Enhanced photocatalytic activity and cycle stability driven by ultrasonic vibration for ferroelectric photocatalysts

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Abstract: Ferroelectric materials have been applied in the photocatalytic field due to the internal electric field generated by the spontaneous polarisation. In this study, it is found that the ferroelectric BaTiO3 catalysts exhibit the excellent photocatalytic property and cycle stability under ultrasonic vibration. In addition, the degraded photocatalytic activity after several cycling tests can be recovered if the BaTiO3 sample is treated by ultrasonic before photocatalytic reaction. The enhanced photocatalytic activity and cycle stability are ascribed to the variational spontaneous polarisation under external strain for ferroelectric materials. Under ultrasonic vibration, the high-frequency alternating strain applied on the BaTiO3 grain changes the internal polarisation electric field. Due to the fast changing polarisation electric field, there is not enough time to form the depolarisation electric field in the BaTiO3 grain. Therefore, the effective electric field existed in BaTiO3 grain is large and can effectively promote the separation of the photo-generated electrons/holes; thus improving the photocatalytic activity. It is suggested that ultrasonic vibration is an efficient method to improve the photocatalytic properties and cycle stability of the ferroelectric photocatalysts.

1 Introduction

Perovskite-type materials with chemical formula ABO3 have been made into electronic devices, such as energy harvester [1], energy storage [2], force sensor [3], electronic capacitor [4–6] etc. In recent decades, parts of them, such as BaTiO3 (BT) [7–9], SrTiO3 [10, 11], BiFeO3 [12], and PbTiO3 [13] are investigated as catalysts for potential environmental applications such as organic contaminant degradation [14], up-conversion luminescence [15], and direct water decomposition [16] in the past decades. Especially, ferroelectric materials show an attractive potential application in photocatalytic field. In the ferroelectric unit cell, the B-site displacement leads to the spontaneous polarisation and generated a polarisation electric field. In addition, the external strain can change the spontaneous polarisation direction and then the internal electric field direction in the grain. The internal electric field can file attract positive/negative charges on the surface. By applying an alternating strain (i.e. ultrasonic vibration), an alternating polarisation electric field can be generated, which induces the charging and discharging on the surface of the ferroelectric grain. Recently, the piezoelectric ZnO or BT materials under ultrasonic excitation have been used to organic contaminant degradation [7, 17] and water splitting [18].

In addition to the above function, the internal polarisation electric field can enhance the photocatalytic properties of the ferroelectric materials under irradiation because the internal electric field in the piezoelectric grain can accelerate the separation and migration of the photogenerated electrons and holes [19–21]. However, the photocatalytic properties of the ferroelectric materials under the irradiation and strain have not been investigated until now.

In this study, the photocatalytic properties and cycle stability of the ferroelectric BT materials under UV–vis illumination and ultrasonic vibration are investigated. Amount of Pt nanoparticles were deposited on the surface of BT powder using sonochemistry method. Analytically pure hexachloroplatinate acid hexahydrate (H2PtCl6·6H2O, 97%) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. The as-prepared BT particles were dispersed in the ethanol solution and then mixed with 1.5, 2.0, 2.5 mol% H2PtCl6·6H2O. Subsequently, the mixed suspension reacted under ultrasonic condition (40 kHz, 600 W) for 2 h to obtain the Pt-loading BT powders, which were labelled with 1.5%-Pt, 2.0%-Pt, 2.5%-Pt, respectively. Meanwhile, the pure BT powders were labelled with 0%-Pt.

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and energy dispersive X-ray spectra (EDX) were carried out on JEOL 2011F (JEOL, Japan) at 200 kV. X-ray diffraction (XRD) was measured by Smartlab (Rigaku, Japan) using Cu Kα radiation. Ultraviolet and visible (UV–vis) absorption spectra and diffuse reflectance
The photocatalytic activity of pure and Pt-loading BT powders was evaluated by degrading RhB dye. Prior to photocatalytic degradation, 0.1 g sample was magnetically stirred with RhB aqueous solutions (100 mL, with a concentration of 0.02 m/M/L) in the dark for 30 min to reach a stable equilibrium situation. The time-resolved photoluminescence (TRPL) spectrum is obtained on a scan UV–vis spectrophotometer (U-4100, HITACHI, Japan) with an integrating sphere assembly, using a standard three-electrode cell with a working electrode, a platinum wire counter electrode, and a standard calomel electrode as a reference electrode. 1 M NaSO₄ aqueous solution was used as the electrolyte solution. The working electrode was prepared according to the following process. Twenty milligrams of as-prepared sample was suspended in 0.5 mL ethanol, and then dip-coated on a 10 mm × 20 mm indium-tin oxide glass electrode. The electrode was then annealed at 100°C for 1 h in vacuum. The steady-state photoluminescence (PL) spectra were measured by a Hitachi F-4600 fluorescence spectrophotometer with excitation at 420 nm. The time-resolved photoluminescence (TRPL) spectrum is measured by a spectrometer (FLS980, Edinburgh Instruments) with an excitation source of a femtosecond pulse at 325 nm.

3 Results and discussion

The crystal structure of the pure and 2.0%-Pt BT powders is detected by XRD patterns in Fig. 1. XRD patterns coincide well with the standard samples (JPCDS No. 72-0138). The strong XRD intensity indicates that the good crystallinity of the BT powders prepared by hydrothermal synthesis in this work. The obvious splitting peaks of (002) and (200) demonstrate that the as-prepared BT powders are tetragonal, which verifies the ferroelectricity of the BT particles. In addition, the XRD diffraction peaks broaden obviously, demonstrating that as-synthesised BT particles are nanoscale, in agreement with TEM results below. When the Pt nanoparticles are loaded on the BT particles, no distinct change is found from the XRD patterns, indicating that the sononchemistry method has little effect on crystal structure and grain size of the BT powders. Besides, Pt diffraction peaks were not detected from the XRD pattern because of the low Pt content.

The morphology, crystal structure and chemical composition of the pure and 2.0%-Pt BT powders are characterised using TEM, HRTEM and EDX in Fig. 2. From the TEM image in Fig. 2a, it can be found that the pure BT sample has irregular morphology with the average size of 50–150 nm. A clear lattice fringe can be detected from the HRTEM image in Fig. 2b, which demonstrates the good crystallinity of the BT particles prepared by hydrothermal synthesis in this work. The interplanar spacing is ~0.280 nm, which well corresponds to the (111) crystal plane of tetragonal BaTiO₃. The good crystallinity and measured interplanar spacing coincide well with the above XRD results. In addition, all the chemical elements including Ba, Ti, and O can be detected from the EDX spectrum in Fig. 2c. Fig. 2d shows the morphology of the 2.0%-Pt samples. Compared with the smooth surface of pure BT sample, the surface of 2.0%-Pt BT particles become rough, indicating that the Pt nanoparticles are attached on the BT powders. The round-shaped Pt particles have a diameter of 5–10 nm. The lattice fringe of the Pt particles is little blurry as seen from the HRTEM image in Fig. 2e, which should be ascribed to the poor crystallinity of the nanoparticles. The lattice fringe with the interplanar spacing of about 0.220 nm matches well with the (111) crystal plane of the Pt (JCPDS No. 65-2868). A tiny number of Pt can be detected from the EDX spectrum in Fig. 2f. Moreover, it can be found that the Pt nanoparticles are tightly attached to the BT particles, suggesting the electrical connection between them.

UV–vis absorption (α) spectra of the pure and Pt-loading BT powders are carried out in Fig. 3a. The strong absorption band can be detected when the wavelength is shorter than ~415 nm for all the samples, which should attribute to the electron transition from the valence band to conduction valance. The band gap energy (E_g) could be calculated by the Tauc plot [27]. The relationship between the incident photon energy and the absorption coefficient (α) is plotted in Fig. 3b which is given in the following equation:

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

where \( h \) is the Plank constant, \( \nu \) is the photon frequency, and \( A \) is a constant. The intercept on x-axis of the plots is \( E_g \). As seen from Fig. 3b, all the samples have a similar band energy gap (~3.08 eV). Therefore, the loading Pt nanoparticles almost have no effect on the band structure of the BT-based powders. However, the absorption of the Pt-loading BT powders obviously enhance compared with the pure BT powders, which should be ascribed to the nanostructured Pt particles. The loading metal nanoparticles can form the Schottky barrier with BT particles, which enhances the electron–hole separation and thus promotes the photocatalytic activity [22, 23]. In addition, the incident irradiations are fiercely absorbed due to the plasmonic resonance between the free electrons and the electrical field of the electromagnetic irradiation, generating a large number of photo-generated charge carriers. The excited free carriers are efficiently injected into the conduction band of BT particles, thus improving the photocatalytic activity [24].
The above-mentioned results can be further supported by the photoluminescence (PL) spectra in Fig. 4a, which reveals the transfer and separation efficiency of photo-generated electron/hole pairs [28]. The PL intensity of the Pt-loading BT samples is lower than that of the pure BT samples, suggesting the attached Pt nanoparticles could promote the separation of photo-generated charge carriers.

Time-resolved transient PL (TRPL) spectra of the pure and 2.0%-Pt BT samples with femtosecond photoexcitation at 325 nm are performed in Figs. 4b and c. In this study, the TRPL decay is modelled with a biexponential distribution of the type [29]:

\[ I(t) = A_{\text{fast}} \exp \left( -\frac{t}{\tau_{\text{fast}}} \right) + A_{\text{slow}} \exp \left( -\frac{t}{\tau_{\text{slow}}} \right) \]

where \( I(t) \) and \( t \) are the TRPL intensity and time, respectively. \( A_{\text{fast}} \) and \( A_{\text{slow}} \) are the fitting fast and slow coefficients, respectively. The fast lifetime \( \tau_{\text{fast}} \) is attributed to recombination of delocalised (untrapped) carriers located in the interior of the BT grain. The slow lifetime \( \tau_{\text{slow}} \) is associated to recombination of localised (trapped) carriers, which is ascribed to the surface-related electrons/holes. The fitting parameters are summarised in Table 1. \( \tau_{\text{fast}} \) of the 2.0%-Pt sample is similar with that of the pure BT sample, demonstrating that the attached Pt nanoparticles have slight effect on the recombination of the interior electrons/holes. However, \( \tau_{\text{slow}} \) of the 2%-Pt sample is almost twice larger than that of pure BT sample. It demonstrates the recombination of localised electrons/holes trapped by the surface defects could be suppressed by the attached Pt nanoparticles, and thus improving the photocatalytic activity. The amplitude-averaged lifetime \( \tau \) is calculated as

\[ \tau = \frac{A_{\text{fast}} \tau_{\text{fast}} + A_{\text{slow}} \tau_{\text{slow}}}{A_{\text{fast}} + A_{\text{slow}}} \]

\( \tau \) of the 2.0%-Pt sample (~3.96 ns) is much longer than that of the pure BT sample (~0.8 ns), also suggesting the higher separation efficiency of photo-generated charge carriers for the Pt loading BT samples.

The photocatalytic activity of the BT-based samples is assessed through the degradation of RhB dye under UV-vis light illumination. The change of relative RhB concentration as a function of irradiation time (t) is shown in Fig. 5a. \( C_0 \) and \( C \) are the initial concentrations of RhB and that at the irradiation time, respectively. RhB degradation under UV-vis light illumination is negligible due to the almost unchanged concentration in the blank experiment. When the catalysts are added, the absorption at a wavelength of 554 nm decreases rapidly, suggesting that RhB has been destroyed. The reaction rate constant is the slope of the ln(\( C_0/C \)) versus \( t \) line as shown in Fig. 5b, which is summarised in Table 2. It can be observed that the photocatalytic activity of the Pt-loading BT sample is higher than that of the pure BT sample, which should be ascribed to the SPR effect of Pt nanoparticles, the injection of the photo-generated electrons into the conduction band of BT particles and the enhanced separation efficiency of photo-generated charge carriers [7–9]. Moreover, the decomposition of RhB increases with increasing Pt loading content, reaching a maximum for 2.0%-Pt sample, and then decreases with further increase in Pt content. The optimum loading content is 2.0 mol%.

At this loading amount, RhB removal rate is about 84.5% after 25 min under UV-vis irradiation. With the further increase of Pt amount, Pt grain size increase and even form the platinum clusters, leading the decreasing active sites for the photocatalytic reaction. Besides, superfluous Pt nanoparticles would hinder light absorption of BT particles, which lowers the efficiency of photocatalytic reaction. The photocatalytic properties are similar with metal nanostructures attached BT particles in the previous reports [30–33].

The photocatalytic degradation of the BT-based samples is also performed under ultrasonic vibrations. The variations of \( \ln(C_0/C) \) as a function of irradiation time are shown in Figs. 5c and d.
ultrasonic frequency in this study is 40 kHz, the direction of the grain size is lower than 100 nm from theoretical and experimental electric field (labelled by the purple arrow), which is defined as the accompanied by the decreasing polarisation electric field. Hence, wall energy [34]. It is well known the multi-domain structure composed of polarisation energy, depolarisation energy and domain electric field across the grain. The polarisation direction is labelled polarisation electric field can accelerate the separation and mobility the grain is very large, and the thermodynamic state is instable. The opposite direction of the polarisation electric field, generating a thus changes the polarisation electric filed. Considering that the ultrasonic vibrations, an alternating external stain is applied on the BT grain. The strain would change the polarisation direction of the BT due to the direct piezoelectric effect as shown in Fig. 6a, and thus changes the polarisation electric filed. Considering that the ultrasonic frequency in this study is 40 kHz, the direction of the external stain and polarisation electric field will change once approximately every $1.25 \times 10^{-5}$ s. In such a short time period, the depolarisation electric field could not form because the migration of the defect space charges is a dynamical process. Therefore, the effective electric field under ultrasonic vibrations is larger than that without ultrasonic driven, which could result in better photocatalytic activity. Moreover, the lifetime of photo-generated electrons/holes is ($\sim 0.8$ and $\sim 3.96$ ns for the pure and 2.0%-Pt BT samples, respectively) much smaller than the period of the external strain. Therefore, the variational internal electric field almost has no effect on the mobility of photo-generated charge carriers.

To deduce the Gibbs free energy of BT system, the defect charge carriers (e.g. free electron, free hole, oxygen vacancy, free ions, labelled by the blue circles in Fig. 6b) would accumulate in opposite direction of the polarisation electric field, generating a depolarisation electric field as shown by the blue arrow accompanied by the decreasing polarisation electric field. Hence, the Gibbs free energy of the BT grain decreases and the thermodynamic state becomes stable. However, the effective electric field (labelled by the purple arrow), which is defined as the difference between polarisation and depolarisation electric field, decreases. Therefore, the depolarisation electric field deteriorates the separation efficiency of the photogenerated charge carriers.

When the photocatalytic degradation is performed under ultrasonic vibrations, an alternating external strain is applied on the BT grain. The strain would change the polarisation direction of the BT grain due to the direct piezoelectric effect as shown in Fig. 6c, and thus changes the polarisation electric field. Considering that the ultrasonic frequency in this study is 40 kHz, the direction of the

d, respectively. The reaction rate constants are calculated by least square method and summarised in Table 2. It can be found that the reaction rate constant under ultrasonic vibrations is higher than that without ultrasonic-driven for the catalyst with the same component, which should be related with the spontaneous polarisation of ferroelectric BT. The schematic diagram in Fig. 6a sketches the effect of the internal electric field on the photo-generated charge carriers. The Gibbs free energy of the ferroelectric grain is composed of polarisation energy, depolarisation energy and domain wall energy [34]. It is well known the multi-domain structure would transform into single domain configuration when the BT grain size is lower than 100 nm from theoretical and experimental analysis [35–38]. From the TEM in Fig. 2, the BT grain size is 50–100 nm. Therefore, the single domain structure is expected in the as-prepared BT sample. Thus, the domain energy is absent in the BT grain. All the Ti ions in the BT grain display the same displacement direction, which will generate an integrated internal electric field across the grain. The polarisation direction is labelled by the red arrow in Fig. 6b. In this case, the polarisation energy in the grain is very large, and the thermodynamic state is instable. The polarisation electric field can accelerate the separation and mobility of the photo-generated electrons/holes (labelled by the red circles in Fig. 6a), improving the photocatalytic activity [39].

To deduce the Gibbs free energy of BT system, the defect charge carriers (e.g. free electron, free hole, oxygen vacancy, free ions, labelled by the blue circles in Fig. 6b) would accumulate in opposite direction of the polarisation electric field, generating a depolarisation electric field as shown by the blue arrow accompanied by the decreasing polarisation electric field. Hence, the Gibbs free energy of the BT grain decreases and the thermodynamic state becomes stable. However, the effective electric field (labelled by the purple arrow), which is defined as the difference between polarisation and depolarisation electric field, decreases. Therefore, the depolarisation electric field deteriorates the separation efficiency of the photogenerated charge carriers.
degraded photocatalytic properties should be ascribed to the accumulation of the defect space charges on the surface and the increasing depolarisation electric field in the BT grain.

Surprisingly, the photocatalytic activity could recover a lot if the ferroelectric particles were treated by ultrasonic vibrations. After five cycling tests, the 2.0%-Pt sample is treated by ultrasonic vibrations. The photocatalytic efficiency of the 2.0%-Pt sample is performed and displayed in the sixth cycling test in Fig. 7a. RhB removal rate is about 88.1% after 25 min in the sixth cycle, indicating that the photocatalytic activity rejuvenates after ultrasonic treatment. During ultrasonic treatment, the polarisation electric filed would change because of the external alternating strain, inducing the dissolution of accumulated defect space charges on the surface of BT grain and the decreasing depolarisation electric field. Hence, the effective electric field increases and improves the photocatalytic properties after ultrasonic treatment.

4 Conclusions
In this study, BT powders are synthesised by a hydrothermal reaction and the Pt nanoparticles were deposited on the surface of BT particles using sonochemistry method. The photocatalytic activity of Pt-loading BT samples is evaluated by degrading RhB. It is found that the photocatalytic properties under ultrasonic vibration are better than that without the external strain applied on the BT particles. The cycling photocatalytic property becomes more stable when the BT samples are treated by ultrasonic before photocatalytic degradation. In addition, the degraded photocatalytic activity after several cycling tests can resurface if the BT sample is treated by ultrasonic vibrations before photocatalytic reaction. Under ultrasonic vibration, a high-frequency alternating strain is applied on the BT grain, inducing the fast changing polarisation electric field. Hence, there is no enough time to form the depolarisation electric field. Hence, there is no enough time to form the depolarisation electric field. Therefore, the effective electric field increases and can effectively promote the separation the photo-generated electron-holes, thus improving the photocatalytic activity. It is suggested that ultrasonic vibration is an efficient method to improve the photocatalytic properties and cycle stability of the ferroelectric photocatalysts. Considering BT could be made into electronic devices (e.g. actuators, sensors, transducer, capacitor) due to its ferroelectric and piezoelectric properties, BT can be fabricated into the promising multifunctional device in the future.

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6 References
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