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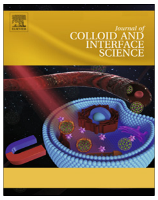

Regular Article

Ferroelectric spontaneous polarization steering charge carriers migration for promoting photocatalysis and molecular oxygen activation

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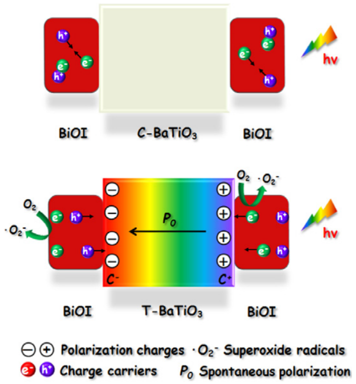
GRAPHICAL ABSTRACT



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ABSTRACT

Introducing a polarization electric field in photocatalyst system is regarded as a new concept for photocatalytic activity enhancement. In this work, we first unearth that the spontaneous polarization of ferroelectric BaTiO$_3$ promotes the photocatalytic and molecular oxygen activation performance of the narrow-band-gap semiconductor BiOI. Ferroelectric tetragonal-phase BaTiO$_3$ (T-BaTiO$_3$) were prepared via calcination of nonferroelectric cubic-phase BaTiO$_3$ (C-BaTiO$_3$), and their polarization ability was verified via ultrasonication-assisted piezoelectric catalytic degradation. Then, the C-BaTiO$_3$/BiOI and T-BaTiO$_3$/BiOI heterostructures are fabricated by a soft-chemical method. To disclose the influence of ferroelectric spontaneous polarization on charge movement behavior, the photocatalytic and molecular oxygen activation properties are monitored by degradation of methyl orange (MO) and superoxide radical ($\cdot O_2^-$) evolution under visible light irradiation ($\lambda > 420$ nm), respectively. The results demonstrated that T-BaTiO$_3$/BiOI far outperforms C-BaTiO$_3$/BiOI and pristine BiOI. The ferroelectric spontaneous polarization of T-BaTiO$_3$ can steer the migration of photogenerated charge carriers and induce efficient separation, accounting for the strengthened photodegradation and reactive oxygen species $\cdot O_2^-$ production rate (11.02×10^{-7} mol L^{-1} h^{-1}). The study may furnish a new reference for developing efficient tactics to advance the photocatalytic and molecular oxygen activation ability for environmental chemistry and biochemistry applications.

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1. Introduction

Semiconductor photocatalysis is gaining increasing attention owing to their large potentials for tackling the current serious environmental and energy issues [1–3]. In particular, reactive oxygen species (ROS), the highly-active and green oxidants generated in photocatalytic process, e.g. superoxide ($\cdot O_2^-$), hydroxyl ($\cdot OH$), peroxyl ($RO_2^{\cdot}$), singlet oxygen ($^1O_2$), are of great importance in the fields of environmental chemistry and biochemistry [4,5]. However, the development of photocatalysis is currently largely confined by the unsatisfied charge separation efficiency of photocatalysts, driving many efforts to develop diverse strategies, traditionally, metal or non-metal doping, hetero/homojunction fabrication, etc., for enhancing their photocatalytic performance [6–10]. Though these strategies show certain potential, there are some drawbacks. e.g. For hetero/homojunction fabrication, it requires that the semiconductors must possess matchable band energy levels to allow the effective charge separation and transfer between bands. Building an electric field in photocatalyst system has been regarded as a new tactic to strengthen the separation of photoinduced charge carriers. The existence of internal electric field allows a driving force for the migration of photogenerated electrons and holes in an opposite direction, thereby enhancing the charge separation [11,12].

Ferroelectrics, in which the strong spontaneous polarization can promote charge separation, are introduced in photocatalysis recently. The spontaneous polarization originating from the displacement of the center of the negative and positive charges in a unit cell could induce the appearance of macroscopic positive (C^+) and negative charges (C^-) on the two opposite sides of ferroelectrics, which would enhance separation of the photogenerated electron-hole pairs [13]. For instance, ferroelectric $BiFeO_3$ can presumably decrease the charge recombination rate from 17 s^{-1} to 0.6 s^{-1} in $BiFeO_3/BiVO_4$ composite, enabling $BiVO_4$ photoanode to show high and stable photoelectrochemical water oxidation performance [14]. Similarly, the charge transfer of Z-scheme $BiVO_4$-$CuInS_2$ catalyst can be enhanced by ferroelectric $BiFeO_3$, leading to an improved photodegradation activity for 2,4-dichlorophenol [15]. Tetragonal-phase $BaTiO_3$ is also a typical ferroelectric material with the Curie temperature of about 120 °C in bulk crystal. However, both the ferroelectric tetragonal phase and nonferroelectric cubic phase can exist at room temperature, as the surface-related strain could make the cubic phase stable at room temperature in small crystallites [13]. Hong et al. found that direct piezoelectrical water splitting can be achieved by $BaTiO_3$ microfibers, but it is not in the piezoelectric tetragonal phase [16]. Benke et al. reported the pyroelectrically driven hydroxyl radicals ($\cdot OH$) evolution by the cooperation of $BaTiO_3$ and Pd nanoparticles [17]. Recently, the sonophotocatalysis of $Ag_2O-BaTiO_3$ hybrid photocatalyst was investigated, and the ultrasonication-assisted piezoelectric polarization of $BaTiO_3$ was demonstrated to be capable of promoting the photoinduced charge separation of Ag_2O [18]. Nonetheless, the effect of ferroelectric self-polarization of $BaTiO_3$ on the movement behavior of photogenerated charge carriers of semiconductors has not been recognized.

Layered bismuth-based (LBB) semiconductor photocatalytic materials recently attract intensive research interests due to the diverse structural configurations and strong photo-oxidation ability from hybridized orbitals of O 2p and Bi 6s. They include not only the classical Sillén-structured bismuth halides BiOX (X = F, Cl, Br, I) [19–22] and Aurivillius structured Bi_2MO_6 (M = W, Mo) [23,24], but also some newly-developed Sillén-structure related $Bi_2O_2[BO_2(OH)]$ [25] and $Bi_2O_2(OH)(NO_3)$ [26]. BiOI, which almost possesses the narrowest band gap (1.7–1.9 eV) among the LBB materials [27,28], triggered widespread research efforts, including heterostructure fabrication with different semiconductors [29–36]. Considering the polar feature of ferroelectrics, coupling BiOI with a ferroelectric, like $BaTiO_3$, may be a feasible way to promote the charge separation of BiOI, which has not been achieved so far.

In this work, ferroelectric tetragonal-phase $BaTiO_3$ (T-$BaTiO_3$) was prepared by calcinating nonferroelectric cubic-phase $BaTiO_3$ (C-$BaTiO_3$), and we first utilize ultrasonication-assisted piezoelectric catalytic degradation to show their difference. Then, the C-$BaTiO_3$ and T-$BaTiO_3$ are separately employed to couple with BiOI to construct C-$BaTiO_3$/BiOI and T-$BaTiO_3$/BiOI heterostructures, respectively. The photocatalytic and molecular oxygen activation performance of samples are monitored, respectively, by degradation of methyl orange (MO) and superoxide radical ($\cdot O_2^-$) evolution under visible light irradiation ($\lambda > 420$ nm). It demonstrated that T-$BaTiO_3$/BiOI shows much higher photo-reactivity than C-$BaTiO_3$/BiOI and pristine BiOI. The efficient charge separation induced by ferroelectric spontaneous polarization of tetragonal-phase $BaTiO_3$ was demonstrated to be responsible for the enhanced photocatalytic and molecular oxygen activation ability. The corresponding mechanism is also proposed as well. Our work may offer a general approach to photocatalytic activity enhancement of semiconductor photocatalysts.

2. Experimental section

2.1. Synthesis

Cubic non-ferroelectric $BaTiO_3$ powder (99.9% trace metal basis, ~100 nm) was obtained from Sigma. Tetragonal ferroelectric $BaTiO_3$ samples are synthesized by thermal treatment of cubic $BaTiO_3$ powder in an alumina crucible at 1200 °C for 24 h in a tube furnace in air based on the Ref. [13], which demonstrated that this high calcination temperature can induce the phase-transformation of $BaTiO_3$ from cubic phase to tetragonal phase.

The $BaTiO_3$/BiOI composites are synthesized through a simple room-temperature precipitation method with assistance of ethylene glycol (EG). 0.4 mmol cubic $BaTiO_3$ or tetragonal $BaTiO_3$ powders are first dispersed in 20 ml EG solution containing 2 mmol $Bi(NO_3)_3\cdot 5H_2O$ (Sigma-Aldrich). After that, 20 ml of KI (2 mmol, Sigma-Aldrich) water solution was dropwise added into the above suspension, and was kept stirring for 1 h. After that, the products were collected with filtration and washed for three times with deionized water and ethanol, and dried at 80 °C for 10 h. The cubic $BaTiO_3$/BiOI and tetragonal $BaTiO_3$/BiOI are denoted as C-$BaTiO_3$/BiOI or T-$BaTiO_3$/BiOI, respectively.

2.2. Characterization

The phase structure of samples is determined by X-ray diffraction (XRD, PANalytical Empyrean, Cu Kα radiation) with Cu K_α radiation ($\lambda = 1.5418$ Å). The scanning step width of 0.02° and the scanning rate of 0.2° S^{-1} were applied to record the patterns in the 2θ range of 10–75°. Field-emission scanning electron microscopy (FESEM, FEI NanoSEM 630) and transmission electron microscopy (TEM, JEOL 1200 EXII) are used to analyze the morphology and microstructure. UV–vis diffuse reflectance spectra (DRS) of samples were obtained using a Varian Cary 6000i spectrophotometer. The spectra were recorded at 250–750 nm referenced to $BaSO_4$. Specific surface area was determined by the nitrogen adsorption-desorption method on a 3020 Micromeritics instrument.

2.3. Photocatalytic degradation experiments

The photocatalytic performance of samples is assessed by degradation of methyl orange (MO) under visible light irradiation