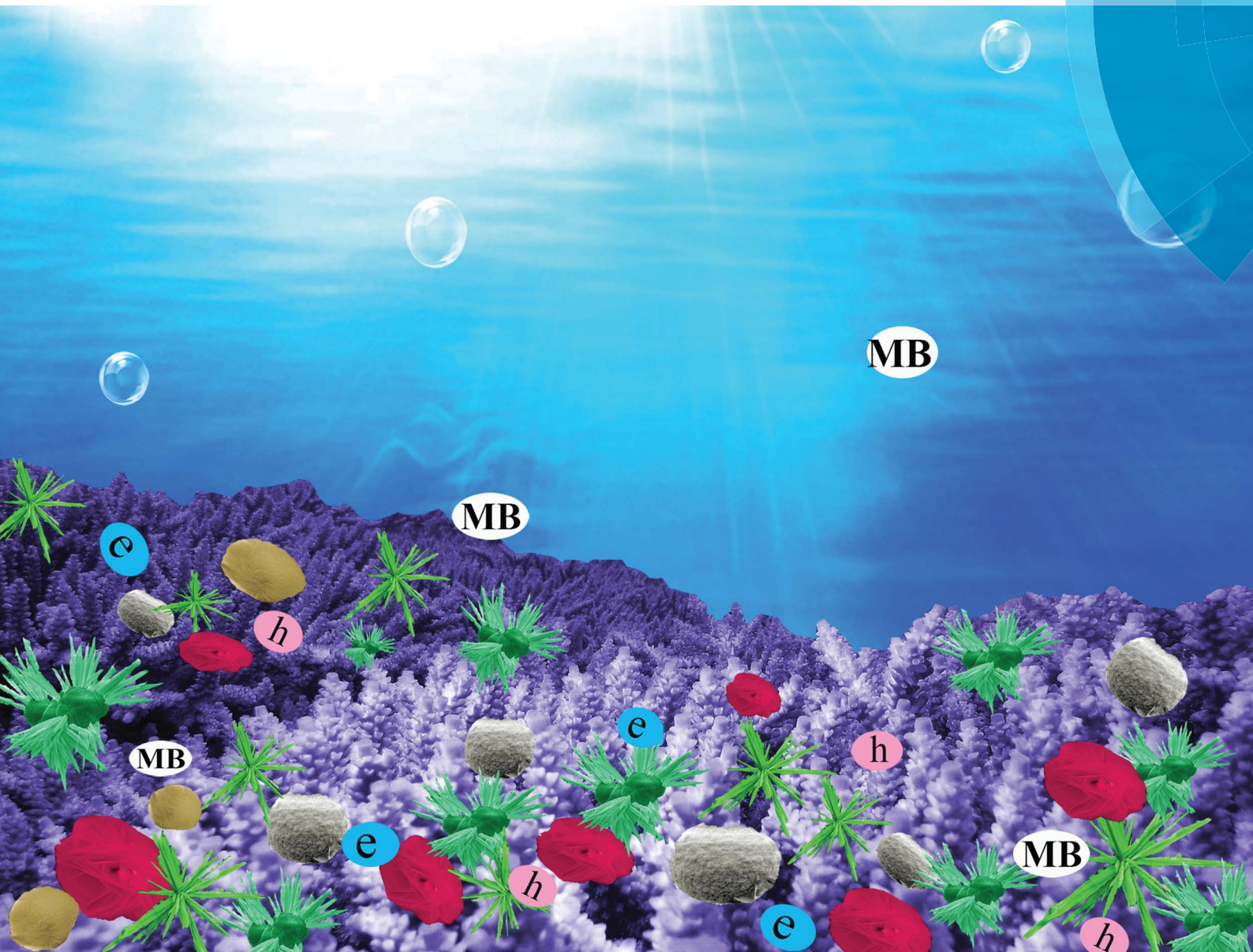


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Garden-like perovskite superstructures with enhanced photocatalytic activity



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 prepared using ZnO flowers as templates. Different three-dimensional SrTiO₃ architectures 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.

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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.^{1–3} In particular, perovskite nanostructures have recently received considerable attention due to their enhanced performance as compared to the bulk counterparts.^{3–6} 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

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.^{8–13}

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 nano-sheets,^{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 nanocubes¹² were produced through modified hydrothermal methods. Clearly, developing a feasible approach to yield diverse hierarchical

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† 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 study revealed that the formation of these diverse hierarchical architectures can be 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. Remarkably, this preparative strategy can be readily extended to produce other hierarchical perovskite materials, including dendrite-shaped BaTiO₃ and nest-shaped CaTiO₃, as well as pyrochlore Pb₂Ti₂O₆ which was further transformed into PbTiO₃ by calcination. Quite intriguingly, in comparison to other semiconductors and perovskite materials (*i.e.*, ZnO, TiO₂, BaTiO₃, CaTiO₃ and PbTiO₃), garden-like SrTiO₃ superstructures exhibited a superior photocatalytic performance in the degradation of methyl blue (MB). To the best of our knowledge, this is the first study of creating diverse yet elaborate 3D hierarchical SrTiO₃ architectures simply by a one-pot reaction.

2. Experimental section

2.1 Fabrication of garden-like SrTiO₃ hierarchical structures

Hierarchically structured garden-like SrTiO₃ grown on transparent conducting substrates was formed by a combination of chemical bath synthesis and subsequent hydrothermal treatment. In a typical synthesis, 20 mL 0.025 M Zn(NO₃)₂ (Sigma-Aldrich, purity ≥98.0%) aqueous solution with 0.0125 M 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, 2 cm × 2 cm, 14 Ω square⁻¹; 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 its conducting side facing up. The chemical bath reaction was performed at 85 °C for 4 h in an oven. Subsequently, the FTO substrate was taken out, rinsed extensively with deionized water, and then immersed in another aqueous solution with 0.1 M (NH₄)₂TiF₆ (Sigma-Aldrich, purity ≥99.99%) and 0.1 M H₃BO₃ (Sigma-Aldrich, purity ≥99.5%) at 25 °C for 2 h, followed by deionized water washing. Subsequently, a hydrothermal treatment was carried out in an aqueous solution containing 0.1 M (CH₃COO)₂Sr (Sigma-Aldrich, purity ≥97.0%) at pH = 13.00 (measured using a pH meter) adjusted by adding 1 M NaOH solution at 180 °C for 24 h. The product was rinsed with dilute HCl solution to remove some existing impurities (*e.g.*, unreacted ZnO). The effects of hydrothermal growth conditions, including the growth time (from 3 h to 40 h), temperature (from 150–200 °C), initial concentrations of (CH₃COO)₂Sr, and acidity

on the resulting hierarchical structures were systematically investigated. Similarly, BaTiO₃ films were obtained by hydrothermal synthesis 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 Pb₂Ti₂O₆ 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

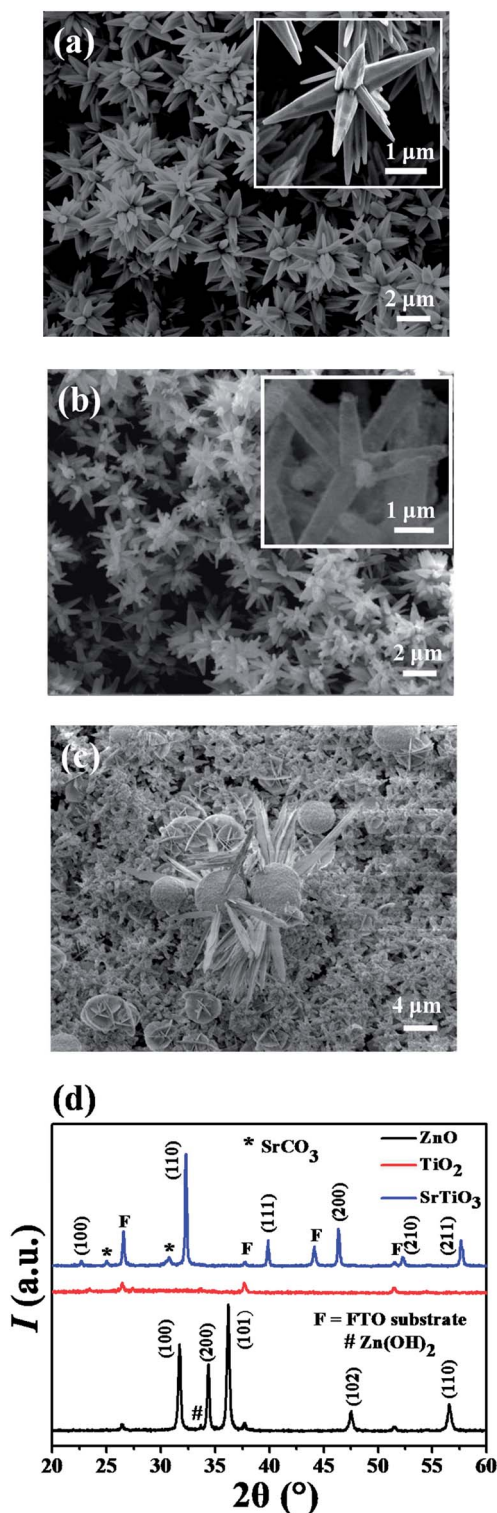


Fig. 1 SEM images of (a) ZnO flowers prepared in aqueous solution (pH = 11.00) containing 0.025 M $\text{Zn}(\text{NO}_3)_2$ and 0.0125 M HMTA at 90 °C for 4 h (the close-up of one ZnO flower is shown as the inset); (b) TiO_2 flowers produced by converting ZnO flowers in aqueous solution containing 0.1 M $(\text{NH}_4)_2\text{TiF}_6$ and 0.1 M H_3BO_3 at 25 °C for 2 h (the close-up of one TiO_2 flower is shown as the inset); and (c) SrTiO_3 garden created by hydrothermally treating TiO_2 flowers in aqueous solution (pH = 13.00) containing 0.1 M $(\text{CH}_3\text{COO})_2\text{Sr}$ at 180 °C for 24 h. (d) XRD patterns of ZnO flowers, TiO_2 flowers and SrTiO_3 garden.

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 $(\text{NH}_4)_2\text{TiF}_6$ and 0.1 M H_3BO_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 literature²⁵ 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 $(\text{CH}_3\text{COO})_2\text{Sr}$ 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 $\text{Zn}(\text{OH})_2$ 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

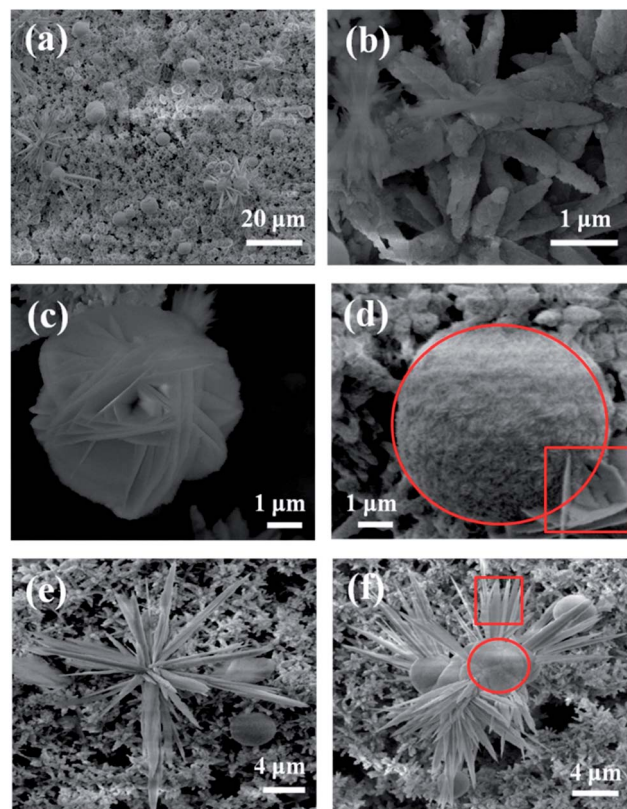


Fig. 2 SEM images of (a) a full top view of a SrTiO_3 garden, (b) SrTiO_3 flowers composed of hollow nanorods, (c) SrTiO_3 flowers assembled with nanosheets, (d) SrTiO_3 bouquet constructed with nanoflakes (see Fig. S2a† for a better view where nanoflakes are clearly evident), (e) SrTiO_3 grass containing long blades, and (f) hierarchically structured SrTiO_3 showing the coexistence of bouquet and grass.

quantity of SrCO_3 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 $\text{Zn} : \text{O} = 1 : 1$ (Fig. S1a and S1d[†]); for TiO_2 , in addition to Ti and O elements, a little of residual Zn from the ZnO template and a little of F adsorbing from the $(\text{NH}_4)_2\text{TiF}_6$ solution used for converting ZnO into TiO_2 were identified (Fig. S1b and S1d[†]); while in the case of SrTiO_3 structure, the atomic ratio of $\text{Sr} : \text{Ti} : \text{O}$ was approximately $1 : 1 : 3$, corresponding well to the molecular formula of strontium titanate (Fig. S1c and S1d[†]).

The detailed features of the SrTiO_3 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

composed of several nanorods with a diameter of the nanorod in the range of 300–500 nm and a length within 1–2 μm . However, these rod-shaped petals had a considerably rough surface (Fig. 2b) in comparison to the translucent hollow TiO_2 nanorods (inset in Fig. 1b). The mesoporous SrTiO_3 nanorod was hollow as evidenced by TEM imaging (Fig. 3a), where the center of the nanorod appeared relatively bright. In addition, another flower-like structure with a diameter of approximately 5 μm , assembled by many thin nanosheets as petals, was also developed (Fig. 2c). These nanosheets with a width in the range of 2–3 μm and a wall thickness of about 20 nm connected with each other to form a network resembling a flower (Fig. 2c). More interestingly, a uniformly shaped bouquet-like structure with a size ranging from 3–5 μm is seen in Fig. 2d. Further scrutiny of the SrTiO_3 bouquet revealed that such a 3D superstructure was constructed from dozens of squeezed and interacted flake-like petals of about 400 nm in width and 15 nm in wall thickness (Fig. S2a[†]). Furthermore, a grass-like structure composed of 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. 2f) can intercalate into the bouquet-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 SrTiO_3 , 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 TiO_2 without any other visible superstructures; however, the XRD measurement (Fig. 4f) revealed that these flowers were cubic SrTiO_3 , suggesting the rapid transformation of amorphous TiO_2 into crystal SrTiO_3 . 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 ripen superstructures comprising diverse morphologies (Fig. 2a and 4d) due to the crystal growth. However, when the growth time

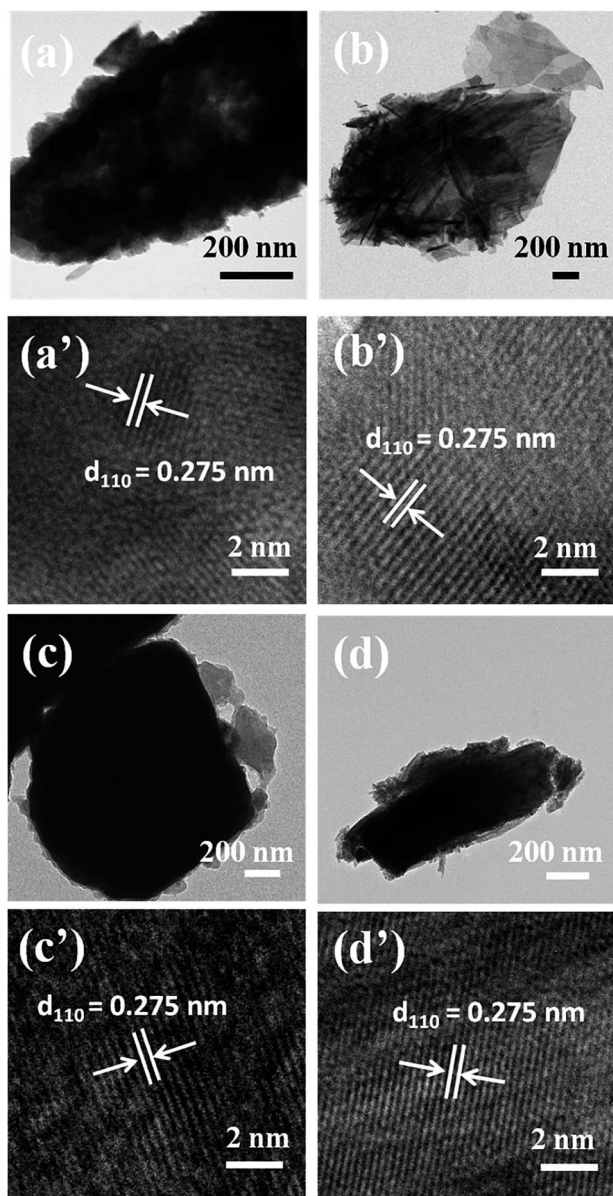


Fig. 3 TEM images of (a) a SrTiO_3 hollow nanorod; (b) several SrTiO_3 nanosheets; (c) part of the SrTiO_3 bouquet; (d) SrTiO_3 blade fragment. (a'–d') HRTEM images, corresponding to TEM images in (a–d).

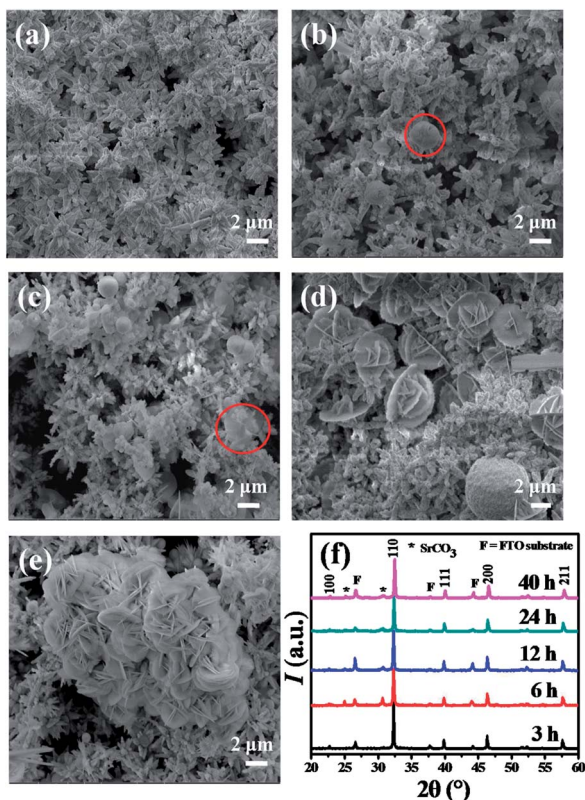


Fig. 4 SEM images of SrTiO₃ gardens produced by hydrothermal treatment for (a) 3 h, (b) 6 h, (c) 12 h, (d) 24 h, and (e) 40 h. (f) The corresponding XRD pattern of SrTiO₃ gardens prepared at different times.

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.¹⁰ 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 (CH₃COO)₂Sr (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,^{5,16,17} 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 MTiO₃ (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 TiO₆ 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).¹⁷ 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.*, Pb₃O₂CO₃ 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

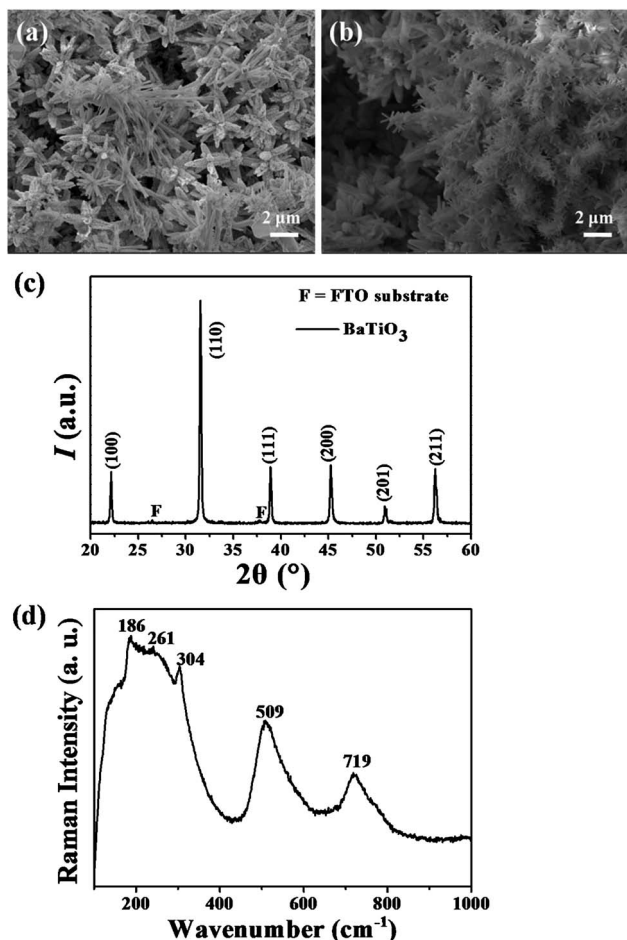


Fig. 5 SEM images of dendritic BaTiO_3 hydrothermally prepared in the 0.05 M $(\text{CH}_3\text{COO})_2\text{Ba}$ solution (pH = 13.50) at 200 °C for (a) 12 h, and (b) 24 h. (c) XRD pattern and (d) the Raman spectrum of the sample in (b).

observation is totally different from a recent report where cubic pyrochlore $\text{Pb}_2\text{Ti}_2\text{O}_6$ was converted into the tetragonal phase by calcination,³¹ 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.³² In addition, Fig. S7b† shows the profile of photoluminescence (PL) emission of PbTiO_3 , which implies that the intrinsic defects of PbTiO_3 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 MTiO_3 ($M = \text{Sr}, \text{Ba}, \text{Ca}$ and Pb) with various microstructures. As reported in the literature, solid ZnO nanorods can be readily converted into hollow TiO_2 nanorods *via* liquid-phase TiO_2 deposition and simultaneous ZnO dissolution by immersing ZnO nanorods in an aqueous solution consisting of $(\text{NH}_4)_2\text{TiF}_6$ and H_3BO_3 .²⁵ This conversion facilitated the subsequent hydrothermal synthesis of perovskite structures. To date, there have been two possible mechanisms to account for the formation of MTiO_3 under hydrothermal conditions:^{4,33} (1) heterogeneous nucleation by which *in situ* transformation of TiO_2 into MTiO_3 occurs due to inward diffusion of dissolved M^{2+} ,³³ (2) homogeneous

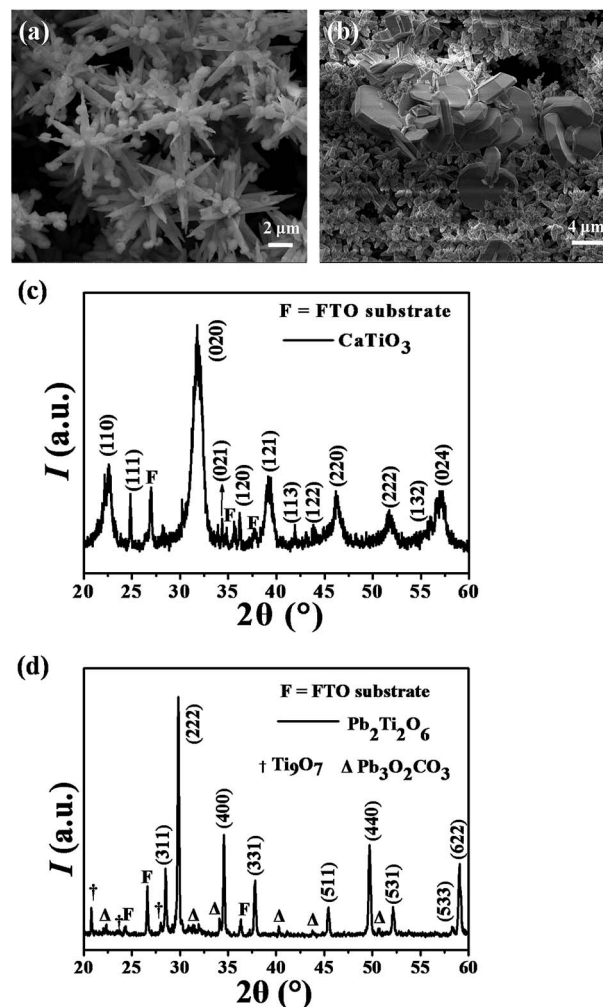
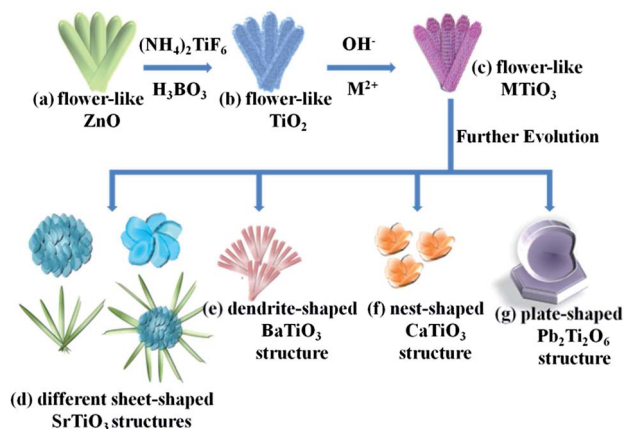


Fig. 6 SEM images of (a) CaTiO_3 hydrothermally prepared in 0.05 M $(\text{CH}_3\text{COO})_2\text{Ca}$ solution at pH = 13.00 at 180 °C for 24 h, and (b) $\text{Pb}_2\text{Ti}_2\text{O}_6$ hydrothermally synthesized in 0.05 M $(\text{CH}_3\text{COO})_2\text{Pb}$ solution at pH = 7.00 at 200 °C for 24 h. (c and d) XRD patterns of (c) CaTiO_3 and (d) $\text{Pb}_2\text{Ti}_2\text{O}_6$, respectively.

nucleation in which the dissolution-precipitation process takes place *via* the dissolution of some soluble TiO_2 as hydroxyl-titanium complexes (*i.e.*, $[\text{Ti}(\text{OH})_6]^{2-}$) and subsequent precipitation of MTiO_3 crystals as a result of the reaction between $[\text{Ti}(\text{OH})_6]^{2-}$ and M^{2+} , either homogeneously in solution or heterogeneously on TiO_2 .⁴ Depending on reaction conditions, both mechanisms may occur simultaneously or one dominates over the other.^{8,27,28,34–36} On the basis of morphological features observed in the present study, we proposed that the formation of MTiO_3 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.*, $[\text{Ti}(\text{OH})_6]^{2-}$) that dissolved from the surface of TiO_2 flowers (Scheme 1b) grown directly from the ZnO template (Scheme 1a) can react with abundant M^{2+} to form



Scheme 1 Schematic illustration of the formation mechanism of MTiO_3 with various superstructures.

MTiO_3 nuclei predominantly on the TiO_2 surface; then the nuclei grow into small nanoparticles.³⁴ The dissolution of TiO_2 and precipitation of MTiO_3 occurring in the vicinity of the flower surfaces can be probably attributed to the rapid reaction between the as-formed $[\text{Ti}(\text{OH})_6]^{2-}$ and M^{2+} to yield MTiO_3 that nucleated on the surface of TiO_2 flowers.³⁴ As the reaction proceeds, the formed MTiO_3 nanoparticles are accumulated on the surface of TiO_2 flowers to produce a particulate layer. After complete consumption of the remaining TiO_2 precursor, mesoporous MTiO_3 flowers composed of hollow nanorods (Scheme 1c) are well replicated from TiO_2 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),^{34,37} 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.*, CaTiO_3 formed at 180 °C for 40 h (Fig. S2c†); SrTiO_3 prepared at 200 °C for 24 h (Fig. S4c and S4d†)). Notably, due to different crystal growth nature, different MTiO_3 structures have their preferred growth orientations, which accounts for diverse final structures,^{27,28} including nanosheets for SrTiO_3 (Fig. S2a†), nanoneedles for BaTiO_3 (Fig. S2b†), nanoslices for CaTiO_3 (Fig. S2c†), and microplates for $\text{Pb}_2\text{Ti}_2\text{O}_6$ (Fig. S2d†). These structures interact with one another and self-organize into elaborate hierarchical superstructures (Schemes 1d–g). In particular, a garden-like SrTiO_3 structure was developed under the selected hydrothermal condition (*i.e.*, 0.1 M $(\text{CH}_3\text{COO})_2\text{Sr}$ at pH = 13.00 at 180 °C for 24 h). Apparently, under this mild reaction condition, the SrTiO_3 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 MTiO_3 materials, from which the absorption coefficient can be calculated based on the Lambert–Beer law.³⁸

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

$$A = \log(I_0/I) \quad (2)$$

$$\alpha = 2.303 A/t \quad (3)$$

where I_0 is the intensity of incident light, I is the intensity of transmitted light, A is the optical absorbance (Fig. S8a†), α 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:^{39,40}

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

$$h\nu = 1240/\lambda \quad (5)$$

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.*, PbTiO_3) or 2 for an indirect inter-band transition (*e.g.*, ZnO , TiO_2 , BaTiO_3 , SrTiO_3 and CaTiO_3), $h\nu$ is the discrete photon energy, λ is the wavelength and β is the absorption constant, respectively.^{10,19,41} Accordingly, the E_g of as-prepared MTiO_3 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 plot 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 TiO_2 after annealing at 450 °C for 2 h, 3.46 eV for SrTiO_3 , 3.09 eV for BaTiO_3 , 3.24 eV for CaTiO_3 , and 3.12 eV for PbTiO_3 , respectively, signifying that their photocatalytic activities exist under UV-light irradiation.

It is worth noting that SrTiO_3 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 TiO_2 (*i.e.*, -1.2 V vs. SCE), suggesting that SrTiO_3 has a stronger reduction ability.^{12,42,43} In the present study, the photocatalytic activity of these hierarchically structured MTiO_3 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 characteristics under UV light illumination. Enhanced photocatalytic performance was obtained in the presence of all as-prepared materials. The order of photocatalytic activity followed $\text{SrTiO}_3 > \text{ZnO} > \text{TiO}_2 > \text{PbTiO}_3 > \text{BaTiO}_3 > \text{CaTiO}_3$. Remarkably, SrTiO_3 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 $\ln(C_0/C) = kt$, where C_0 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.^{11,24} As indicated in

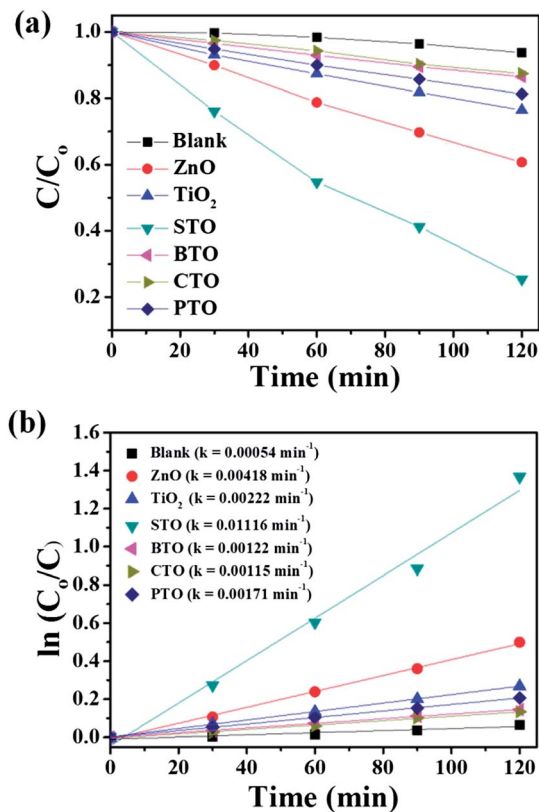


Fig. 7 Photocatalytic degradation rates of MB under UV light irradiation using different catalysts. (a) C/C_0 vs. t , and (b) $\ln(C_0/C)$ vs. t . STO, BTO, CTO, and PTO represent SrTiO_3 , BaTiO_3 , CaTiO_3 , and PbTiO_3 , respectively.

Fig. 7b, very low apparent reaction rate constants of $0.54 \times 10^{-3} \text{ min}^{-1}$, $1.15 \times 10^{-3} \text{ min}^{-1}$, $1.22 \times 10^{-3} \text{ min}^{-1}$, and $1.71 \times 10^{-3} \text{ min}^{-1}$ were obtained in the cases of the self-photolysis of MB, the photocatalysis by CaTiO_3 , BaTiO_3 and PbTiO_3 , respectively. ZnO and TiO_2 photocatalysis displayed relatively higher reaction rates of $4.54 \times 10^{-3} \text{ min}^{-1}$ and $2.22 \times 10^{-3} \text{ min}^{-1}$, respectively. In contrast, SrTiO_3 exhibited the highest reaction rate of $11.16 \times 10^{-3} \text{ min}^{-1}$, reflecting a 146% enhancement of photocatalytic efficiency when compared to that of ZnO. In addition, different SrTiO_3 structures prepared at different times were also examined. As demonstrated in Fig. S9a and S9b,[†] the reaction rate of MB decomposition increased from $1.07 \times 10^{-3} \text{ min}^{-1}$ to $7.00 \times 10^{-3} \text{ min}^{-1}$ and to $11.16 \times 10^{-3} \text{ min}^{-1}$ as hydrothermal growth time increased from 0 h (amorphous TiO_2 only) to 3 h and to 24 h, respectively. However, prolonged growth for 40 h led to reduced photocatalytic activity ($6.31 \times 10^{-3} \text{ min}^{-1}$). Obviously, this was possibly due to the crystal and morphological differences of samples, namely, amorphous TiO_2 flowers at 0 h (Fig. 1b), pure flower-like SrTiO_3 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.⁴⁴ Accordingly, Fig. S9c[†]

reveals that after 1 h dark adsorption the order of adsorption capacity of SrTiO_3 samples followed SrTiO_3 (24 h) > SrTiO_3 (3 h) > SrTiO_3 (40 h) > SrTiO_3 (0 h; *i.e.*, pure TiO_2 flowers), which correlated well with the photocatalytic results. It is noteworthy that in comparison to other materials, SrTiO_3 still showed the best adsorption capacity, which may be considered as an additional major reason for its highest photocatalytic activity. Alternatively, the SrTiO_3 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.^{19,45} 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 H_2O , OH^- or O_2 to form oxygen species (*e.g.*, OH^\cdot) 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 SrTiO_3 to degrade the MB molecules.¹⁹ Taken together, SrTiO_3 with the garden-like superstructures prepared from 0.1 M $(\text{CH}_3\text{COO})_2\text{Sr}$ 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 SrTiO_3 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 SrTiO_3 was performed. Interestingly, this approach is general and can be utilized to produce other perovskite (*e.g.*, BaTiO_3 and CaTiO_3) and pyrochlore ($\text{Pb}_2\text{Ti}_2\text{O}_6$) structures. Remarkably, in this work the garden-like SrTiO_3 superstructures exhibited superior photocatalytic performance in photodegradation of MB dyes as compared to other semiconductor photocatalysts (*i.e.*, ZnO, TiO_2 , BaTiO_3 , CaTiO_3 and PbTiO_3), primarily due to their hierarchical architectures with enhanced diffusion and improved dye adsorption capacity.

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