Garden-like perovskite superstructures with enhanced photocatalytic activity†

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By subjecting amorphous flower-like TiO2 to a facile hydrothermal synthesis in the presence of Sr2+, garden-like perovskite SrTiO3 superstructures were achieved. The amorphous TiO2 was preformed using ZnO flowers as templates. Different three-dimensional SrTiO3 architectures were coexisted in the garden, including SrTiO3 flowers composed of several hollow sword-shaped petals, many sheet-shaped petals or numerous flake-shaped petals, and SrTiO3 grass consisting of a number of long blades. These SrTiO3 superstructures were simultaneously grown on fluorine-doped tin oxide (FTO) substrates. On the basis of a comprehensive study on the effects of growth time, temperature, initial concentrations of precursor, and pH, the formation of these various hierarchical architectures was attributed primarily to the dissolution of amorphous TiO2 and precipitation of perovskite crystals, followed by the Ostwald ripening process of perovskite nanocrystals and self-organization of perovskite building blocks. Interestingly, this approach can be readily extended to create other perovskite structures, including dendritic BaTiO3 and nest-like CaTiO3, as well as PbTiO3 transformed from plate-like pyrochlore Pb2Ti2O6 after post-thermal treatment. Garden-like SrTiO3 superstructures showed a superior photocatalytic performance when compared to other as-prepared semiconductors and perovskite materials (i.e., ZnO, TiO2, BaTiO3, CaTiO3 and PbTiO3), probably due to their intrinsic photocatalytic activity and special garden-like features with a coexistence of various structures that significantly facilitated the adsorption and diffusion of methyl blue (MB) molecules and oxygen species in the photochemical reaction of MB degradation.

Moreover, SrTiO3 is also a cubic-perovskite-type semiconductor with a band gap of approximately 3.2 eV. It has been widely recognized as an effective photocatalyst for water splitting and degradation of organic pollutants owing to its excellent thermal and photo-stabilities, photocatalytic activity, and good structural stability as the framework for metal ion doping.8−11 It is noteworthy that the properties of functional materials not only depend strongly on the chemical composition, but also are sensitive to the crystal structure, size and morphology. Therefore, in recent years great efforts have been concentrated on the controllable preparation of materials with versatile structures and tailored properties.5,6,14−18 The self-organization of nanoscale functional building blocks, including nanosheets,19−21 nanorods,5,22,23 nanoparticles,12,17,24 to form complex hierarchical structures offers great potential for use in energy conversion and storage applications. It is noteworthy that there has been little work on the fabrication of hierarchically structured SrTiO3. For example, dendrite-like SrTiO3 structures were obtained by a hydrothermal process,22 and mesoporous SrTiO3 spheres composed of nanoparticles24 and hollow SrTiO3 microspheres constructed by the assembly of nanocubes23 were produced through modified hydrothermal methods. Clearly, developing a feasible approach to yield diverse hierarchical

1. Introduction

Perovskite-type oxides MTiO3 (M = Ca, Ba, Sr, Pb, etc.) have been extensively studied because of their unique properties for a wide range of applications in catalytic, superconductor, thermoelectric, ferroelectric, piezoelectric, and dielectric devices.1−4 In particular, perovskite nanostructures have recently received considerable attention due to their enhanced performance as compared to the bulk counterparts.5−6 Among various MTiO3, such as a typical ternary perovskite-type oxide with large dielectric nonlinearity, temperature-dependent dielectric ability, and low microwave losses, SrTiO3 is a functional material for microwave devices operating at low temperature.7

† Electronic supplementary information (ESI) available: FESEM images and the XRD pattern of SrTiO3 films (effects of growth temperature, initial precursor concentration, and pH value), EDS analysis of ZnO, TiO2 and SrTiO3, the XRD pattern and PL spectra of PbTiO3, UV-vis spectra of different films, and UV photo-degradation of MB. See DOI: 10.1039/c3nr05564g
structures of SrTiO₃ with effective catalytic responses remains challenging.

In this work, a large variety of SrTiO₃ hierarchical architectures (i.e., garden-like superstructures) were successfully created by a facile hydrothermal treatment of amorphous flower-like TiO₂ preformed using the ZnO flowers as templates. The introduction of ZnO templates was motivated by exploiting an amorphous yet 3D structured TiO₂ prototype as the titanium source for the SrTiO₃ formation. The time-dependent evolution of ammonia. A hexamethylenetetramine (HMTA, Sigma-Aldrich, purity ≥99.0%) was prepared, having a pH of 11.00 adjusted by adding ammonia. A fluorine-doped tin oxide (FTO) substrate (F:SnO₂, 150 μm; Pilkington Glass, USA) ultrasonically cleaned for 30 min in a mixed solution of acetone and ethanol with a volume ratio of 1:1, followed by rinsing with deionized water for 15 min was placed in a sealed glass bottle containing the Zn(NO₃)₂ aqueous solution prepared above with 0.0125 M hexamethylenetetramine (HMTA, Sigma-Aldrich, purity ≥99.0%) for 4 h. These well-defined ZnO structures were synthesized hydrothermally in 0.05 M (CH₃COO)₂Ba (Sigma-Aldrich, purity ≥99.0%) solution (pH = 13.50) at 200 °C, and CaTiO₃ films were prepared hydrothermally in 0.05 M (CH₃COO)₂Ca (Sigma-Aldrich, purity ≥99.0%) solution (pH = 13.00) at 180 °C, while Pb₂TiO₃ films were synthesized hydrothermally in 0.05 M (CH₃COO)₂Pb (Sigma-Aldrich, purity ≥99.0%) solution (pH = 7.00) at 200 °C, followed by annealing at 600 °C to transform them into PbTiO₃.

2.2 Photocatalytic degradation of MB molecules

The photocatalytic activity of samples was evaluated by the degradation of methyl blue (MB) dye. The photocatalytic experiments were conducted in a quartz glass reactor. The reactor was equipped with a water jacket to control the reaction temperature. A 200 W high-pressure mercury lamp (GCQ200, Shanghai Jiguang Special Lighting Electrical Appliance Factory) emitting at a wavelength of 365 nm was employed as the UV light source. All experiments were performed under continuous stirring, using 30 mL of 10 mg L⁻¹ MB aqueous solution, and air was bubbled through a gas disperser into the reactor. The change of MB concentration with the degradation time was analyzed using a UV-vis spectrophotometer (Unico UV-2102 PC) at a wavelength of 664 nm.²¹

2.3 Characterization

The morphology and lattice structures of samples were examined by field emission scanning electron microscopy (FESEM; FEI Quanta 250, operating at 10 kV in high vacuum) and transmission electron microscopy (TEM; JEOL 2100, operating at 200 kV). A SEM equipped with an energy dispersive X-ray spectrometer (EDS, FEI Quanta 250, operating at 10 kV in high vacuum) was used to analyze the composition of the nanostructures. The phase identification of the materials was conducted by X-ray diffraction (XRD; SCINTAG XDS-2000, Cu Kα radiation; operating at a scan rate of 0.04° s⁻¹ and a step size of 0.02° in 2θ). The light absorption of the films was measured by UV-visible spectroscopy (Varian; UV-vis-NIR spectrophotometer, Cary 5000). The Raman spectrum was recorded on a Renishaw Raman microspectrometer system 2000 equipped with a He–Ne laser (632.8 nm). The laser power was 5.6 mW on a sample with a light spot of diameter about 1 mm. Room-temperature photoluminescence (PL) was recorded using a fluorescence spectrophotometer (Hitachi High-Tech, F-7000) equipped with a xenon lamp as an excitation source (excitation at 325 nm).

3. Results and discussion

Fig. 1 shows the SEM images and XRD patterns of as-prepared products. As indicated in Fig. 1a, flower-like ZnO structures were formed via a chemical bath procedure in the basic solution (pH = 11.00) containing 0.025 M Zn(NO₃)₂ and 0.0125 M HMTA at 85 °C for 4 h. These well-defined ZnO flowers comprising several tapering sword-like petals with a length of approximately 2 μm and an average diameter of about 400 nm (inset in
Fig. 1a) were used as templates and converted into TiO$_2$ flowers (Fig. 1b) after a 2 h-immersion in the aqueous solution containing 0.1 M (NH$_4$)$_2$TiF$_6$ and 0.1 M H$_3$BO$_3$ at 25 °C. The TiO$_2$ flower almost retained the structure of ZnO templates (inset in Fig. 1b). The TiO$_2$ petals appeared to be translucent hollow rods as reported in the literature and had a rough surface (inset in Fig. 1b), which is distinctly different from the smooth surface of solid rod-shaped ZnO petals (inset in Fig. 1a). Subsequently, a hydrothermal treatment was performed to transform TiO$_2$ into hierarchical SrTiO$_3$ (Fig. 1c) in a basic (pH = 13.00) 0.1 M (CH$_3$COO)$_2$Sr solution at 180 °C for 24 h. Interestingly, different SrTiO$_3$ architectures emerged on the FTO substrate (Fig. 1c and 2a), resembling a garden growing several plants, including the original flower-shaped structures composed of several nanorods (i.e., sword-shaped petals; Fig. 2b) and new flowers made of many nanosheets (i.e., sheet-shaped petals; Fig. 2c). Fig. 1d displays XRD patterns of the above-mentioned three products, in which the typical peaks were well-indexed to the standard hexagonal (wurtzite) structure (JCPDS no. 36-1451) for the ZnO film with a minor Zn(OH)$_2$ phase. The amorphous structure was, however, present in the TiO$_2$ film. The final product can be assigned to cubic SrTiO$_3$ (JCPDS no. 73-0661), which has an excellent crystalline nature, suggesting the successful transformation of TiO$_2$ into SrTiO$_3$. We note that there is a small
quantity of SrCO₃ impurity in the product. Moreover, the EDS analysis further showed that only Zn and O elements in the ZnO template had an atomic ratio of Zn : O = 1 : 1 (Fig. S1a and S1d†); for TiO₂, in addition to Ti and O elements, a little of residual Zn from the ZnO template and a little of F adsorbing from the (NH₄)₂TiF₆ solution used for converting ZnO into TiO₂ were identified (Fig. S1b and S1d†); while in the case of SrTiO₃, the atomic ratio of Sr : Ti : O was approximately 1 : 1 : 3, corresponding well to the molecular formula of strontium titanate (Fig. S1c and S1d†).

The detailed features of the SrTiO₃ garden are shown in Fig. 2 (SEM images) and Fig. 3 (TEM images). A full view of the garden is shown in Fig. 2a, indicating the coexistence of various structures in the garden. Fig. 2b presents the original flower structure, the atomic ratio of Sr : Ti : O was approximately 1 : 1 : 3, corresponding well to the molecular formula of strontium titanate (Fig. S1c and S1d†). The long blade-like building blocks emanating radially from a core with a length in the range of 4–8 μm and a width of 300 nm was synchronously grown (Fig. 2e). Noticeably, two different structures can emerge at the same time during the growth, for example, some long blade-like structures (marked with a red square in Fig. 2e) can intercalate into the bouquets-like structure (red circle in Fig. 2f), while some larger sheet-shaped petals (red square in Fig. 2d) implanted into the bouquet-like structure that was made of numerous smaller flake-shaped petals (red circle in Fig. 2d). Fig. 3a–d display the TEM images of the fragments of four representative building blocks, that is, a hollow nanorod (Fig. 3a, corresponding to Fig. 2b), several nanosheets (Fig. 3b, corresponding to Fig. 2c), a part of bouquet (Fig. 3c, corresponding to Fig. 2d) and a nanoblade (Fig. 3d, corresponding to Fig. 2e), respectively. The corresponding high resolution TEM (HRTEM) images of the four building blocks are shown in Fig. 3a’–d’. All of them had the same fringe spacing of approximately 0.275 nm. This corresponds to the (110) lattice spacing of the cubic phase of SrTiO₃, in accordance with the XRD measurement (Fig. 1d).

To further scrutinize the growth process of hierarchical architectures, the time-dependent evolution study and control experiments were performed and the resulting samples were examined by SEM and XRD. The typical SEM images of the samples obtained at different hydrothermal reaction times are shown in Fig. 4a–e. As evidenced in Fig. 4a, the sample obtained after 3 h only contained flower-like structures converted from TiO₂ without any other visible superstructures; however, the XRD measurement (Fig. 4f) revealed that these flowers were cubic SrTiO₃, suggesting the rapid transformation of amorphous TiO₂ into crystal SrTiO₃. As the hydrothermal reaction time increased to 6 h, some scattered bud-like protuberances (red circle in Fig. 4b) for bouquets were created and situated on the flower surface (Fig. 4b). Quite interestingly, the sheet-like building blocks (red circle in Fig. 4c) for the new flower-like structure (Fig. 2c) emerged as the reaction progressed (Fig. 4c). The prolonged reaction for 24 h yielded dense and ripened superstructures comprising diverse morphologies (Fig. 2a and 4d) due to the crystal growth. However, when the growth time

![Fig. 3 TEM images of (a) a SrTiO₃ hollow nanorod; (b) several SrTiO₃ nanosheets; (c) part of the SrTiO₃ bouquet; (d) SrTiO₃ blade fragment. (a’–d’) HRTEM images, corresponding to TEM images in (a–d).](image-url)
was extended up to 40 h, several flowers were aggregated together, forming a bulky wreath-like morphology. In addition, Fig. S3† shows the photoluminescence (PL) emission of SrTiO3 samples, which can be characterized by a typical multi-phonon process, namely, a system where the relaxation occurs via several routes, involving the participation of numerous states within the bandgap of the material due to intrinsic defects of the material.26 The intensity of PL decreased with an increase in hydrothermal time, suggesting the gradually reduced recombination between electrons and holes trapped in the intermediate states to the band gap of SrTiO3 samples.26 Remarkably, the corresponding XRD (Fig. 4f) and PL (Fig. S3†) results implied that the appearance of this luxuriant garden may probably be ascribed to the transformation of unstable structures (i.e., original flowers in Fig. 2b) into stable structures with reduced defects (i.e., sheet-shaped flowers in Fig. 2c). These flower-like structures undergo the dissolution-recrystallization process, namely, the well-known Ostwald ripening process,27,28 as will be discussed in more detail later.

In addition, the effects of the variation of hydrothermal conditions, including temperature, precursor concentration and pH, on the formation of hierarchical architectures were also explored. First, hydrothermal synthesis at lower temperature (180 °C) was found to only yield some rounded nanosheets with a width of about 6 μm and a wall thickness of 20 nm (Fig. S4a and S4b†), which loosely interacted with their adjacent nanosheets. In contrast, higher temperature synthesis (200 °C) introduced an increased reaction rate, thus leading to the complete transformation of original flowers into small but dense and irregular nanosheets of about 3 μm wide, which are randomly connected with their neighbors (Fig. S4c and S4d†). Subsequently, the study of the precursor concentration effect showed that a lower concentration of \((\text{CH}_3\text{COO})_2\text{Sr}\) (0.05 M) resulted in the formation of a small quantity of rounded nanosheets with 3 μm in size (Fig. S5a and S5b†), while a higher concentration (0.2 M) resulted in many bougainvillea-like architectures composed of 2 μm wide fine sheet-shaped petals (Fig. S5c and S5d†). Finally, it was found that OH− played an important role in the generation of SrTiO3 since it was impossible to obtain any crystalline SrTiO3 when the pH was lower than 12.00 (Fig. S6a and S6b†). On the other hand, when the pH was increased up to 13.50, fine bundles composed of gracile nanowhiskers and small bud-like structures were apparently obtained (Fig. S6c and S6d†).

Due to their unique dielectric, piezoelectric, and ferroelectric properties,3-17 in addition to SrTiO3, other perovskite structures, such as BaTiO3, CaTiO3, and PbTiO3 have also been intensively investigated. However, we note that many reported preparative routes are only capable of synthesizing one or two kinds of perovskites. In the present study, the synthesis of perovskite MTOI₃ (M = Ba, Ca, and Pb) was carried out by adjusting the reaction parameters used in the similar hydrothermal reaction. Under optimized conditions, the creation of well-defined superstructures can be readily realized for these three perovskite structures, that is, dendritic BaTiO3 (Fig. 5a and 5b), nest-like CaTiO3 (Fig. 6a), and plate-like pyrochlore Pb₂Ti₂O₆ (Fig. 6b) were observed. The XRD measurement revealed that BaTiO3 had high crystallinity (Fig. 5c, JCPDS no. 83-1880). Moreover, Fig. 5d shows the Raman spectrum of the BaTiO3 sample where the Raman peaks located at 186, 261 and 509 cm⁻¹ are related to the transverse optical (TO) modes of A1 symmetry, the peak at 304 cm⁻¹ is assigned to the B1 mode, and the peak at 719 cm⁻¹ corresponds to the highest frequency longitudinal optical mode (LO) with A1 symmetry. The existence of the Raman peak at 304 cm⁻¹ suggests the asymmetry within the TiO₂ octahedra of BaTiO3 on a local scale, indicating the presence of the tetragonal BaTiO₃ phase.29,30 However, for CaTiO₃, the XRD pattern showed that the as-prepared product can be indexed to an orthorhombic lattice (Fig. 6c; JCPDS no. 82-0229).29 Quite interestingly, cubic pyrochlore Pb₂Ti₂O₆ (Fig. 6d; JCPDS no. 26-0142) was formed,23 which is often observed as an intermediate phase during the preparation of the perovskite PbTiO₃ material. It is difficult to obtain the single-phase of Pb₂Ti₂O₆ because of the close stoichiometry to perovskite (Pb : Ti : O = 1 : 1 : 3) and metastable nature of Pb₂Ti₂O₆ at high temperature.23 However, under hydrothermal conditions, well-crystallized cubic pyrochlore Pb₂Ti₂O₆ remained rather stable although a trace of impurities existed (Fig. 6d, additional peaks in the XRD pattern were from impurities, e.g., Pb₂O₃CO₃ and Ti₃O₇). After thermal annealing at 600 °C for 2 h, cubic pyrochlore Pb₂Ti₂O₆ was transferred into cubic PbTiO₃ (Fig. S7a† JCPDS no. 40-0099). Notably, this
observation is totally different from a recent report where cubic pyrochlore Pb₂Ti₂O₆ was converted into the tetragonal phase by calcination, partially due to the morphological difference between the present study and that reported in the literature as the change of crystal size can affect both lattice structure and polarization. In addition, Fig. S7b† shows the profile of photoluminescence (PL) emission of PbTiO₃, which implies that the intrinsic defects of PbTiO₃ were largely reduced via the thermal transformation as reflected by the reduced intensity of PL spectra.

We now turn our attention to elucidate the possible growth mechanism of MTiO₃ (M = Sr, Ba, Ca and Pb) with various microstructures. As reported in the literature, solid ZnO nanorods can be readily converted into hollow TiO₂ nanorods via liquid-phase TiO₂ deposition and simultaneous ZnO dissolution by immersing ZnO nanorods in an aqueous solution consisting of (NH₄)₂TiF₆ and H₃BO₃. This conversion facilitated the subsequent hydrothermal synthesis of perovskite structures. To date, there have been two possible mechanisms to account for the formation of MTiO₃ under hydrothermal conditions: (1) heterogeneous nucleation by which in situ transformation of TiO₂ into MTiO₃ occurs due to inward diffusion of dissolved M²⁺, and (2) homogeneous nucleation in which the dissolution–precipitation process takes place via the dissolution of some soluble TiO₂ as hydroxyl–titanium complexes (i.e., [Ti(OH)₆]³⁻) and subsequent precipitation of MTiO₃ crystals as a result of the reaction between [Ti(OH)₆]³⁻ and M²⁺, either homogeneously in solution or heterogeneously on TiO₂. Depending on reaction conditions, both mechanisms may occur simultaneously or one dominates over the other. On the basis of morphological features observed in the present study, we proposed that the formation of MTiO₃ superstructures may be governed by the dissolution and precipitation mechanism (i.e., mechanism (2) as noted above), followed by the Ostwald ripening process of perovskite nanocrystals and self-organization of perovskite building blocks. The evolution process is illustrated in Scheme 1. At the first stage, in the basic solution titanium species (i.e., [Ti(OH)₆]³⁻) that dissolved from the surface of TiO₂ flowers (Scheme 1b) grown directly from the ZnO template (Scheme 1a) can react with abundant M²⁺ to form

Fig. 5 SEM images of dendritic BaTiO₃ hydrothermally prepared in the 0.05 M (CH₃COO)₂Ba solution (pH = 13.50) at 200 °C for (a) 12 h, and (b) 24 h. (c) XRD pattern and (d) the Raman spectrum of the sample in (b).

Fig. 6 SEM images of (a) CaTiO₃ hydrothermally prepared in 0.05 M (CH₃COO)₂Ca solution at pH = 13.00 at 180 °C for 24 h, and (b) Pb₂Ti₂O₆ hydrothermally synthesized in 0.05 M (CH₃COO)₂Pb solution at pH = 7.00 at 200 °C for 24 h. (c and d) XRD patterns of (c) CaTiO₃ and (d) Pb₂Ti₂O₆, respectively.
MTIO₃ nuclei predominantly on the TiO₂ surface; then the nuclei grow into small nanoparticles. The dissolution of TiO₂ and precipitation of MTIO₃ occurring in the vicinity of the flower surfaces can be probably attributed to the rapid reaction between the as-formed [Ti(OH)₆]²⁻ and M²⁺ to yield MTIO₃ that nucleated on the surface of TiO₂ flowers. As the reaction proceeds, the formed MTIO₃ nanoparticles are accumulated on the surface of TiO₂ flowers to produce a particulate layer. After complete consumption of the remaining TiO₂ precursor, mesoporous MTIO₃ flowers composed of hollow nanorods (Scheme 1c) are well replicated from TiO₂ flowers. Subsequently, new architectures grow at the expense of small and less crystalline particles. According to the well-known dissolution-recrystallization process (i.e., Ostwald ripening process), the reduction in surface energy drives the crystal growth and morphological evolution due to the difference in solubility between large particles and small particles. Finally, as the reaction continues under prolonged reaction time and high temperature, nanoparticles disappear due to the dissolution (e.g., CaTiO₃ formed at 180 °C for 40 h (Fig. S2c†); SrTiO₃ prepared at 200 °C for 24 h (Fig. S4c and S4d†)). Notably, due to different crystal growth nature, different MTIO₃ structures have their preferred growth orientations, which accounts for diverse final structures, including nanosheets for SrTiO₃ (Fig. S2a†), nanoneedles for BaTiO₃ (Fig. S2b†), nanoslices for SrTiO₃ (Fig. S2c†), and microplates for Pb₂Ti₂O₆ (Fig. S2d†). These structures interact with one another and self-organize into elaborate hierarchical superstructures (Schemes 1d–g). In particular, a garden-like SrTiO₃ structure was developed under the selected hydrothermal condition (i.e., 0.1 M (CH₃COO)₂Sr at pH = 13.00 at 180 °C for 24 h). Apparently, under this mild reaction condition, the SrTiO₃ crystal nucleus successfully evolved into various morphologies (Scheme 1d). However, under other experimental conditions (i.e., low and high temperatures, low and high precursor concentrations), the crystal nucleus grew uniformly, and only one final structure was developed. Clearly, more theoretical and experimental studies are needed to elucidate this result, and will be investigated in future work.

Fig. S8a† shows the UV-vis absorption spectra of as-prepared MTIO₃ materials, from which the absorption coefficient can be calculated based on the Lambert–Beer law. 

\[
I = I_0 \exp(-\alpha t) \quad (1)
\]

\[
A = \log(I/I_0) \quad (2)
\]

\[
\alpha = 2.303 \frac{A}{t} \quad (3)
\]

where \(I_0\) is the intensity of incident light, \(I\) is the intensity of transmitted light, \(A\) is the optical absorbance (Fig. S8a†), \(\alpha\) is the absorption coefficient, and \(t\) is the film thickness, respectively. Subsequently, the optical band gap energy \(E_g\) can be analyzed by the Tauc formula:

\[
(\alpha h\nu)^{1/n} = \beta(h\nu - E_g) \quad (4)
\]

\[
h\nu = 1240/A \quad (5)
\]

where \(n\) depends on the characteristics of the transition in a semiconductor, which is either 1/2 for a direct inter-band transition (e.g., PbTiO₃) or 2 for an indirect inter-band transition (e.g., ZnO, TiO₂, BaTiO₃, SrTiO₃, and CaTiO₃), \(h\nu\) is the discrete photon energy, \(\lambda\) is the wavelength and \(\beta\) is the absorption constant, respectively. Accordingly, the \(E_g\) of as-prepared MTIO₃ materials can thus be determined from the plot of \((\alpha h\nu)^{1/n}\) vs. \(h\nu\) by extrapolating the intercept of the tangent of to \((\alpha h\nu)^{1/n} = 0\) (Fig. S8b and S8c†). As shown in Fig. S8b†, the band gap energies \(E_g\) are 3.14 eV for ZnO, 3.18 eV for amorphous TiO₂ after annealing at 450 °C for 2 h, 3.46 eV for SrTiO₃, 3.09 eV for BaTiO₃, 3.24 eV for CaTiO₃, and 3.12 eV for Pb₂Ti₂O₆, respectively, signifying that their photocatalytic activities exist under UV-light irradiation.

It is worth noting that SrTiO₃ has superior photocatalytic activity as the bottom of its conduction band (CB) is determined by the Ti 3d states, which is even more negative (i.e., −1.4 V vs. SCE) (using SCE as the reference electrode) than that of anatase TiO₂ (i.e., −1.2 V vs. SCE), suggesting that SrTiO₃ has a stronger reduction ability. In the present study, the photocatalytic activity of these hierarchically structured MTIO₃ materials was evaluated through the photodegradation of methyl blue (MB) under UV light activation. The variations of dye concentration at the time interval of 30 min are shown in Fig. 7a. It is not surprising that 7% of MB was degradable after 120 min in the absence of a catalyst because of its self-degradation character. The photocatalytic performance was obtained in the presence of all as-prepared materials. The order of photocatalytic activity followed SrTiO₃ > ZnO > TiO₂ > Pb₂TiO₆ > BaTiO₃ > CaTiO₃. Remarkably, SrTiO₃ led to 75% removal of MB after the 2 h photodegradation, showing the best photocatalytic performance among the six catalysts.

The photocatalytic decomposition of MB can be described by the Langmuir–Hinshelwood kinetic model. The first-order linear relationship can be expressed as \(\ln(C_o/C) = kt\), where \(C_o\) and \(C\) are the initial concentration of MB dye and the concentration of MB at time \(t\) (the irradiation time), and \(k\) is the apparent first-order reaction constant. As indicated in
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Fig. 7 Photocatalytic degradation rates of MB under UV light irradiation using different catalysts. (a) C/C0 vs. t, and (b) ln(C0/C) vs. t. STO, BTO, CTO, and PTO represent SrTiO3, BaTiO3, CaTiO3, and PbTiO3, respectively.

Fig. 7b, very low apparent reaction rate constants of 0.54 × 10^{-3} min^{-1}, 1.15 × 10^{-3} min^{-1}, 1.22 × 10^{-3} min^{-1}, and 1.71 × 10^{-3} min^{-1} were obtained in the cases of the self-photolysis of MB, the photocatalysis by CaTiO3, BaTiO3 and PbTiO3, respectively. ZnO and TiO2 photocatalysis displayed relatively higher reaction rates of 4.54 × 10^{-3} min^{-1} and 2.22 × 10^{-3} min^{-1}, respectively. In contrast, SrTiO3 exhibited the highest reaction rate of 11.16 × 10^{-3} min^{-1}, reflecting a 146% enhancement of photocatalytic efficiency when compared to that of ZnO. In addition, different SrTiO3 structures prepared at different times were also examined. As demonstrated in Fig. S9a and S9b, the reaction rate of MB decomposition increased from 1.07 × 10^{-3} min^{-1} to 7.00 × 10^{-3} min^{-1} and to 11.16 × 10^{-3} min^{-1} as hydrothermal growth time increased from 0 h (amorphous TiO2 only) to 3 h and to 24 h, respectively. However, prolonged growth for 40 h led to reduced photocatalytic activity (6.31 × 10^{-3} min^{-1}). Obviously, this was possibly due to the crystal and morphological differences of samples, namely, amorphous TiO2 flowers at 0 h (Fig. 1b), pure flower-like SrTiO3 structure after 3 h (Fig. 4a), peculiar garden-like hierarchical architecture after 24 h (Fig. 2a and 4d), and large agglomerates after 40 h (Fig. 4e). It is well accepted that dark adsorption is a prerequisite for good photocatalytic activity. In general, 2D thin nanosheet structures have a large surface area and a good diffusion state, which substantially facilitate the dye loading. Accordingly, Fig. S9c reveals that after 1 h dark adsorption the order of adsorption capacity of SrTiO3 samples followed SrTiO3 (24 h) > SrTiO3 (3 h) > SrTiO3 (40 h) = SrTiO3 (0 h; i.e., pure TiO2 flowers), which correlated well with the photocatalytic results. It is noteworthy that in comparison to other materials, SrTiO3 still showed the best adsorption capacity, which may be considered as an additional major reason for its highest photocatalytic activity. Alternatively, the SrTiO3 garden-like structure was partially built from layered structures (i.e., hydrothermally treated for 24 h); and the layer- or sheet-like architectures have been proven to be more favorable for diffusion and separation of photoexcited charge carriers. Due to their layer- or sheet-like configuration, only through very short distance the generated holes can easily diffuse to the sheet surface where they are subsequently captured by surrounding H2O, OH− or O2 to form oxygen species (e.g., OH+) which then react with MB. Consequently, the recombination process of charge carriers is substantially reduced, and thus the excited electrons can also effectively diffuse to the surface of SrTiO3 to degrade the MB molecules. Taken together, SrTiO3 with the garden-like superstructures prepared from 0.1 M (CH3COO)2Sr at pH = 13.00 at 180 °C for 24 h yielded the best performance among other materials in the MB degradation in this work.

4. Conclusion

In summary, garden-like cubic SrTiO3 superstructures were directly grown on transparent conducting substrates by a combination of chemical bath synthesis and hydrothermal treatment. This in situ growth approach rendered the formation of diverse yet elaborate superstructures in one sample. A comprehensive study on the effects of growth time, temperature, initial concentration of precursor, and acidity on the creation of diversified morphologies of SrTiO3 was performed. Interestingly, this approach is general and can be utilized to produce other perovskite (e.g., BaTiO3 and CaTiO3) and pyrochlore (Pb2Ti2O6) structures. Remarkably, in this work the garden-like SrTiO3 superstructures exhibited superior photocatalytic performance in photodegradation of MB dyes as compared to other semiconductor photocatalysts (i.e., ZnO, TiO2, BaTiO3, CaTiO3, and PbTiO3), primarily due to their hierarchical architectures with enhanced diffusion and improved dye adsorption capacity.

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Notes and references
