hand, Ag coupling promotes the O_2 adsorption to trap photoelectrons. This work shows an effective approach to improve the photoelectric properties of BOB by modulating the lifetime, thermodynamic energy of photoelectrons and promoting O_2 adsorption, which will pave a new way to obtain high performance materials for photoelectric devices.

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通过 SnO_2 和Ag共修饰促进光生电子捕获氧气改善BiOBr纳米盘的光电特性

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摘要 针对BiOBr纳米材料导带位置偏正导致的可见光生电子寿命短、电荷分离差和氧气捕获能力差等关键科学问题, 本文通过简单的一步水热法合成高光伏响应的Ag-SnO₂-BiOBr复合纳米材料. 通过气氛控制表面光电压、瞬态光电压技术和光电化学实验等深入揭示了Ag-SnO₂-BiOBr复合纳米材料的电荷转移和分离机制. 结果表明, SnO₂可作为适当能量水平的可见光生电子接收平台, 有效延长光生电子的寿命, 提高其利用率并促进光生电荷分离. 共修饰Ag有效改善了SnO₂和BiOBr的表面氧吸附能力, 进一步促进了BiOBr可见光生电子的有效分离, 因此表现出高的光伏响应, 分别是SnO₂/BiOBr、Ag/BiOBr和BiOBr的3.8、1.3和15.4倍. 本工作对深入研究含铋半导体材料的光电特性和电荷分离机理具有重要的意义, 为后续设计光伏传感等光电器件提供实验和理论依据.