Nanoscale Surface Disorder for Enhanced Solar Absorption and Superior Visible-Light Photocatalytic Property in Ti-Rich BaTiO₃ Nanocrystals

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Supporting Information

ABSTRACT: Lattice disorder has emerged as a novel strategy to realize visible-light photocatalytic activity, but many existing studies often involved reduction states simultaneously. Photocatalysts based on only the lattice disorder but without the reduction states are still quite lacking and challenging. To this end, we explored a new type of lattice disorder in terms of the surface atom nonstoichiometry strategy in BaTiO₃. Well-dispersed tetragonal BaTiO₃ nanocrystals with a uniform size (∼20 nm) and cuboid morphology were hydrothermally synthesized through controlling over t-butylamine and oleic acid. HRTEM coupled with structural evolution analysis reveals the existence of a Ti-rich layer on BaTiO₃ nanocrystals with surface atom disorder, which gives an overall Ti/Ba ratio of 1.50:1. This is mainly dominated by the oriented adsorption between oleic acid and surface Ba²⁺ of the nucleus during solution reaction. Such a surface disorder and Ti-rich nonstoichiometry effect could facilitate the enhanced visible-light absorption with a wavelength span of 400–700 nm that enables the superior visible-light photocatalytic property, which is not subject to the reduction states. This work demonstrates a first white material presenting a new type of lattice disorder that would be helpful for a wide range of photocatalyst explorations.

1. INTRODUCTION

Solar-driven photocatalyst has attracted considerable attention because it provides a relatively simple and environment-friendly route that enables directly harvesting and converting sunlight into chemical energy.¹ To explore the high-performance photocatalysts, great endeavors have been devoted, on the one hand, to improve the capability of absorbing visible/infrared light, and on the other, to suppress the combination of photogenerated electrons and holes. For nearly all the wide-gap semiconductors with an intrinsic band gap of g > 3.0 eV, such as, TiO₂, ZnO, MTO (M = Ba/Sr/Ca), MTaO₃ (M = K/Na), etc., chemical modifications through the controllable doping of metal and/or nonmetal ions to generate donor/acceptor levels in the band gap²⁻⁶ or noble metals and heterocompound loading to facilitate charge transfer and separation⁷⁻⁹ are necessary. However, the diversity in the origin of mid-gap energy levels, for example, reduced states, interstitial states, F⁻ centers, vacancies, defect coupling, etc., makes no consensus understanding in the photocatalytic mechanisms. More seriously, these effects, due to the associated trapping centers and mid-levels, usually lead to rapid photogenerated charge carrier recombination that undermines the photocatalytic performances.

Recently, a conceptually different approach, that is, hydrogenation that introduced surface disorder in TiO₂ nanophase, was achieved by Chen et al.¹³ with exploration of black titania. This “black” only refers to the lattice disorder in a material with yielding mid-gap states whose energy distributions differ from that of a single defect in a crystal. The fascinating black concept, with showing quite promising potentials, has been widely expanded and adopted for synthesizing various black visible-light photocatalysts, for example, black Ti₃O₄, Nb₂O₅, BiVO₄, BaTiO₃ or related hybrids, etc. As a matter of fact, these newly developed black photocatalytic materials are more or less involved with the reduction states, somewhat similar to the case of Ti³⁺ self-doped TiO₂;¹⁻²,²¹ this obviously not coincided exactly with the original lattice disorder induced black but might be subject to the catalytic roles that the reduction states mainly play in. Consequently, challenging questions are still open. For instance, what is another new type of a visible-light catalyst with only the lattice disorder? Further, is it possible to explore a white material with visible-light activity only based on the lattice disorder?

In this work, a new type of surface disorder, that is, surface atom nonstoichiometry, was proposed in order to gain affirmative answers as schematically seen in Figure 1a. Assuming that the disorder/amorphous structure with...
unsaturated surface atoms enables offering the larger surface area and more active sites than that of the crystalline type, the surface band gap of the electronic state may become diffuse to narrow the gap in terms of the localized band tail for the visible-light response. This assumption has been proven very recently in binary semiconductors, for example, (Mo,W)-(S,Se)\textsuperscript{24–26} with existing structural amorphous states, which showed higher photocatalytic efficiency than their crystalline states. Herein, we selected a typical wide-gap semiconductor, BaTiO\textsubscript{3}, as a prototype oxide in order to construct the surface disorder and Ti-rich nonstoichiometry for achieving the outstanding visible-light photocatalytic property.

2. RESULTS AND DISCUSSION

Single-phase BaTiO\textsubscript{3} nanocrystals were synthesized by a tailored hydrothermal method, where NaOH and t-butylamine were used to control over the phase, size, and morphology, while oleic acid was utilized for the purpose of the surface disorder and nonstoichiometry tuning. The synthesized particles crystallize in perovskite-structured BaTiO\textsubscript{3} without any other possible impurities like BaCO\textsubscript{3} or TiO\textsubscript{2}, indicating the pure-phase nature of BaTiO\textsubscript{3} (XRD in Figure 2a). Further confirmed by TEM (Figure 1c,d), as-synthesized BaTiO\textsubscript{3} has a well-defined cuboid morphology and uniform size of around 25 nm. Careful HRTEM observations reveal that these BaTiO\textsubscript{3}
nanoparticles were well crystallized in the inner core as seen in the clear lattice fringes with a spacing of 0.41 nm, but strikingly, their surfaces were capped by an amorphous or atomic disorder thin layer. This layer has a thickness of about 2–3 nm as highlighted in Figure 1e (arrows). Therefore, the surface disorder was achieved in BaTiO3 nanocrystals, as expected.

To identify the formation mechanism of surface disorder, Fourier transform infrared (FT-IR) spectrum of BaTiO3 nanocrystals was measured (Figure 1b). The infrared absorptions at the low-wavenumber region, that is, 600–380 cm\(^{-1}\), are the Ti–O vibration characteristics in the BaTiO3 lattice.\(^{27}\) Except for the absorbed H\(_2\)O at 3418 and 1626 cm\(^{-1}\) that are assigned to O–H stretching vibration (\(\nu_1\)) and O–H deformation vibration (\(\delta_2\)), respectively, surface coordination groups were observed additionally. Peaks at 2923 and 2853 cm\(^{-1}\) correspond to the vibrational modes of methyl and methylene groups within oleic acid molecules. Two absorption bands of \(\nu_1\)(COO\(^-\)) at 1525 cm\(^{-1}\) and \(\nu_1\)(COO\(^-\)) at 1375 cm\(^{-1}\) suggest the existence of acetate groups bonded to Ba atoms as a bridging ligand.\(^{28}\) These observations indicate that the oleic acid molecules are responsible for the formation of the surface disorder in BaTiO3 nanocrystals, as schematically proposed in Figure 1a. The six-coordinated Ti precursor, acting as a sort of Ti-based octahedron monomer, can easily condense by vertex connections to capture the Ba species, for example, Ba\(^{2+}\) or [Ba(OH)]\(^+\), to form BaTiO3 directly.\(^{29}\) The carboxylic side of oleic acid molecules would bond to exposed Ba\(^{2+}\) within the crystalline surface preferentially, while the other side of the stretched carbon chains spread around the nucleus, due to the steric hindrance effect of their long hydrophobic tails, would impede the Ba species to effectively diffuse toward the nucleus’ surface. As a result of the Ba deficiency, the Ti-rich surface disorder layer forms.

Whereas the surface amorphous/disorder layer was clearly presented for BaTiO\(_3\) nanocrystals, what are the nature of this disordered surface and the crystalline core? Raman spectroscopy was first performed to determine the phase structure and space group of present BaTiO\(_3\) through discernible phonon modes. As shown in Figure 2a, these Raman peaks rightly correspond to the phonon modes of the tetragonal phase of BaTiO\(_3\) (space group \(P4mm\)), with eight Raman modes that are described by \(3A_1[(TO)+(LO)]+4E[(TO)+(LO)]+3B_1\).\(^{30}\) Two broad bands situated at 260 and 521 cm\(^{-1}\) are assigned to \(A_1(TO)\) and \(E(TO)+A_1(TO)\) modes, respectively, and \(E(TO+LO)\) and/or \(B_1\) modes at 305 cm\(^{-1}\) were observed to further confirm the tetragonal phase for present BaTiO\(_3\) nanocrystals.\(^{31}\) Another band centered at 720 cm\(^{-1}\), also characteristic in tetragonal BaTiO\(_3\), is related to the highest frequency longitudinal optical mode (LO) of the \(A_1\) symmetry of TiO\(_6\) octahedra.\(^{32}\)

With respect to the characteristics, for example, compositions and structures, of the surface amorphous layer, high-temperature annealing was utilized to crystallize the BaTiO\(_3\) nanocrystals, which enables quantitative analysis through structural evolution and chemical composition determinations. As shown in Figure 2b, the BaTiO\(_3\) sample after sintering at 500 °C does not exhibit any differences to the as-prepared one, indicating that such a disorder layer is quite stable. Sintering at 800 °C gives rise to, in addition to tetragonal BaTiO\(_3\), a new phase, that is, monoclinic BaTi\(_5\)O\(_{11}\) (space group \(P2_1/n\)). XRD structural refinement was further performed to determine this phase and ratio by a least-squares method using the GSAS program.\(^{33}\) As seen in Figure 2c, well refinement with a fit parameter of \(w_R = 10.006\%\) and a flat difference curve confirms highly satisfactory reliability, which yields a molar ratio of 86.14:13.86 for tetragonal BaTiO\(_3\) to monoclinic BaTi\(_5\)O\(_{11}\). This implies that the original molar ratio of Ti/Ba in as-prepared BaTiO\(_3\) apparently deviates from the standard stoichiometry, which instead is calculated to be 1.55(±0.04):1. Further sintering at higher temperatures, for example, 1100 °C, to allow complete crystallization produces a new phase transition, from which the resulting XRD consists of tetragonal BaTiO\(_3\) and monoclinic BaTi\(_5\)O\(_{11}\) (space group \(C2/m\)). Structural refinement gives a 1.48(±0.02):1 molar ratio of Ti/Ba, consistent with the above result. Obviously, the excessive Ti stems from the surface layer, that is, such a surface disordered layer is dominated by Ti-rich non-stoichiometry. It thus concludes that surface-disordered and Ti-rich BaTiO\(_3\) (SurTi-BaTiO\(_3\)) nanocrystals, for the first time, were achieved. To gain a comparative conclusion, a mixture of commercial BaTiO\(_3\) and TiO\(_2\) with a similar refinement ratio, that is, \(R_{BaTiO_3}/R_{TiO_2} = 1.05\), was sintered at high temperatures (Figure S1). This gives a similar phase transition behavior that an additional Ti-rich phase, that is, BaTi\(_5\)O\(_{10}\), forms with the dominated BaTiO\(_3\) phase when sintering at 1100 °C, again suggesting the Ti-rich surface for the as-synthesized BaTiO\(_3\) nanocrystals.

The present disorder and Ti excess in SurTi-BaTiO\(_9\) due to having an altered materials’ surface, may have significant influences on the optical bands and electronic structures. UV–vis diffuse spectroscopy was thus performed (Figure 3a) for...
Figure 4. Photocatalytic properties of as-prepared BaTiO3 nanocrystals under visible-light irradiation. (a) Decomposition efficiency on the RhB dye. Commercial bulk BaTiO3 was also performed for comparison, showing no visible photocatalytic activity. (b) Kinetic fits [−ln(C/C0) vs time] for RhB degradation. (c) Cycling tests on the photocatalytic activity for as-prepared BaTiO3 nanocrystals and (d) schematic mechanism of photocatalytic degradation with narrowed optical band gap induced by surface disorder.

these purposes. In order to reach a clearer comparison, commercial BaTiO3 was also involved, which is characterized similarly in the tetragonal phase (XRD and Raman in Figure S2). It is striking that the SurTi-BaTiO3 nanocrystals demonstrate the apparent absorption in the entire visible-light region with a tail prolonging to around 700 nm, sharply distinct from that of the commercial BaTiO3 we measured (Figure 3a) or the BaTiO3 nanoparticles and bulks previously reported. For these latter cases, there is no absorption intensity beyond a wavelength of approximately 400 nm because BaTiO3 is typically a direct wide-gap semiconductor with an optical band gap of approximately 3.2 eV. Regardless of inducing visible-light absorption, the surface disorder does not alter the band gap (Eg) for SurTi-BaTiO3 nanocrystals, which is calculated to be 3.26 eV (Figure 3a, inset) using the Kubelka–Munk function, quite close to that of commercial BaTiO3. However, the enhanced visible-light absorption for the visible-light photocatalysis, which implies a process of only photoproduced charges and subsequent separation other than the surface.

Table 1. Pseudo-First-Order Apparent Rate Constant (k_{app}) and R² of RhB Degradation Reaction for the Commercial BaTiO3 and SurTi-BaTiO3 Nanocrystals

| samples            | k_{app} (min⁻¹) | R²  |
|--------------------|-----------------|-----|
| commercial BaTiO3  | 2.37 × 10⁻¹      | 0.942|
| SurTi-BaTiO3       | 1.20 × 10⁻¹      | 0.995|

1.20 × 10⁻¹ min⁻¹, orders higher than that of commercial BaTiO3. The activity factor k (k = k_{app}/m) for SurTi-BaTiO3 is thus calculated to be 2.4 min⁻¹ g⁻¹, which is much larger than those previously reported for oxides, exhibiting the superior photocatalytic efficiency.

It is especially noted that no other changes in the crystal phases and charge states (Figures S4 and S5) happen after photocatalysis, which implies a process of only photoproduced charges and subsequent separation other than the surface.
chemical or redox reactions. As a consequence, the SurTi-BaTiO₃ nanocrystals demonstrate excellent photocatalytic stability. As shown in Figure 4c, the RhB degradation efficiency could be well maintained after five times of cycling test. We noted that a slight decline in degradation efficiency is due to the SurTi-BaTiO₃ nanocrystal loss during recycling. This again indicates the superior photocatalytic performance and, most importantly, the intrinsic photocatalytic nature for the present surface-disordered and Ti-rich BaTiO₃ nanocrystals.

As stoichiometric BaTiO₃ is visible-light photocatalytically inert because of its large band gap of 3.24 eV, the disordered and Ti-rich surface layer for SurTi-BaTiO₃ nanocrystals should be responsible for the superior photocatalytic property. This is steadily supported by the fact that SurTi-BaTiO₃ possesses relatively strong visible-light absorption with an energy span of 3.2–2.1 eV (Figure 3a), which apparently stems from the surface contributions, forming a BaTiO₃@SurTi-BaTiO₃ structure. This thus gives rise to a photocatalytic mechanism like “core−shell” as presented in Figure 4d. The surface disorder/amorphous structure in SurTi-BaTiO₃ behaves somewhat what like loose and porous structures to facilitate the dye adsorption process and possesses more active sites offered by a greater number of unsaturated atoms on their surfaces compared to the crystalline structure; meanwhile, the narrower band gap induced by the localized band tail and gap states of the electronic state within the surface disorder layer also plays a significant role in the visible-light response. The photo-generated charge carriers only happen in the surface layer, which then migrate to the outmost surface of SurTi-BaTiO₃ nanocrystals where the redox reaction is triggered with the surface absorption species such as OH⁻ and O₂ to generate active radicals, for example, O₂⁻ and OH⁻ within near aqueous solution. These active radicals, like those previously reported, enable breaking the molecular groups of RhB to the final decomposition effect.

3. CONCLUSIONS

In summary, well-dispersed tetragonal BaTiO₃ nanocrystals with a uniform size and cuboid morphology were synthesized through controlling over t-butylamine and oleic acid. Strikingly, the nanocrystals show, for the first time, the surface disorder that is featured in the Ti-rich nonstoichiometry. Such a surface disorder effect could improve the solar absorption with a wavelength span of 400–700 nm, which results in the superior visible-light catalytic property. This work demonstrates a first white material exhibiting the visible-light photocatalytic performance. Therefore, the proposed new mechanism, that is, the surface lattice disorder that is not involved in the reduction states, would be quite promising in photocatalyst explorations for many wide-gap materials.

4. EXPERIMENTAL SECTION

4.1. Sample Preparations. Surface-disordered and Ti-rich BaTiO₃ nanocrystals were synthesized by a hydrothermal method. Typically, 0.7887 g of Ba(OH)₂·8H₂O was dissolved in 50 mL of deionized water, which was followed by adding 1.21 mL of bis(ammonium lactate) titanate dihydroxide (TALH) (50 wt % aqueous solution) under magnetic stirring to form a white suspension. A certain amount of 5 M NaOH aqueous solution to tune the pH to around 13.0 and t-butylamine with its ratio to Ba²⁺ of 8:1 were added into the above suspension to control over the phase, size, and morphology, while oleic acid was utilized for the purpose of the surface disorder and nonstoichiometry tailoring. The as-prepared solution was transferred to a Teflon-lined autoclave (100 mL) for the hydrothermal reactions that were carried out at 220 °C for 24 h. After the reaction, white precipitates formed, which were subsequently filtered, washed thoroughly with diluted HCl solution, deionized water, and ethanol, and further dried at 60 °C to obtain the final SurTi-BaTiO₃ nanocrystals.

For comparison purposes, the commercial BaTiO₃ (99.99%) used in this work was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The XRD pattern and room-temperature Raman spectrum are shown in Figure S2. Commercial TiO₂ (anatase, 99.99%) from Shanghai Aladdin Biochemical Technology Co., Ltd. was used to conduct the sintering experiments.

4.2. Characterizations. The phase purity and crystallinity of the as-prepared samples were examined by X-ray diffraction (XRD) (Rigaku SmartLab SE, Cu Kα radiation, λ = 0.15406 nm). Raman spectra were collected on a confocal Raman microscope (Renishaw iVia) with an excitation line of 514.5 nm at room temperature. The particle size and morphology of the samples were characterized by transmission electron microscopy (TEM) (JEOL, JEM-2100). The infrared spectra of the samples were measured on a Fourier transform IR spectrophotometer (Thermo Fisher Nicolet iS10). The optical diffuse reflectance spectra were recorded on a UV−vis spectrometer (Perkin Elmer Lambda 650S). The XPS spectrum was carried out using an X-ray photoelectron spectroscopy (Thermo Fisher Scientific K-Alpha⁹, mono Al Kα radiation).

4.3. Photocatalytic Studies. The photocatalytic activity of the as-synthesized SurTi-BaTiO₃ nanocrystals was evaluated through decomposing the Rhodamine B (RhB) dye. The blank and commercially stoichiometric BaTiO₃ samples were used for comparison purposes. Specifically, 50 mg of the (as-synthesized and stoichiometric) samples were put into a quartz reactor with 50 mL of 10 ppm (10 mg/L) RhB solution. This reactor was first kept in a dark environment for 10 h under magnetic stirring to reach a dark adsorption−desorption equilibrium. Then, a visible-light source (λ > 450 nm) with a 500 W xenon long-arc lamp was exposed to the central cold trap of the reactor to irradiate the samples. During irradiation, 4 mL of solution was taken out from the reactor at an interval time of 3 min, which was centrifuged to obtain a clear solution with the residual RhB dye for absorption spectroscopic measurement. The absorption characteristic of the centrifuged solution was measured on a UV−vis spectrometer (Perkin Elmer Lambda 650S), which was used to monitor the degradation process and evaluate the photocatalytic performances.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00739.

XRD patterns of the mixture of BaTiO₃ and TiO₂ after high-temperature sintering, room-temperature Raman spectrum and XRD pattern of commercial BaTiO₃ UV−vis spectrum of the residual RhB dye during the
decomposition process, and XRD and XPS data of SurTi-BaTiO3 after photocatalysis (PDF)

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**Author Contributions**
W.H. conceived the idea. W.H., G.L., and J.X. analyzed the data. G.L., J.W., L.X., and Y.L. conducted the experiments under the supervision from W.H. and J.X. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

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