SrTiO$_3$/Bi$_4$Ti$_3$O$_{12}$ Nanoheterostructural Platelets Synthesized by Topotactic Epitaxy as Effective Noble-Metal-Free Photocatalysts for pH-Neutral Hydrogen Evolution

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ABSTRACT: Low-temperature hydrothermal epitaxial growth and topochemical conversion (TC) reactions offer unexploited possibilities for the morphological engineering of heterostructural and non-equilibrium shape (photo)catalyst particles. The hydrothermal epitaxial growth of SrTiO$_3$ on Bi$_4$Ti$_3$O$_{12}$ platelets is studied as a new route for the formation of novel nanoheterostructural SrTiO$_3$/Bi$_4$Ti$_3$O$_{12}$ platelets at an intermediate stage or (100)-oriented mesocrystalline SrTiO$_3$ nanoplatelets at the completed stage of the TC reaction. The Bi$_4$Ti$_3$O$_{12}$ platelets act as a source of Ti(OH)$_6^{2−}$ species and, at the same time, as a substrate for the epitaxial growth of SrTiO$_3$. The dissolution of the Bi$_4$Ti$_3$O$_{12}$ platelets proceeds faster from the lateral direction, whereas the epitaxial growth of SrTiO$_3$ occurs on both bismuth-oxide-terminated basal surface planes of the Bi$_4$Ti$_3$O$_{12}$ platelets. In the progress of the TC reaction, the Bi$_4$Ti$_3$O$_{12}$ platelet is replaced from the lateral ends toward the interior by SrTiO$_3$, while Bi$_4$Ti$_3$O$_{12}$ is preserved in the core of the heterostructural platelet. Without any support from noble-metal doping or cocatalysts, the SrTiO$_3$/Bi$_4$Ti$_3$O$_{12}$ platelets show stable and 15 times higher photocatalytic H$_2$ production (1265 μmol·g$^{−1}$·h$^{−1}$; solar-to-hydrogen (STH) efficiency = 0.19%) than commercial SrTiO$_3$ nanopowders (81 μmol·g$^{−1}$·h$^{−1}$; STH = 0.012%) in pH-neutral water/methanol solutions. A plausible Z scheme is proposed to describe the charge-transfer mechanism during the photocatalysis.

KEYWORDS: hydrothermal epitaxial growth, topochemical conversion, perovskites, SrTiO$_3$, Aurivillius-phase layer structures, Bi$_4$Ti$_3$O$_{12}$, hydrogen evolution

1. INTRODUCTION

Utilizing sunlight to drive chemical reactions over semiconductor photocatalysts represents a promising strategy to overcome the world’s problems related to energy shortages and environmental pollution. The production of storable, green H$_2$ fuel from water-splitting reactions addresses these challenges.$^{1−6}$ At the moment, the process still suffers from too-low efficiencies to become economically viable. However, recent findings about the importance of heterojunctions,$^{1}$ mesocrystallinity,$^{6}$ type of exposed facets,$^{2}$ and preferential orientation$^{7}$ for improved photocatalytic performance increasingly promote an interest in the morphological engineering of functional nanostructures. In particular, the integration of two different functional materials with different band gaps and band-edge positions has attracted a great deal of scientific and technological attention.$^{3,5}$ Such heterojunction systems lead to an improvement of the photocatalytic efficiency by enhancing the photogenerated charge carriers’ separation.$^{5}$ However, designing heterostructural photocatalysts in terms of achieving the target characteristics and boosted photocatalytic performance remains challenging. The same is true for the creation of single-phase photocatalyst particles with morphologies that are different from the thermodynamic equilibrium crystal shape. The engineering of the functional characteristics of the particles based on an understanding of the nucleation and growth can ensure that rational morphological design prevails over serendipity.

Topochemical conversion (TC) reactions from Aurivillius perovskite platelets (Bi$_4$Ti$_3$O$_{12}$ and MBi$_4$Ti$_4$O$_{15}$ (M = Sr, Ba)) in molten salts (NaCl/KCl) were intensively studied for the preparation of MTiO$_3$ perovskite nanoparticles with non-equilibrium, platelet-shape crystallites.$^{9−12}$ However, slow ionic diffusion in the solid-state lattice at much lower hydrothermal synthesis...
temperatures (100–200 °C) provides a better insight and understanding of the reactions at the interface compared to that in molten salt TC.5,13 Hydrothermal TC reactions initiated by the epitaxial growth of a new phase on the precursor (template) particles enable the formation of heterostructures at an intermediate state of the transformation or after complete conversion with the formation of new-phase particles with a preserved morphology and having a crystallographic relationship with the parent phase.13 In the field of hydrothermal TC reactions, Kalyani et al. performed an in-depth study of the epitaxial growth of SrTiO3 on anatase (TiO2) nanowires and their complete TC to SrTiO3 mesocrystalline nanowires.14 Exploring the TC reaction mechanisms for various template precursors will help us to engineer more complex heterostructures in the future.

In this study, we present an example of employing the TC reaction concept in the rational design of new heterostructural and mesocrystalline nanoparticles under hydrothermal conditions. We have studied the hydrothermal epitaxial growth of SrTiO3 on Bi4Ti3O12 template platelets with the intermediate formation of new nanostructured SrTiO3/Bi4Ti3O12 platelets and after the complete transformation formation of (100)-oriented SrTiO3 mesocrystalline nanoplatelets.

One of the reasons for the selection of the SrTiO3/Bi4Ti3O12 heterostructure was the interesting photocatalytic properties of the individual materials.2,5,7,16 SrTiO3 meets the thermodynamic criteria for an overall photocatalytic water-splitting reaction in terms of the appropriate band-edge positions and bandgap.5,7,17 Several efficient H2-evolution photocatalysts based on SrTiO3 were developed using various design strategies, aiming to improve the light-harvesting capabilities and the charge-carrier separation.2,7,18–24 For example, Zhang et al. prepared (100)-oriented SrTiO3 mesocrystalline superstructural platelets by hydrothermal topotactic epoxicy from a TiO2 mesocrystalline precursor template that consisted of assembled anatase nanocrystals with a dominant exposure of [001] facets. The authors proved that these (100)-oriented SrTiO3 platelets exhibited 3 times higher photocatalytic efficiency for H2 evolution compared to conventional disordered SrTiO3 systems. The abovementioned study revives the interest in further photocatalytic investigations of SrTiO3 nanostructures with controlled morphologies and orientations. Similar to SrTiO3, Bi4Ti3O12 was also explored as a photocatalyst for H2 generation. However, according to several reports, pure Bi4Ti3O12 does not exhibit an outstanding H2 evolution activity,16,25 although modifications such as reduction (Bi4Ti3O12→Bi3Ti2O6)1,6 and substitution with Cr (Bi4Ti3O12→Cr2Ti2O6)1,6,27,28 were confirmed to enhance considerably visible-light photocatalytic H2 evolution from water/methanol solutions (2–4 times). For both types of modified Bi4Ti3O12, the improvement was ascribed to the narrowing of the band gap and the decreased recombination of the photogenerated charges.1,6,25

The other motivation for choosing the SrTiO3/Bi4Ti3O12 system is related to the presence of similar perovskite units in both phases,16 which promises the successful epitaxial growth of SrTiO3 on Bi4Ti3O12. The first attempt to prepare Bi4Ti3O12/SrTiO3 composite microplatelets was made by Zhao et al.,17 who also used a combination of molten-salt-synthesized Bi4Ti3O12 platelets and alkaline hydrothermal conditions for the growth of SrTiO3. However, their Bi4Ti3O12 platelets were larger (side length: 10–15 μm, 1–2 μm in this study). The major difference was in the hydrothermal step where the titanium precursor (tetrabutyl titanate) was added for the formation of SrTiO3 where the titanium was not proposed to originate from the dissolution of Bi4Ti3O12, as in our study. Accordingly, the reported morphology of the 10–15 μm Bi4Ti3O12 platelets with sub-micrometer attachments25 was completely different from the SrTiO3/Bi4Ti3O12 heterostructural platelets described in this study. Therefore, we believe that the presented SrTiO3/Bi4Ti3O12 composite nanostructures are unique and their functional properties are worth investigating. Our study is focused on a detailed microstructural examination of the platelets at different stages of TC in order to understand the SrTiO3/Bi4Ti3O12 interface and gain a detailed insight into the mechanism of hydrothermal epitaxial growth and the TC reaction. The epitaxial growth of SrTiO3 on a layered structure of Bi4Ti3O12 is expected to be more complex and illustrative than the epitaxial growth on mono metal oxides. Moreover, the anisotropic shape of the primary Bi4Ti3O12 platelets with different dissolution rates of the basal and lateral surfaces is an interesting characteristic of this system that also influences the morphological evolution. The described TC mechanism provides general guidelines for the morphological engineering of nanoheterostructures through hydrothermal epitaxial growth. This study emphasizes the key parameters that must be considered for the selection of a heterostructural system, which include the structural matching at the interface, the thermodynamic stability and solubility of the involved materials, and the supersaturation. A light-induced, good, and stable H2 production rate from a pH-neutral solution established these novel, noble-metal-free SrTiO3/Bi4Ti3O12 nanoheterostructural platelets as promising candidates in the field of photocatalytic H2 evolution.

2. EXPERIMENTAL SECTION

2.1. Synthesis Conditions. 2.1.1. Chemicals and Materials. All the chemicals were of analytical grade and were used as received without further purification. In the syntheses, the following reagents were involved: KCl (Sigma-Aldrich, ≥99.0%), NaCl (Merck, ≥99.7%), TiO2 (P25, Degussa), Bi2O3 nanopowder (Sigma Aldrich, 99.8%), HNO3 (VWR, 68%), SrCl2·6H2O (Sigma-Aldrich, ≥99.0%), NaOH (Fisher Chemicals, ≥98.7%). Water used for the study was purified with a system to produce ultrapure water (Purelab Option-Q2, ELGA). Commercially available SrTiO3 nanopowder was used as a reference photocatalyst (Sigma-Aldrich, 20–40 nm).

2.1.2. Synthesis of Bi4Ti3O12 Template Platelets. Bi4Ti3O12 platelets were synthesized in molten KCl/NaCl salt using Bi2O3 (1.9453 g) and TiO2 (0.5 g) nanopowders as the starting materials. To synthesize the Bi4Ti3O12 platelets, the molar ratio of NaCl:KCl:Bi2O3:TiO2 was optimized as 50:50:2:3. The synthesis was performed at 800 °C with a holding time of 2 h with heating and cooling rates of 10 °C/min. Details of the procedure and selected parameters are described elsewhere.25 After the synthesis, the Bi4Ti3O12 platelets were separated from the salt by washing with ultrapure water. To ensure the complete removal of any surface contamination,25 the platelets were soaked in 2-M HNO3 for a short time (5 min) and washed again with ultrapure water. The product particles were freeze-dried to obtain a powder with well-separated platelets.

2.1.3. Hydrothermal TC of Bi4Ti3O12 to SrTiO3. The TC reaction of the Bi4Ti3O12 template particles to SrTiO3 platelets was carried out via the hydrothermal route. Bi4Ti3O12 particles were used as templates for the non-equilibrium plate-like growth of SrTiO3 and as well as a source of Ti, whereas SrCl2·6H2O was the source of strontium. A large excess of SrCl2·6H2O was used to ensure supersaturation conditions and promote the nucleation of SrTiO3 on both basal surface planes of the Bi4Ti3O12 platelets. First, SrCl2·6H2O was
dissolved in ultrapure water, and then Bi$_4$Ti$_3$O$_{12}$ platelets were added to the solution in an amount corresponding to the Sr:Ti molar ratio of 12:1. Suspensions were sonicated for 25 min followed by the addition of NaOH solutions. In the precurs suspension before the hydrothermal reaction, the concentrations of the SrCl$_2$, 6H$_2$O, Bi$_4$Ti$_3$O$_{12}$, and NaOH platelets were 0.0388, 0.00107, and 6 M, respectively. The hydrothermal syntheses were performed by stirring at 200 °C in a Berghof high-pressure reactor using a Teflon (PTFE) insert. The reaction time was varied from 1 to 15 h. After the hydrothermal synthesis, the product particles were separated from the reaction solution by centrifugation and washed several times with ultrapure water. The solid product was soaked in 1 M HNO$_3$ for 5 min to remove the side products, and afterward, the particles were again repeatedly washed with ultrapure water to completely remove any traces of acid. At the end, the particles were freeze-dried to obtain the final product.

### 2.2. Characterization of the Samples.

**X-ray powder diffraction** was employed using a Bruker AXS D4 Endeavor with Cu Kα radiation (1.5406 Å) for the powder samples and for the platelets cast on the Si monocrystalline substrate. The weight ratio of SrTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$ platelets in various weight ratios. These XRD measurements were performed for preferentially oriented platelets cast on the Si monocrystalline substrate.

A field-emission scanning electron microscope (FE-SEM, JSM 7600 F, JEOL, Japan) was used to observe the morphology of the particles. A nanoscale analysis of the platelets was performed using a 200 kV scanning transmission electron microscope (STEM, Jeol ARM 200 CF, JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDXS, Jeol Centurio 100). Samples of platelet-like particles for the STEM analyses were prepared using two approaches. For observations along the shorter zone axis of the platelets, the powdered sample was sonicated in absolute ethanol and a droplet of the suspension was applied to the lacy, carbon-coated copper grid. This resulted in a spontaneous alignment along the preferential orientation with the largest surface parallel to the carbon film substrate. The thickness of the platelets of up to 100 nm allowed STEM analyses without any further thinning. For edge-on observations of the platelet-like particles with a side length between 1 and 2 microns, the particles had to be thinned to electron transparency. This was accomplished by embedding the powders in epoxy resin and further mechanical and ion milling (Gatan PIPS Model 691, USA).

The Brunauer—Emmett—Teller (BET) surface areas of the powders were measured by nitrogen adsorption with a Micromeritics Gemini II 2370 nitrogen-adsorption apparatus (Norcross, GA). Band-gap energies of the synthesized platelets were determined from their diffuse reflection spectra with BaSO$_4$ as a reference.

**2.2.1. Photocatalytic H$_2$ Evolution.**

The photocatalytic H$_2$ evolution measurements were carried out in a 50 mL quartz round-bottom flask at ambient temperature and atmospheric pressure using mixing to achieve the particle suspension. A commercial solar simulator equipped with a Xenon arc lamp (300 W, Newport) and an AM 1.5G filter was used as the light source. In a typical photocatalytic measurement, 20 mg of photocatalyst was suspended in 40 mL of aqueous solution containing 25 vol % methanol and the suspension was sonicated for 30 min to obtain a well-dispersed particle suspension. Before light irradiation, the quartz flask was sealed with a rubber septum and purged with a nitrogen flow for 40 min to remove the excess oxygen in the reaction mixture. Finally, the sealed quartz flask was placed under light irradiation. All the photocatalysts were subjected to 4 h of light irradiation, and the H$_2$ evolution was measured periodically every hour. The generated gas composition (1 mL) was analyzed with a gas chromatograph (GC, SRI-8610C) equipped with a thermal conductivity detector (TCD), and high-purity nitrogen was used as the carrier gas.

### 3. RESULTS AND DISCUSSION

The transformation of Bi$_4$Ti$_3$O$_{12}$ into SrTiO$_3$ under hydrothermal conditions is governed by the chemistry at the interface and the concentrations of the dissolved titanium and strontium species (supersaturation). In this particular TC reaction, the Bi$_4$Ti$_3$O$_{12}$ platelets act as a source of titanium and as the substrate for the epitaxial growth of SrTiO$_3$. To control and direct the growth of SrTiO$_3$ on the surface of the Bi$_4$Ti$_3$O$_{12}$ platelets, the characteristics of the latter must be studied first.
3.1. Structural Studies of Bi₄Ti₃O₁₂ Template Platelets. In the first step of our investigations, we characterized the Bi₄Ti₃O₁₂ platelets down to the atomic scale. Knowledge about the morphology, the termination of the Bi₄Ti₃O₁₂ crystallites, and the nature of the surface after applying different treatment procedures following the synthesis in molten salt (and after washing with water or acid) is important for selecting the optimum strategy for the treatment of the synthesized Bi₄Ti₃O₁₂ powders and gives fundamental knowledge for steering and understanding the heterogeneous nucleation of SrTiO₃ on Bi₄Ti₃O₁₂ templates. Orthorhombic Bi₄Ti₃O₁₂ platelets grown in NaCl/KCl molten salt at 800 °C for 2 h are shown in Figure 1a. The crystallites have a typical tabular or platelet-like morphology with a side length of up to a few microns and a thickness of well below a micron. The platelet-like morphology represents the equilibrium shape of Bi₄Ti₃O₁₂ reflecting its layered crystal structure. High-angle annular dark field (HAADF)–STEM analysis of the Bi₄Ti₃O₁₂ platelets after the removal of the residual salt by soaking in water and additionally in 2 M HNO₃ for a short time is shown in Figure 1b–e. A low-magnification image of edge-on-oriented Bi₄Ti₃O₁₂ platelets (Figure 1b) shows that most of the crystallites have a thickness below 100 nm (1 unit cell = 3.2882 nm; PDF: 01-084-6889). The morphology of the Bi₄Ti₃O₁₂ platelets indicates a significantly faster growth in the direction of the layers and a slower thickening perpendicular to the layers, typical for minerals with a layered structure.

Atomic-resolution STEM was used to investigate the termination of the platelets. Figure 1c shows HAADF-STEM images of Bi₄Ti₃O₁₂ platelets oriented along the [100] Bi₄Ti₃O₁₂ and [110] Bi₄Ti₃O₁₂ zone axes. The experimental images are overlaid with an atomic model of Bi₄Ti₃O₁₂ (PDF: 01-084-6889) showing the layered structure composed of [Bi₂O₂]²⁺ sheets and pseudo-perovskite [Bi₂TiO₆]²⁻ blocks. Both images were recorded near the surface of the platelets and reveal that the crystallites are terminated by [Bi₂O₂]²⁺ sheets. Several crystallites were examined and the analyses confirmed that all the Bi₄Ti₃O₁₂ platelets have this termination on both basal-plane surfaces. Observations of the crystallites at lower magnifications also showed that the basal-plane surface of the Bi₄Ti₃O₁₂ platelets is atomically flat on a large scale (Figure 1d), perhaps even across the whole crystallite since the presence of steps and terraces on the basal surface were never observed in the TEM. In contrast to the basal-plane surfaces, the lateral surfaces of the crystallites contain growth steps where the TiO₆ octahedra are exposed (Figure 1e). HAADF-STEM images recorded at the edge of the crystallite also imply weaker bonding of the adatoms on the exposed surface of the lateral side of the platelet (see the inset in Figure 1e). These basic differences between the basal and lateral surfaces reflect the layer-by-layer growth mode and probably influence the Bi₄Ti₃O₁₂ dissolution rates in different crystallographic orientations. It is expected that the dissolution of the Bi₄Ti₃O₁₂ platelets will proceed faster from the lateral stepped surface. The [Bi₂O₂]²⁺-terminated Bi₄Ti₃O₁₂ platelets with atomically flat basal-plane surfaces are an ideal substrate for the epitaxial growth of the perovskite SrTiO₃ phase due to the good match of the two phases in the 001 Bi₄Ti₃O₁₂|| 001 SrTiO₃ and 110 Bi₄Ti₃O₁₂||110 SrTiO₃ orientational relationship. The lattice spacings of {110}Bi₄Ti₃O₁₂ and {100}SrTiO₃ are 0.3842 and 0.3905 nm, meaning that the structural match of both phases is good, a prerequisite for successful epitaxial growth.

3.2. Background for the Selection of the TC Synthesis Conditions. The TC reaction of the Bi₄Ti₃O₁₂ platelets to SrTiO₃ particles with a preserved, plate-like morphology under hydrothermal conditions is expected to proceed by the dissolution of Bi₄Ti₃O₁₂ and the concurrent precipitation of SrTiO₃ on the surface of the Bi₄Ti₃O₁₂ platelets with the only source of titanium ions being the dissolving Bi₄Ti₃O₁₂ crystals, whereas the concentration of Sr²⁺ ions is controlled based on the amount of strontium salt (SrCl₂·6H₂O).

The lack of relevant thermodynamic data for Bi₄Ti₃O₁₂ limits the theoretical predictions for its dissolution and for the formation of equilibrium compounds (SrTiO₃, Bi₂O₃, and Bi₂TiO₅) as a function of the physicochemical conditions (pH, synthesis temperature (T), and concentrations of ions). Hence, the first approximate experimental conditions for the formation of SrTiO₃ from Bi₄Ti₃O₁₂ were established based on the reported thermodynamic modeling for the crystallization of SrTiO₃ from TiO₂ under hydrothermal conditions and previous empirical studies of SrTiO₃ growth on different titane precursors. Lencka and Riman calculated a phase-stability diagram for the Sr–Ti hydrothermal system of anatase and hydrous TiO₂ gel. Later, Kalyani et al. extended the diagram to rutile. Their results show that the formation of SrTiO₃ from titane precursors requires a basic pH, where the Ti(OH)₆⁻ ions are the predominant aqueous titanium species. Considering that Sr(OH)₂ exhibits a high solubility in aqueous media at higher temperatures of 100 °C ≤ T ≤ 300 °C, the formation of SrTiO₃ under hydrothermal conditions is presented using the following equation:

\[
\text{Ti(OH)}_6^{2-}(aq) + \text{Sr}^{2+}(aq) \rightarrow \text{SrTiO}_3(s) + 3\text{H}_2\text{O}
\]  

(1)

In our system, under alkaline conditions, the Sr²⁺ ions from the dissolved SrCl₂ precipitate first as Sr(OH)₂, which then dissolves at higher temperatures (100 °C ≤ T ≤ 200 °C). The Ti(OH)₆⁻ species form presumably by the dissolution of Bi₄Ti₃O₁₂ in alkaline media according to eq 2.

\[
\text{Bi}_4\text{Ti}_3\text{O}_12 + 12\text{H}_2\text{O} + 6\text{OH}^- \Rightarrow 4\text{Bi(OH)}_3^+ + 3\text{Ti(OH)}_6^{2-}
\]  

(2)

It is expected that the precipitation of the SrTiO₃ on Bi₄Ti₃O₁₂ platelets (heterogeneous nucleation) also proceeds following eq 1. According to the theory of heterogeneous nucleation, the energy for the formation of a critical nucleus is proportional to the third power of the interfacial free energy and inversely proportional to the square of the supersaturation. In other words, the energy barrier for the nucleation of SrTiO₃ on Bi₄Ti₃O₁₂ is lowered by the close structural match between the Bi₄Ti₃O₁₂ substrate and the precipitating SrTiO₃ phase and by the higher concentrations of Ti(OH)₆⁻ and Sr²⁺ ions (supersaturation). Taking into account the orientation relationship of [001]Bi₄Ti₃O₁₂||[001]-SrTiO₃ and [110]Bi₄Ti₃O₁₂||[110]SrTiO₃, the theoretical lattice match between Bi₄Ti₃O₁₂ and SrTiO₃ is good. The supersaturation (eq 3) in our system is defined as the ratio between the product of the activities of aqueous species immediately before the SrTiO₃ formation and the solubility product \( K_s \), which is the reciprocal of the equilibrium constant of eq 1:

\[
S = \frac{a(\text{Ti(OH)}_6^{2-})a(\text{Sr}^{2+})}{K_s}
\]  

(3)
In our reaction system, the concentration of Ti(OH)\(_6^{2-}\) is a complex function of Bi\(_4\)Ti\(_3\)O\(_12\) dissolution and SrTiO\(_3\) precipitation. Therefore, possibilities for the direct control of the supersaturation in terms of Ti(OH)\(_6^{2-}\) are limited. In contrast, tailoring of the supersaturation with respect to the Sr\(^{2+}\) ions is easily feasible with the initial amount of strontium salt. To ensure the supersaturation conditions for SrTiO\(_3\) formation, the selected strontium concentration with respect to the whole titanium content was higher than that required by the SrTiO\(_3\) stoichiometry. The optimal concentration of Bi\(_4\)Ti\(_3\)O\(_12\) was determined during our preliminary experiments to be 0.00107 M.\(^{30}\) This relatively low concentration was also selected to avoid the eventual precipitation of bismuth titanium compounds (e.g., Bi\(_{12}\)TiO\(_{20}\)) that would compete with SrTiO\(_3\) for the Ti(OH)\(_6^{2-}\) species.

Before studying the Bi\(_4\)Ti\(_3\)O\(_12\)-to-SrTiO\(_3\) transformation, the stability of the initial Bi\(_4\)Ti\(_3\)O\(_12\) template platelets at 200 °C and in highly alkaline conditions (6 M NaOH) without the presence of Sr\(^{2+}\) ions was verified. The solubility and dissolution rates of the Bi\(_4\)Ti\(_3\)O\(_12\) platelets in the alkaline media should be moderate to prevent their complete dissolution and the disintegration of the substrate for epitaxial growth, as was observed in some other systems.\(^{35,36}\) A qualitative evaluation of the stability of the Bi\(_4\)Ti\(_3\)O\(_12\) platelets under applied alkaline hydrothermal conditions (6 M NaOH, 200 °C/15 h) in the absence of SrCl\(_2\) revealed no significant change in the platelet’s average side length, while the general platelet-like morphology was well preserved in spite of the harsh conditions. The major difference was observed on the lateral surfaces where the beginning of the exfoliation was observed. This is a result of the limited incongruent dissolution of [Bi\(_4\)O\(_2\)]\(^{2+}\) sheets and the pseudo-perovskite [Bi\(_4\)Ti\(_3\)O\(_10\)]\(^{12-}\) blocks from the lateral direction (Figure S1, Supporting Information). Considering the low concentration of Bi\(_4\)Ti\(_3\)O\(_12\) platelets (0.00107 M), their solubility in 6 M NaOH is relatively low. Nevertheless, under similar hydrothermal conditions in the presence of dissolved Sr\(^{2+}\) ions, it is assumed that SrTiO\(_3\) formation according to eq 1 is the driving force for Bi\(_4\)Ti\(_3\)O\(_12\) dissolution. The transformation of the initial Bi\(_4\)Ti\(_3\)O\(_12\) template particles to SrTiO\(_3\) platelets was studied for a system with a strontium content that is 12 times higher than required by the SrTiO\(_3\) stoichiometry. The strontium concentration (0.0388 M) was 4 times larger than in our previous study.\(^{30}\) With a higher supersaturation, we aim to decrease the energy barrier for the nucleation of SrTiO\(_3\) and promote its growth over the whole basal-plane surfaces of Bi\(_4\)Ti\(_3\)O\(_12\) platelets and consequently ensure that the SrTiO\(_3\)/Bi\(_4\)Ti\(_3\)O\(_12\) heterostructural and final SrTiO\(_3\) particles maintain the platelet-like shape of the initial template.\(^{33,34}\)

### 3.3. Mechanistic Interpretation of the Bi\(_4\)Ti\(_3\)O\(_12\)-to-SrTiO\(_3\) TC Process

The progress of the hydrothermal TC reaction was first inspected by XRD. Figure 2 and Figure S2 (Supporting Information) show the XRD patterns of the acid-washed platelets (free of side products) after different reaction times. The XRD patterns of the initial Bi\(_4\)Ti\(_3\)O\(_12\) platelets with a high (001) preferential orientation are also shown in Figure 2 and Figure S2 for comparison. The formation of the SrTiO\(_3\) was already observed after 1 h of the hydrothermal reaction (6 M NaOH, Sr/Ti = 12). The amount of SrTiO\(_3\) compared to Bi\(_4\)Ti\(_3\)O\(_12\) increased with a prolongation of the reaction time. Only SrTiO\(_3\) with a (100) preferential orientation and no Bi\(_4\)Ti\(_3\)O\(_12\) were detected after 15 h (Figure 2 and Figure S2).

In the figures, SrTiO\(_3\) and Bi\(_4\)Ti\(_3\)O\(_12\) are labeled as STO and BIT, respectively.

The side-products can carry valuable information about the TC mechanism. An insight into all the reactions accompanying the TC of Bi\(_4\)Ti\(_3\)O\(_12\) to SrTiO\(_3\) was obtained with an XRD analysis of the whole reaction product (Figure S3, Supporting Information). The results revealed the formation of SrTiO\(_3\), SrCO\(_3\), and Bi\(_2\)O\(_3\). SrCO\(_3\) formed through a reaction of Sr(OH)\(_2\) with carbonate impurities in the NaOH chemical and with atmospheric CO\(_2\). The formation of SrCO\(_3\) also continued after the completed reaction and the opening of the autoclave when the alkaline suspension with excessive and unreacted Sr(OH)\(_2\) is exposed to the atmosphere for a longer time. The formation of bismuth oxide, on the other hand, is a result of condensation of bismuth hydroxide Bi(OH)\(_3\), which forms during the Bi\(_4\)Ti\(_3\)O\(_12\) dissolution. No bismuth titanium compounds (e.g., Bi\(_{12}\)TiO\(_{20}\)) were detected. This proves that the dissolved titanium is consumed for the crystallization of SrTiO\(_3\) and not for the formation of bismuth titanium compounds (e.g., Bi\(_{12}\)TiO\(_{20}\)). Single-phase SrTiO\(_3\) was obtained after the dissolution of the side-products in 1 M HNO\(_3\) (Figure 2 and Figure S2, Supporting Information). A deeper insight into the process of the transformation from the initial Bi\(_4\)Ti\(_3\)O\(_12\) platelets to SrTiO\(_3\) was obtained by a microstructural investigation of the samples after the different times for the TC reaction. The partially and fully transformed platelets were examined by SEM and STEM from top and cross-sectional views. An SEM image of the powder sample after 1 h of reaction is shown in Figure 3a. The initial morphology of the Bi\(_4\)Ti\(_3\)O\(_12\) platelets is clearly preserved; however, the particles appear to have a core-rim structure. The XRD pattern of the platelets (cast from the isopropanol suspension of the platelets on the Si monocrystalline substrate) revealed the presence of Bi\(_4\)Ti\(_3\)O\(_12\) and SrTiO\(_3\) phases with preferential (001) and (100) orientations, respectively (Figure 2).

The sample after 1 h of transformation was investigated in more detail using the HAADF-STEM. A typical particle is shown in Figure 3b, and here, the core-rim structure is even more evident. In the dark-field (DF) image, the core of the particles is much brighter, indicating a higher atomic density in the core region, whereas the rim is more electron-transparent.
due to the lower average atomic density or lesser thickness. More information about the chemical composition and the distribution of the elements in the particles were obtained from EDS mapping (Figure 3c) and EDS line profiles (Figure S4, Supporting Information). The results show that the core of the platelet is Bi-rich, whereas Sr is present everywhere with a higher amount in the rim. Signals from Ti and O were also detected in both parts of the platelets. The distribution of Sr all over the platelet indicates that the growth of SrTiO$_3$ occurs on the whole area of both basal surfaces, including both surface areas over the central part (core). According to the results of the STEM/EDS analyses, the core of the partially transformed Bi$_4$Ti$_3$O$_{12}$ platelets is mainly Bi$_4$Ti$_3$O$_{12}$, covered by SrTiO$_3$ on both sides, whereas the rim is newly formed SrTiO$_3$, which replaced Bi$_4$Ti$_3$O$_{12}$ in the dissolution–precipitation process.

The platelet after 1 h of topochemical transformation can be regarded as a heterostructure of Bi$_4$Ti$_3$O$_{12}$ and SrTiO$_3$. Figure 3d (bright-field (BF) image) is a close-up of another partially transformed platelet in the middle region with the focus set on the surface layer. It shows the nucleation of nanosized crystallites, which occasionally show a rectangular morphology, as expected for the cubic SrTiO$_3$ structure. The presence of regions with distinctly different gray levels suggests that the crystallization of SrTiO$_3$ on the Bi$_4$Ti$_3$O$_{12}$ surface occurs in several layers and that the first layer is nanocrystalline, while...
the platelet (Figure 4e) reveals that, here, the atomic layers of dots with bright contrast (Figure 3e). During the epitaxial hydrothermal reaction) Bi$_4$Ti$_3$O$_{12}$ disintegrates to Ti(OH)$_6$ and the core (SrTiO$_3$/Bi$_4$Ti$_3$O$_{12}$/SrTiO$_3$) where (during the reactions, results in Bi$_2$O$_3$, as already con-

SrTiO$_3$ nanocrystallites. Bismuth oxide-rich inclusions remain captured between the platelets (Figure 4a). A HAADF-STEM examination of the A closer look at the Bi$_4$Ti$_3$O$_{12}$ layer in this part of the platelet (Figure 4e) reveals that, here, the atomic layers of the Bi$_4$Ti$_3$O$_{12}$ structure, the [Bi$_2$O$_2$]$_{2-}$ sheets and the perovskite [Bi$_2$Ti$_3$O$_{10}$]$_{2-}$ blocks, are subjected to intensive dissolution. The same process was already observed in the top-view (Figure 3e). Bi$_4$Ti$_3$O$_{12}$ disintegration is much faster from the lateral directions than from the top, as predicted on the basis of the difference of the basal and lateral surfaces with respect to the concentration of kink sites. Figure 4f,g were recorded in the region between the central part and the edge of the partially recrystallized Bi$_4$Ti$_3$O$_{12}$ particle. Here, the epitaxial orientation relationship between SrTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$ in [100]SrTiO$_3$|[001]Bi$_4$Ti$_3$O$_{12}$ is clearly visible and confirms that the orientation of SrTiO$_3$ is dictated by the structure of the underlying Bi$_4$Ti$_3$O$_{12}$ template. The fact that SrTiO$_3$ growth on the Bi$_4$Ti$_3$O$_{12}$ is epitaxial confirms that the reaction is TC. In this part of the crystal, the SrTiO$_3$ layer was thinned to electron transparency (the Bi$_4$Ti$_3$O$_{12}$ part was completely etched away in some areas) and one of the most interesting features of the SrTiO$_3$ platelets that form during the TC transformation from Bi$_4$Ti$_3$O$_{12}$ under hydrothermal conditions is revealed, i.e., the presence of an atomic bismuth-rich layer (Bi-rich layer), inside the SrTiO$_3$ platelet (Figure 4g). Similarly, the STEM image of the platelet close to the edge (Figure 4h) in the section of complete transformation to SrTiO$_3$ (rim region in Figure 3) revealed the formation of two parallel SrTiO$_3$ platelets that both contain an atomic Bi-rich layer running along the middle part of both platelets. We believe that these Bi-rich layers correspond to the [Bi$_2$O$_2$]$_{2-}$-terminated top layers of the initial Bi$_4$Ti$_3$O$_{12}$ platelet.

An additional insight into the transformation process is obtained from the analysis of partially transformed heterostructure platelets in the edge-on orientation (Figure 4). An SEM image of the platelets in this orientation after 1 h of the TC reaction (200 °C, Sr/Ti = 12, 6 M NaOH) shows that a typical platelet contains a groove running along its edges, apparently splitting the platelet into two thinner parallel platelets (Figure 4a). A HAADF-STEM examination of the partially transformed platelets in an edge-on orientation reveals that the initial Bi$_4$Ti$_3$O$_{12}$ platelets actually start to separate into two parallel platelets aligned with the upper and lower basal-plane surfaces of the Bi$_4$Ti$_3$O$_{12}$ platelet. The process starts at the edges and proceeds toward the interior of the platelet (Figure 4b,c; DF–BF pair of STEM figures). One of the particles thinned to electron transparency almost along the whole area (cross-section) was investigated in more detail in three different regions—in the central part and toward the edge of the partially transformed platelet (Figure 4d–h).

Figure 4d,e was taken in the central part where the particle has a sandwich structure composed of residual Bi$_4$Ti$_3$O$_{12}$ in the middle, which is surrounded by SrTiO$_3$ above and below the Bi$_4$Ti$_3$O$_{12}$. A closer look at the Bi$_4$Ti$_3$O$_{12}$ layer in this part of the platelet (Figure 4e) reveals that, here, the atomic layers of the Bi$_4$Ti$_3$O$_{12}$ structure, the [Bi$_2$O$_2$]$_{2-}$ sheets and the perovskite [Bi$_2$Ti$_3$O$_{10}$]$_{2-}$ blocks, are subjected to intensive dissolution. The same process was already observed in the top-view (Figure 3e). Bi$_4$Ti$_3$O$_{12}$ disintegration is much faster from the lateral directions than from the top, as predicted on the basis of the difference of the basal and lateral surfaces with respect to the concentration of kink sites. Figure 4f,g were recorded in the region between the central part and the edge of the partially recrystallized Bi$_4$Ti$_3$O$_{12}$ particle. Here, the epitaxial orientation relationship between SrTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$ in [100]SrTiO$_3$|[001]Bi$_4$Ti$_3$O$_{12}$ is clearly visible and confirms that the orientation of SrTiO$_3$ is dictated by the structure of the underlying Bi$_4$Ti$_3$O$_{12}$ template. The fact that SrTiO$_3$ growth on the Bi$_4$Ti$_3$O$_{12}$ is epitaxial confirms that the reaction is TC. In this part of the crystal, the SrTiO$_3$ layer was thinned to electron transparency (the Bi$_4$Ti$_3$O$_{12}$ part was completely etched away in some areas) and one of the most interesting features of the SrTiO$_3$ platelets that form during the TC transformation from Bi$_4$Ti$_3$O$_{12}$ under hydrothermal conditions is revealed, i.e., the presence of an atomic bismuth-rich layer (Bi-rich layer), inside the SrTiO$_3$ platelet (Figure 4g). Similarly, the STEM image of the platelet close to the edge (Figure 4h) in the section of complete transformation to SrTiO$_3$ (rim region in Figure 3) revealed the formation of two parallel SrTiO$_3$ platelets that both contain an atomic Bi-rich layer running along the middle part of both platelets. We believe that these Bi-rich layers correspond to the [Bi$_2$O$_2$]$_{2-}$-terminated top layers of the initial Bi$_4$Ti$_3$O$_{12}$ platelet.

The incorporation of the Bi-rich layer is also a consequence of the strong bonding between the termination layer of Bi$_4$Ti$_3$O$_{12}$ and growing SrTiO$_3$. Layer-by-layer growth (Frank–van der Merwe mechanism), evident from our observations (Figure 3d), is also the result of strong bonding at the interface. The Bi-rich layer remains bonded to SrTiO$_3$ even after progressive dissolution of the remaining Bi$_4$Ti$_3$O$_{12}$ template. When the dissolution front of Bi$_4$Ti$_3$O$_{12}$ (inside the groove) reaches the Bi-rich layer, it remains attached to the epitaxial SrTiO$_3$ layer and the growth of the SrTiO$_3$ also proceeds from the inner side, and the Bi-rich layer becomes a coherent part of the newly formed SrTiO$_3$ where it is usually observed to be approximately in the middle of each SrTiO$_3$ platelet (Figure 4h). It is obvious that the formation of two
parallel platelets with an incorporated Bi-rich layer is the consequence of SrTiO3 epitaxial growth on the both bismuth-oxide-terminated basal-plane surfaces of the Bi4Ti3O12 platelets and continued SrTiO3 growth on the inner side of the Bi-rich layers (Figure 4h).

It is clear from Figure 4h that the distance between the two Bi-rich layers, which actually represent a part of the [Bi2O2]2+ terminating sheets on both sides of the starting Bi4Ti3O12 platelet, is approximately 60 nm and corresponds to a typical thickness for starting Bi4Ti3O12 template platelets (Figure 1). The attachment of SrTiO3 nanocubes on both sides of the SrTiO3 layers is also occasionally observed (Figure 4h). The conversion of Bi4Ti3O12 to SrTiO3, as reconstructed from investigations of edge-on-oriented, partially recrystallized platelets, is schematically shown in Figure 4i. The dissolution of the initial Bi4Ti3O12 platelets starts from the lateral surfaces (Figure 4i, step 1) with a high concentration of atomic steps and where both types of structural units ([Bi2O2]2+ sheets and the pseudo-perovskite [Bi2Ti3O10]2− blocks) are exposed. The edging atoms are weakly bonded (Figure 1e). When the solution becomes locally saturated with Sr2+ and Ti(OH)62−, nucleation of SrTiO3 occurs in the areas with the lowest energy barrier. As noted earlier, the interfacial free energy for SrTiO3 nucleation on the basal-plane surfaces of Bi4Ti3O12 is low due to the close structural match at the interface and therefore, SrTiO3 nucleation can immediately occur when saturation conditions are achieved. The areas close to the edges are subjected to higher concentrations of Ti(OH)62− from the beginning of the reaction, and therefore, SrTiO3 nucleation starts there (Figure 4i, step 2). Then, with the progressive dissolution of the Bi4Ti3O12, the growth of SrTiO3 continues on both basal surfaces of the Bi4Ti3O12 platelet. However, when the Bi4Ti3O12 inside the groove completely dissolves to both the initially terminating Bi-rich layers, attached to the newly formed SrTiO3, the epitaxial growth of SrTiO3 also proceeds on the inner side of these Bi-rich layers and they become coherently integrated into the SrTiO3 platelets on both sides. In the end, the Bi-rich layers lie approximately in the middle of each SrTiO3 platelet half (Figure 4i, step 3; see also Figure 4h). The reactions of Bi4Ti3O12 dissolution and SrTiO3 precipitation (epitaxial growth) continue until there is complete dissolution of the Bi4Ti3O12 matrix crystal. The SrTiO3 platelets after 15 h of the reaction at 200 °C in 6 M NaOH and with a Sr:Ti ratio of 12 are shown in Figure 5. The general plate-like shape of the initial Bi4Ti3O12 template particles is well preserved (Figure 5a); however, the integrity/crystallinity of the SrTiO3 platelets reflects the specifics of the recrystallization mechanism. The final platelets usually consist of two intergrown SrTiO3 platelets, as shown by the STEM analysis of the sample after 15 h of hydrothermal treatment (Figure 5b). The presence of Bi4Ti3O12 between the SrTiO3 platelets is not observed, indicating that all the Bi4Ti3O12 molecules dissolved and Ti(OH)62− was used for the formation of SrTiO3. In the edge-on-oriented platelets, the two parallel Bi-rich atomic layers, which are a peculiarity of the studied hydrothermal TC reaction, were observed along the whole length of both SrTiO3 platelet halves (Figure 5c).

From our calculation, a 60 nm-thin Bi4Ti3O12 platelet would result in the formation of an approximately 42 nm-thin SrTiO3 platelet (Figure S5, Supporting Information) or two parallel 21 nm-thin platelets; however, in the process of Bi4Ti3O12 dissolution, the smallest Bi4Ti3O12 crystallites most probably dissolve and then these Ti(OH)62− species are consumed for SrTiO3 growth on the larger Bi4Ti3O12 platelets. Therefore, the typical thickness of the final SrTiO3 platelets is slightly larger and comparable to that of the initial Bi4Ti3O12 platelets.

The crystallinity of the fully transformed SrTiO3 platelets was analyzed in the top view (Figure 5d–f). A low-magnification STEM image of a thinner SrTiO3 platelet is shown in Figure 5d. The crystal is relatively dense at the edges where the transformation starts, and the porosity of the platelet increases toward the central region of the platelet. A higher-magnification STEM image taken in the central part of the platelet with the FFT calculated from the whole area is shown in Figure 5e. It is clear that the matrix consists of epitaxially oriented nanocrystallites that formed (100)-oriented SrTiO3 mesocrystalline platelets with some pores and nanosized inclusions with brighter contrast. The analysis showed that these are amorphous Bi-rich inclusions, which were trapped and overgrown by SrTiO3 during the processes of Bi4Ti3O12 dissolution and SrTiO3 crystallization. The density of the amorphous Bi-rich inclusions appears to be higher in the central part of the SrTiO3 platelets.
The observed morphological development resulted in an interesting variation of the BET specific surface area through the progress of the TC reaction. Actually, the measured BET values of the SrTiO<sub>3</sub>/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> heterostructures increased in the first 6 h of the TC reaction, reaching a maximum at ~20 m<sup>2</sup> g<sup>-1</sup>, and then the BET values decreased and approached that of SrTiO<sub>3</sub> (~10 m<sup>2</sup> g<sup>-1</sup>), which was still higher than the BET value of the initial Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (2~3 m<sup>2</sup> g<sup>-1</sup>) (Table S1, Supporting Information). The high specific surface area of the SrTiO<sub>3</sub>/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> heterostructures is most probably related to the emerging groove and the high surface roughness of the growing SrTiO<sub>3</sub> layers. Smoothening of the surface of the SrTiO<sub>3</sub> platelets with the completion of the TC reaction is the reason for the lower specific surface area of the final SrTiO<sub>3</sub> platelets compared to that of the heterostructures.

3.4. Photocatalytic Performance. To demonstrate the potential of the developed Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>-SrTiO<sub>3</sub> heterostructures and mesocrystalline SrTiO<sub>3</sub> platelets, the as-prepared materials were tested and assessed in terms of the photocatalytic activity for H<sub>2</sub> evolution in pH-neutral aqueous media (H<sub>2</sub>O/CH<sub>3</sub>OH = 75/25). The results were compared to those involving commercial SrTiO<sub>3</sub> nanopowders that were evaluated under the same conditions (Figure 6a). The Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> platelets with the smallest specific surface area, approximately 2~3 m<sup>2</sup> g<sup>-1</sup> (Supporting Information, Table S1), were found to exhibit the lowest H<sub>2</sub> evolution rate among the studied materials, only 7.5 μmol·g<sup>-1</sup>·h<sup>-1</sup>. Mesocrystalline (100)-oriented SrTiO<sub>3</sub> platelets (65 μmol·g<sup>-1</sup>·h<sup>-1</sup>) and commercial nanocrystalline SrTiO<sub>3</sub> powders (81 μmol·g<sup>-1</sup>·h<sup>-1</sup>) show comparable photocatalytic activities, although the specific surface area of the platelets (10 m<sup>2</sup> g<sup>-1</sup>) was lower than that of the commercial nanopowder (24 m<sup>2</sup> g<sup>-1</sup>). An extraordinarily higher H<sub>2</sub> evolution rate (1265 μmol·g<sup>-1</sup>·h<sup>-1</sup>) was observed for the heterostructural SrTiO<sub>3</sub>/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> platelets (Figure 6a and Table S1, Supporting Information). In this study, the enhanced photocatalytic performance for H<sub>2</sub> evolution is only presented for the heterostructural SrTiO<sub>3</sub>/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> platelets with a SrTiO<sub>3</sub>/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> weight ratio of 60/40 and BET = 20 m<sup>2</sup> g<sup>-1</sup> (Figure S6, Supporting information). We confirmed several times that the heterostructural platelets exhibiting a BET surface area of >15 m<sup>2</sup> g<sup>-1</sup> typically show a considerably higher H<sub>2</sub> evolution rate than the pure SrTiO<sub>3</sub> platelets and the commercial SrTiO<sub>3</sub> nanopowders. The results support the important role of the heterojunction for an improvement of the photocatalytic efficiency. A systematic study of the mutual electronic structure transfer (Figure 6b). It is already determined that E<sub>F</sub>/SrTiO<sub>3</sub> lies in a more negative position than E<sub>F</sub>/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub>. During Fermi-level rearrangement, due to the higher Fermi energy of SrTiO<sub>3</sub>, the electrons tend to move from SrTiO<sub>3</sub> to Bi<sub>4Ti<sub>3</sub>O<sub>12</sub>. This phenomenon causes the SrTiO<sub>3</sub> and Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> sites to be positively and negatively charged, respectively. As a result, a weak internal electric field is generated at the solid–solid interface. Therefore, the photo-generated electrons prefer to migrate from a CB of Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> to a VB of SrTiO<sub>3</sub> via this low-resistance pathway. This prevents the electron/hole recombination, and this study supports the possible execution of a Z-scheme transfer (Figure 6b). For this experiment, the coupling of SrTiO<sub>3</sub> and Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> greatly facilitates the photocatalytic performance and separation of electron/hole pairs under light irradiation and, as a result, the H<sub>2</sub> evolution rate is enhanced significantly. Here, the holes at VB/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> were consumed by the hole-scavenger methanol. PL spectroscopy with an excitation wavelength of 320 nm was used to evaluate the separation efficiencies of the photo-excited charge carriers in the studied photocatalyst platelets (Figure 7). The Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> platelets show strong PL emission peaks at approximately 415 and 450 nm, which is in line with the reported PL spectra of Bi<sub>4Ti<sub>3</sub>O<sub>12</sub>. As compared to pure Bi<sub>4Ti<sub>3</sub>O<sub>12</sub>, the SrTiO<sub>3</sub>/Bi<sub>4Ti<sub>3</sub>O<sub>12</sub> heterostructures show a significantly lower PL emission peak at 415 nm.
intensity. This result suggests the inhibition of charge recombination in the SrTiO3/Bi4Ti3O12 heterostructure, resulting in an improvement of its photocatalytic activity. In contrast to Bi4Ti3O12, the SrTiO3 platelets do not show a significant visible PL, which is typical for non-defective SrTiO3.

In terms of band-gap energy, the SrTiO3/Bi4Ti3O12 heterostructural platelets are, similar to SrTiO3, UV-active photocatalysts. Due to the small portion of UV light in the incident light spectra, the SrTiO3-based photocatalysts do not show a high solar-to-hydrogen (STH) efficiency. It has been reported that a modification of the SrTiO3 by doping and/or cocatalyst deposition led to a variation of the STH from 0.037 to 0.65% (Table S3, Supporting Information). The highest STH efficiency (0.65%) was reported by Domen and co-workers for Al-doped SrTiO3 loaded with Rh/Cr2O3 and CoOOH cocatalysts. An STH greater than 1% was demonstrated for La- and Rh-codoped SrTiO3 (H2 evolution) combined with Mo-doped BiVO4 (O2 evolution) and Au in the Z-scheme-based photocatalysts. In the current study, SrTiO3/Bi4Ti3O12 heterostructural platelets without any noble-metal doping or cocatalyst loading exhibit an STH efficiency of 0.19%, which is moderate but comparable to several other reported STH values for noble-metal decorated SrTiO3 photocatalysts (Table S3, Supporting Information). Considering that the SrTiO3/Bi4Ti3O12 heterostructure was evaluated for the first time in terms of photocatalytic H2 evolution, we believe that there is still room for improvement in its STH efficiency.

4. CONCLUSIONS

The epitaxial growth of SrTiO3 on Bi4Ti3O12 template platelets was studied under alkaline hydrothermal conditions at 200 °C to illustrate the TC reaction for the formation of novel SrTiO3/Bi4Ti3O12 heterostructural platelets and (100)-oriented SrTiO3 mesocrystalline platelets. In the presented TC reaction, the Bi4Ti3O12 platelets act as a source of dissolved Ti(OH)4 species and also serve as a substrate for epitaxial growth of SrTiO3. The heterogeneously layered structure of the Bi4Ti3O12 platelets with different dissolution rates of the basal and lateral surfaces results in an interesting morphological development and additionally offers a unique track and insight into the hydrothermal TC mechanism. Dissolution of the initial Bi4Ti3O12 platelet from the lateral ends into the interior and the simultaneous epoxal growth of SrTiO3 on both bismuth-oxide-terminated basal-surface planes of the template platelet result in the formation of two parallel SrTiO3 platelets separated by a groove that deepens with the progress of the TC reaction, whereas Bi4Ti3O12 constitutes the core of the SrTiO3/Bi4Ti3O12 heterostructural platelet. When the TC reaction is completed, the newly formed platelet-like particle consists of two parallel SrTiO3 platelets, both of which have an incorporated monoatomic Bi-rich layer, the remains of the top layers of the parent Bi4Ti3O12 platelet.

The intermediate heterostructural SrTiO3/Bi4Ti3O12 and the final SrTiO3 platelets develop approximately 5–10 times higher specific surfaces (10–20 m2·g−1) than the initial Bi4Ti3O12 platelets, mainly due to the newly formed groove and the high surface roughness of the growing SrTiO3. The photocatalytic activity for the H2 evolution and the STH efficiency of the as-prepared SrTiO3/Bi4Ti3O12 platelets free of noble-metal cocatalysts are reproducible, stable, and 18 times (1265 μmol·g−1·h−1; STH = 0.19%) higher than that of the (100)-oriented SrTiO3 mesocrystalline platelets (65 μmol·g−1·h−1; STH = 0.01%) and 15 times more than that of the commercial SrTiO3 nanopowders (81 μmol·g−1·h−1; STH = 0.012%). The enhanced photocatalytic activity of the SrTiO3/Bi4Ti3O12 heterostructural platelets is explained by the efficient transfer of the photogenerated carriers from Bi4Ti3O12 to SrTiO3 and separation of electron/hole pairs at the interface. The reduced recombination of photoinduced charge carriers in the SrTiO3/Bi4Ti3O12 heterostructural platelets was confirmed by the decreased intensity of the photoluminescence.

The detailed insight into the mechanism of epitaxial growth for SrTiO3 on Bi4Ti3O12 expands the possibilities for using the hydrothermal TC reaction concept in the design of highly preferentially oriented heterostructures or mesocrystallites, involving other template particles and growing phases for the preparation of new efficient photocatalyst systems.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c16253.

Electron microscopy analyses, XRD patterns, photocatalytic data, and the calculation of the band structures (PDF)

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Notes

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