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Research Article

Rapid Thermal Processing and Improved Photocatalysis of Bi_2O_3-$BaTiO_3$ Heterojunction

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Bi_2O_3-$BaTiO_3$ heterojunction with high photocatalysis efficiency was directly synthesized by rapid thermal processing (RTP). Bi_2O_3 and $BaTiO_3$ were mixed in ratio and treated by RTP and conventional thermal processing (CTP), respectively. RTP samples have obvious Bi_2O_3 diffraction peaks, while CTP samples show pure $BaTiO_3$ tetragonal perovskite. More small particles and layered existed in RTP samples. Photodegradation of MB solutions shows that RTP can promote photocatalytic efficiency. Its main lies in the following points: RTP can remove grain boundary defects by strengthening the bond grains; RTP can limit the solution region of the two substances to a certain range to get the best built-in electric field width; and RTP can strengthen the tetragonal $BaTiO_3$ phase to hasten ion movement. Therefore, RTP can achieve much higher photocatalytic efficiency by improving the build heterojunction. This work provides a direct and efficient route to get improvement and high performance of heterojunction.

1. Introduction

Heterojunction formed by compound semiconductors was pointed as an effective method to improve the photocatalysis efficiency for the strengthening of carrier mobility, to separate electron-hole pairs, and so on [1]. $BaTiO_3$ has a potential fit band gap to show photocatalysis. Research showed that it could produce much efficiency in heterojunction with other oxides [2]. The semiconductor combination of Bi_2O_3-$BaTiO_3$ has been designed, and its photocatalytic properties have been widely studied [3]. Bi_2O_3 and $BaTiO_3$ can form type II heterojunction, which can not only get a high generating rate of electron-hole pairs but also effectively inhibit electron-hole pair recombination [4]. These two were considered important reasons for the improved photocatalytic efficiency of this composite semiconductor.

To build a heterostructure, the control of the combined is the essence of the process [5]. By adapting and combining two semiconductors, different photocatalytic effects can be achieved. Among them, heat treatment plays an important part [6]. By changing the heat treatment factors, including heating temperature, heating rate, and heating atmosphere, the combination of the two semiconductors can be controlled to realize the effect of regulating and performance of the heterojunction.

CTP is to rise to the target temperature at a conventional heating rate, maintain the target temperature for a certain time, and then cool down at a cooling rate. In this process, the bonding between the powders in the precursor changes qualitatively, and the powder completes crystallization [7]. Due to the slow heating rate and long heat treatment time, it is not only not conducive to energy conservation but also prone to grain boundary diffusion and viscous flow inhomogeneously. Therefore, local recrystallization is prone to occur in this process, accompanied by grain growth inhomogeneously and abnormally large grains, resulting in unnecessary local defects [8]. These are unfavorable for interface bonding in heterojunction construction. This is one of the important problems to be solved in CTP research.

RTP is an effective method for material tailings [9]. Using the extremely rapid heating rate of RTP to carry out combined heterojunction may bring extra performance compared to CTP. It can build notable grain boundaries, improve the crystal bond for control defects, and induce specific area stress distribution [10]. Based on the characteristics, this approach has the potential to increase performance heterojunction.

In this paper, we carried out a study on the improved photocatalysis of Bi_2O_3-$BaTiO_3$ heterojunction particles combined with RTP. The data consistently showed that the heterojunction combined by this route had improved photocatalysis due to their improved construction. Heterojunction combined with RTP deserves high research interest.

2. Experimental

The precursor compound for thermal treatment was obtained by mixing 1%, 2%, 3%, 4%, and 5% mol bismuth trioxide (Bi_2O_3 with purity 99.99%) with barium titanate ($BaTiO_3$ with purity 99.5%), which followed by ball milling of 24 hours. All these compounds with different Bi doping ratios were divided into 2 groups. Besides, a group of undoped $BaTiO_3$ was also processed as a comparison. Two different thermal treatments were conducted on two groups of the precursor compound. The first group (BT2BiR~BT10-BiR) was treated by RTP, with the heating temperature set at 1130°C for 600 s. The RTP samples were heated at a rate of 200°C/s to 430°C and held for 50 s, then heated at the same rate to 730°C and held for 50 s, and then heated at the same rate again to 1130°C and held for 600 s. The second group (BT2BiC~BT10BiC) was sintered by CTP at 1100°C for 240 min. The CT samples were heated at a rate of 4°C/min to 1050°C and then heated at a rate of 1°C/min to 1130°C and held for 240 min. The photocatalytic for the degradation of methylene blue (MB) was evaluated by agitating the solution and irradiating the samples using a 250 W high-pressure Hg lamp. The initial concentration of MB was 10 mg/L with a catalyst loading of 1 g/L for measurement. Regents and chemicals in this work were purchased from Aladdin Industrial Corporation (Shanghai, China).

RTP was conducted by RTP-300 Rapid Thermal Processor (Beijing Ruiyisi Technology Co. Ltd.). The structure and morphology of the samples were characterized by X-ray diffraction (Philips X-ray diffractometer system) and field emission scanning electron microscopy (FESEM, JEOL JSM-6700F equipped with selected area electron diffraction and energy-dispersive X-ray spectroscopy). The UV absorption spectrum was measured using a Shimadzu UV-3600 plus (Kyoto, Japan) spectrophotometer.

3. Results and Discussion

XRD patterns of all products are displayed in Figures 1 and 2. To supplement, pure $BaTiO_3$ was further characterized. It can be observed that all samples have a main crystal phase that corresponds to a tetragonal perovskite structure $BaTiO_3$ (JCPDS, 05-0626). Figure 1 shows that the samples treated by CTP have no second phase. It means that Bi_2O_3 has dissolved into the $BaTiO_3$ crystal lattice as mentioned in earlier research. But in Figure 2, increasing peaks at 28.04° and 32.9° (Bi_2O_3 JCPDS, 27-0050) with increasing doping concentration show distinct results. Bi_2O_3 does not dissolve into the $BaTiO_3$ crystal lattice when treated by RTP but forms a heterojunction structure with $BaTiO_3$. In the composite photocatalyst, the heterojunction formed by discrete semiconductors was pointed as the key to efficiency improvement [11].

SEM images of all products are displayed in Figure 3. Firstly, on the surface of a big crystal grain treated by RTP, more small particles exist than in CTP. As mentioned in the literature, when metal oxide is doped into $BaTiO_3$, it can be gradually dissolved into the material by a long enough heat treatment time [12]. However, in the RTP, the dissolving process can be shortened by the rapid temperature increase and reduction. This can effectively suppress to form solid solutions but improve the form of heterojunction. As a result, more small particles can be seen. Secondly, some layered and sharp shapes can also be observed in RTP samples. This is because RTP treatment can strengthen the bond grains at the grain boundaries and remove grain boundary defects, which will cause local stress to spread [13]. This will be expected to result in layered, sheet-like, and sharp shapes.

Photodegradation of MB solutions with reaction time for different is presented in Figures 4 and 5. It can be seen from the figures that Bi doping can improve the photocatalytic efficiency of $BaTiO_3$. Moreover, RTP samples show higher photocatalytic efficiency with the same proportion of doping. It can be observed that as the proportion of Bi doping increases, the rate of sample degradation of MB is increasing. At the same time, the rate of RTP samples is greater than that of CTP samples. In addition, the degradation rates of samples with a doping concentration below 8% increase with the increase of doping concentration, but the degradation rate of samples with a doping concentration of 10% decreases slightly compared to 8%. This shows that there is a limit ratio of Bi_2O_3-$BaTiO_3$ composite under this preparation procedure. This shows that on the one hand, Bi doping can effectively improve the photocatalytic efficiency of $BaTiO_3$, and on the other hand, RTP treatment can also promote the photocatalytic efficiency. Since the samples in this study are all non-nanoparticles with low specific surface area, their photocatalytic efficiency is low compared to those reported in the literature for smaller sizes.

When a beam of light shines on a semiconductor material, if the light is stronger than the forbidden bandwidth, the electrons and holes in the semiconductor will form unstable electron-hole pairs [14]. This will lead to the generation of electrons in the conduction band and holes in the valence band. These electron-hole pairs are unstable and will recombine. But if there are pollutants in the solution, the electrons and holes will undergo redox reactions with the pollutant ions on the surface. Thus, the recombination of electron-hole pairs was prevented. And the pollutants can be degraded.

In photocatalysis, several factors play a crucial role [15]: (1) producing rate of electron-hole pairs [16]. This is related to the semiconductor band gap. The narrower the semiconductor band gap, the easier it is for the energy of incident light to excite electron-hole pairs, which can provide more

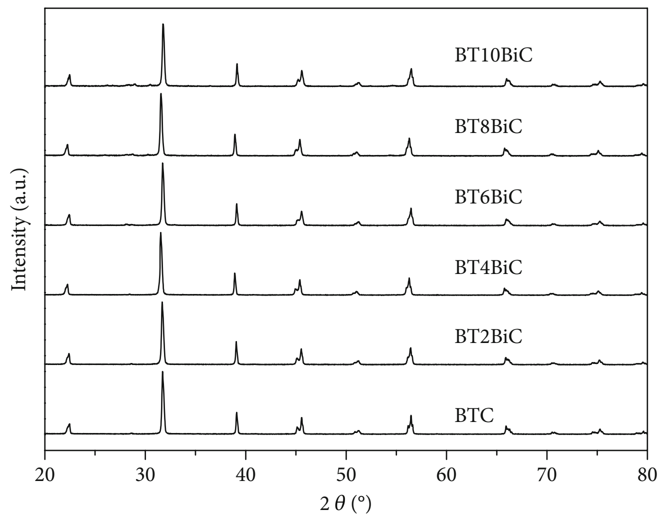

Figure 1: XRD patterns of BT and BT2BiC~BT10BiC.

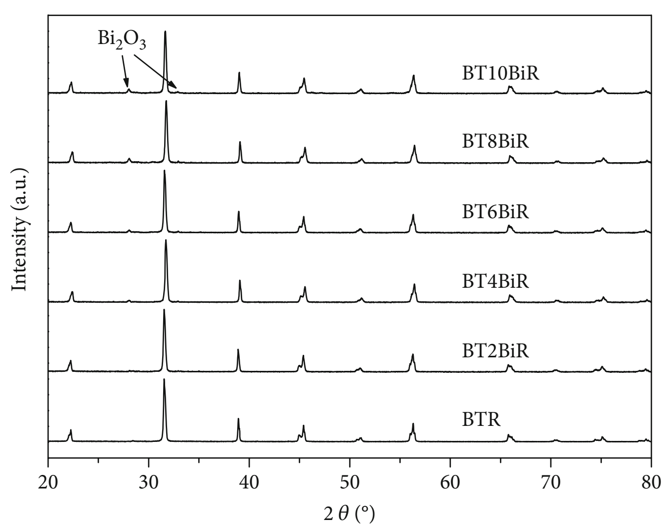

Figure 2: XRD patterns of BT and BT2BiR~BT10BiR.

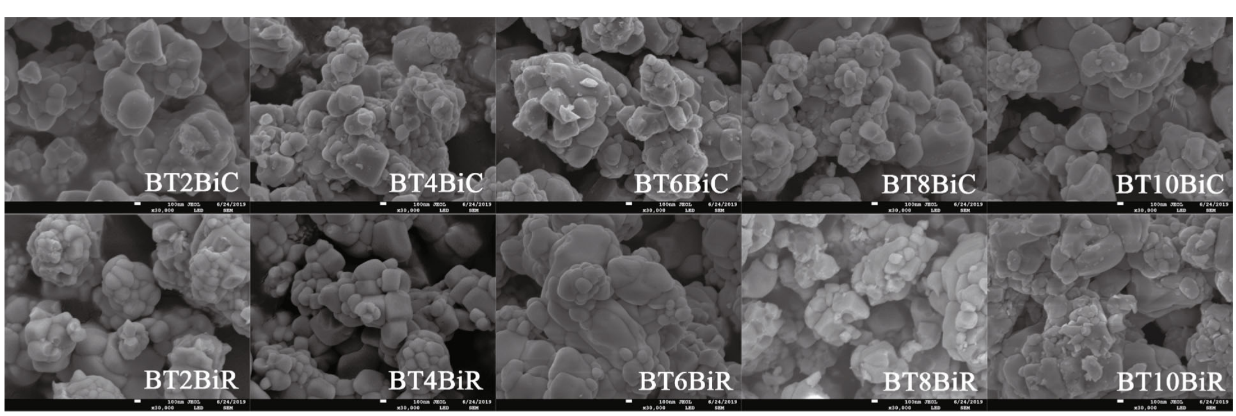

Figure 3: SEM images of BT2BiC~BT10BiC and BT2BiR~BT10BiR.

ions for photocatalysis. (2) Restraint of electron-hole pair recombination [17]. Photoexcited electrons and holes will recombine without reacting with pollutant ions. If there is more recombination, the electron-hole pairs that have a role in the photocatalysis will be reduced. Therefore, how to promote separate electrons and holes has become another key to

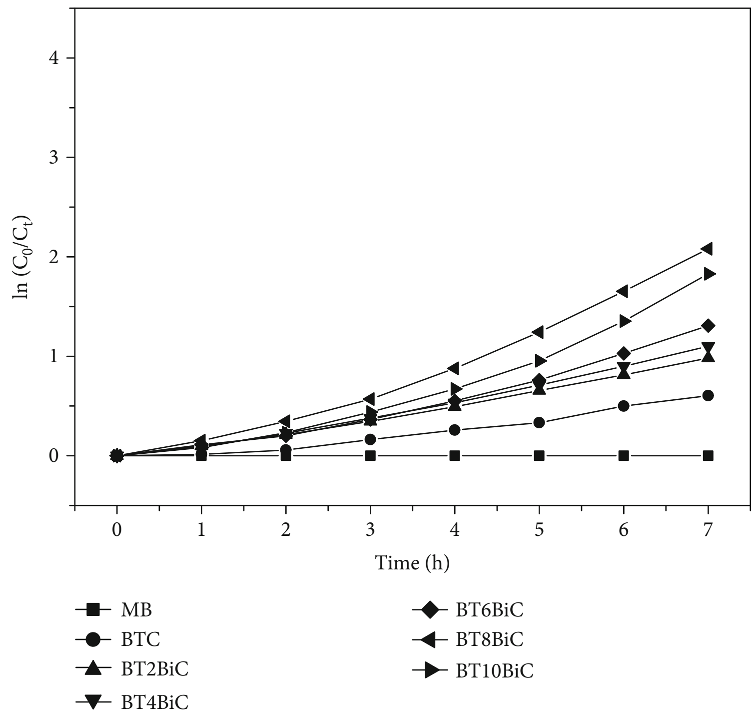

Figure 4: Photodegradation of MB solutions for BT and BT2BiC~BT10BiC.

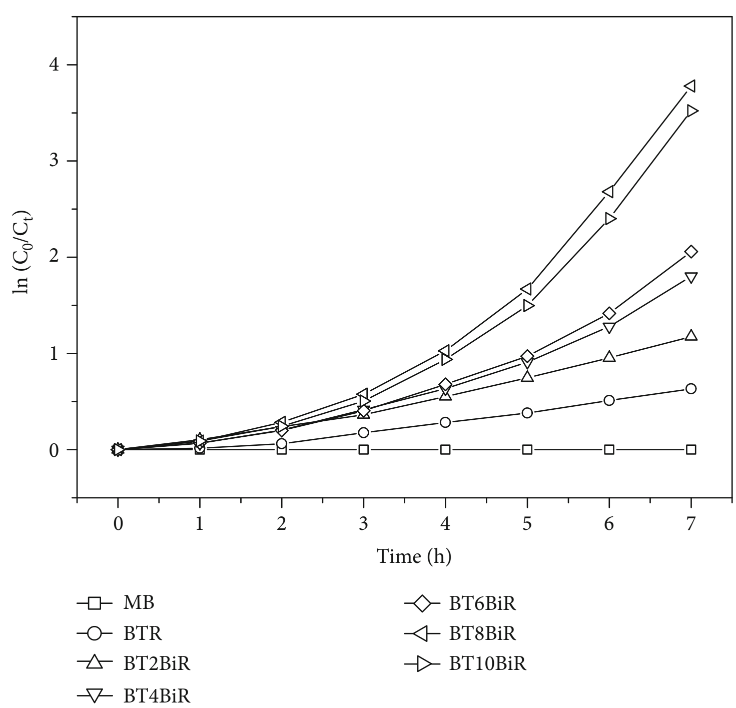

Figure 5: Photodegradation of MB solutions for BT and BT2BiR~BT10BiR.

improving photocatalytic efficiency. (3) Effective specific surface area for photocatalytic reaction. Since the photocatalytic reaction occurs on the surface area, the electrons and holes must be in contact with the pollutant ion to be able to undergo a degradation reaction. So the effective specific surface area will also play an important role.

To form semiconductor heterojunction is an effective way to improve the photocatalytic efficiency. In the study of heterojunction composed of two semiconductors, there are two common types [18]: type I is where the band gap of one material is within the range of the other material, so both photoexcited electrons and holes gather on one

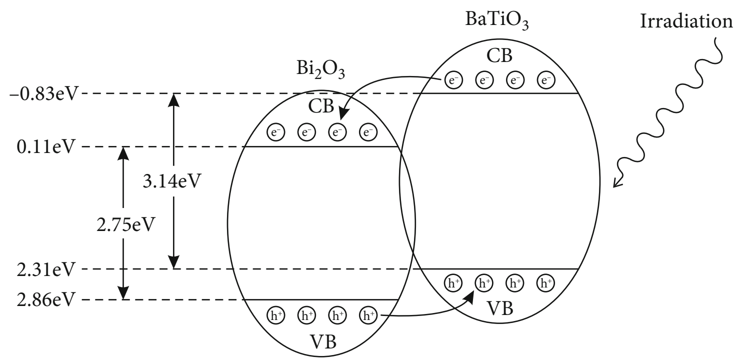

Figure 6: Band potentials and photocatalysis mechanism of Bi_2O_3-$BaTiO_3$ heterojunction.

material during migration, and type II heterojunction is because the conduction band bottom and valence band top of the two materials are interlaced, so the photoexcited electrons and holes gather on different materials, respectively, which can effectively promote separate electron-hole pairs. As shown in Figure 6, the band gaps of $BaTiO_3$ and Bi_2O_3 are estimated to be 3.2 and 2.75 eV, respectively [3]. And CB edge potentials of $BaTiO_3$ and Bi_2O_3 are -0.83 eV and 0.11 eV, respectively. VB edge potentials of $BaTiO_3$ and Bi_2O_3 are 2.31 eV and 2.86 eV, respectively. Therefore, they make up a typical type II heterojunction. This semiconductor heterojunction can narrow down the effective band gap to get a higher yield rate of electron-hole pairs.

Meanwhile, under act light, since the bottom of the conduction band of Bi_2O_3 is lower than that of $BaTiO_3$, an electron potential well is formed. So the photoexcited electrons will gather on the side of Bi_2O_3. Similarly, since the valence band top of $BaTiO_3$ is higher than that of Bi_2O_3 to form a hole potential well, the photoexcited holes will gather on the $BaTiO_3$ side. This can promote the efficient separation of photoexcited electrons and holes. This separation increases reacting electrons and holes with pollutant ions, improving the efficiency of photocatalysis [3, 4]. This shows that improving the heterojunction can effectively improve all of the photocatalysis, promoting and improving the photocatalytic rate.

In this study, RTP samples have higher photocatalytic performance, and we believe the main are as follows. (1) RTP can remove grain boundary defects by strengthening the bond grains at the grain boundaries of heterojunction (which can concentrate the chemical bonds between grains), providing effective support for grain bonding [9]. In the construction of Bi_2O_3-$BaTiO_3$ heterojunction, the bonding degree of the heterojunction directly decides and performs the resulting performance. The grain bonding of the RTP samples is strong, so the photocatalytic efficiency can be improved. (2) To tackle the problem of strengthening grain bonding, the traditional treatment method is to reduce the defects and cracks in the surface area by slowing down the heating rate during heat treatment [19]. However, this method has one drawback; that is, as a dopant, Bi_2O_3 will gradually diffuse into the grains of $BaTiO_3$ during long-term heat treatment, and this diffusion will form a built-in electric field in the heterojunction structure. However, if the width of the built-in electric field is too long, it will weaken the field strength. Owing to the built-in electric field, strength provides the separation driving force of electrons and holes. Then, the driving force to separate the electrons and holes can become weaker, which will hinder the following electron-hole migration in different directions. Therefore, the ideal method is to limit the solution region of the two substances to a certain range to obtain the best built-in electric field width [20]. RTP can easily achieve this by heating treatment for a short time. (3) RTP can strengthen the tetragonal $BaTiO_3$ phase [21]. The fact that the tetragonal of $BaTiO_3$ can accelerate ion movement is considered an important reason for the high photocatalytic rate of heterojunction [22]. Compared with the cubic phase, the tetragonal phase has stronger photocatalytic degradation. Through this, RTP can improve the photocatalytic effect of Bi_2O_3-$BaTiO_3$ heterojunction.

In conclusion, these can bring novel results to the research of RTP construction of semiconductor heterojunction. This method has many potential applications in combining and performing the control of semiconductors. It needs more investigation in further studies.

4. Conclusions

Based on RTP, a direct and effective method to improve the combination and performance of the heterojunction was developed. Bi_2O_3 and $BaTiO_3$ were mixed in specific ratios. Then, RTP and CTP were performed, respectively, in heating treatment procedures. XRD patterns show that the samples treated by RTP have remarkable Bi_2O_3 diffraction peaks. However, samples treated by CTP show pure $BaTiO_3$ tetragonal perovskite. More small particles and layered existed in RTP samples. A significant photocatalytic effect of BTBiR particles was characterized compared to the weaker effect of BTBiC particles and the little effect of pure BT. Since suitable band gap width and electron-hole pair separation are the main reasons for the high photocatalytic efficiency of heterojunction, RTP can achieve much higher photocatalytic efficiency by improving the build heterojunction. First, RTP can remove grain boundary defects by strengthening the bond grains. Next, RTP can limit the solution region of the two substances to a certain range to get the best built-in electric field width. Then, RTP can strengthen the tetragonal

$BaTiO_3$ phase with hasten ion movement. Much investigation of the properties and potential applications of heterostructures combined with RTP is highly desired.

Data Availability

The XRD, SEM images, and photodegradation data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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