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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 Sr³⁺, garden-like perovskite SrTiO₃ superstructures were achieved. The amorphous TiO₂ was preformed using ZnO flowers as template. 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 crystal, 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 Pb₂Ti₃O₆ 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), due probably to its intrinsic photocatalytic activity and special garden-like feature 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.

1. Introduction

Perovskite-type oxides M(TiO₃) (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. In particular, perovskite nanostructures have recently received considerable attention due to their enhanced performance as compared to the bulk counterparts. Among various M(TiO₃), 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. 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.

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. The self-organization of nanoscale functional building blocks, including nanosheets, nanorods, nanoparticles, to form complex hierarchical structures offer 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 were obtained by a hydrothermal process, and mesoporous SrTiO₃ spheres composed of nanoparticles and hollow SrTiO₃ microspheres constructed by the assembly of nanocubes were produced through modified hydrothermal methods. Clearly, developing feasible approach to yield diverse hierarchical 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 template. The introduction of ZnO template was motivated by exploiting an amorphous yet 3D structured TiO₂ prototype as 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 crystal, 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 Pb₂Ti₃O₆ 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 SrTiO$_3$ architectures simply by a one-pot reaction.

2. Experimental Section

2.1 Fabrication of garden-like SrTiO$_3$ hierarchical structures.

Hierarchically structured garden-like SrTiO$_3$ 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(NO$_3$)$_2$ (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. An ultrasonic-doped tin oxide (FTO) substrate (F:SnO$_2$, 2 cm × 2 cm, 14 Ω/square; 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 deionized water rinsing for 15 min was placed in a sealed glass bottle containing the Zn(NO$_3$)$_2$ 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 (NH$_4$)$_2$TiF$_6$ (Sigma-Aldrich, purity ≥99.99%) and 0.1 M H$_2$BO$_3$ (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 (CH$_3$COO)$_2$Sr (Sigma-Aldrich, purity ≥97.0%) at pH = 13.00 (measured by pH meter) adjusted by adding 1 M NaOH solution at 180 °C for 24 h. The product was rinsed by dilute HCl solution to remove some existent 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 (CH$_3$COO)$_2$Sr, and acidity on the resulting hierarchical structures were systematically investigated. Similarly, BaTiO$_3$ films were obtained by hydrothermal synthesis in 0.05 M (CH$_3$COO)$_2$Ba (Sigma-Aldrich, purity ≥99.0%) solution (pH = 13.50) at 200 °C, and CaTiO$_3$ films were prepared hydrothermally in 0.05 M (CH$_3$COO)$_2$Ca (Sigma-Aldrich, purity ≥99.0%) solution (pH = 13.00) at 180 °C, while Pb$_2$Ti$_3$O$_8$ films were synthesized hydrothermally in 0.05 M (CH$_3$COO)$_2$Pb (Sigma-Aldrich, purity ≥99.0%) solution (pH = 7.00) at 200 °C, followed by a 600 °C annealing to transform it into PbTiO$_3$.

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 MB aqueous solution, and air was bubbled through the 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.

2.3 Characterizations.

The morphology and lattice structures of samples were examined by field emission scanning electron microscopy (FESEM; FEI Quanta 250, operated at 10 kV in high vacuum) and transmission electron microscopy (TEM; JEOL 2100, operated at 200 kV). A SEM equipped with an energy dispersive X-ray spectrometer (EDS, FEI Quanta 250, operated 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 Ka radiation; operated at a scan rate of 0.04° s$^{-1}$ and a step size of 0.02° in 20). The light absorption of the films was measured by UV-visible spectroscopy (Varian; UV-vis-NIR spectrophotometer, Cary 5000). 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

Figure 1 shows the SEM images and XRD patterns of as-prepared products. As indicated in Figure 1a, flower-like ZnO structures are formed via a chemical bath procedure in the basic solution (pH = 11.00) containing 0.025 M Zn(NO$_3$)$_2$ and 0.0125 M HMTA at 85 °C for 4 h. These well-defined ZnO flowers consisting several tapering sword-like petals with a length of approximately 2 μm and an average diameter of about 400 nm (inset in Figure 1a) were used as template and converted into TiO$_2$ flowers (Figure 1b) after a 2-h-immersion in the aqueous solution containing 0.1 M (NH$_4$)$_2$TiF$_6$ and 0.1 M H$_2$BO$_3$ at 25 °C. The TiO$_2$ flower almost retained the structure of ZnO template (inset in Figure 1b). The TiO$_2$ petals appeared to be translucent hollow rods as reported in literature and had a rough surface (inset in Figure 1b), which is distinctly different from the smooth surface of solid rod-shaped ZnO petals (inset in Figure 1a). Subsequently, a hydrothermal treatment was performed to transform TiO$_2$ into hierarchical SrTiO$_3$ (Figure 1c) in a basic (pH = 13.00) 0.1 M (CH$_3$COO)$_2$Sr solution at 180 °C for 24 h. Interestingly, different architectures SrTiO$_3$ emerged on FTO substrate, resembling a garden growing several plants, including the original flower-shaped structures composed of several nanorods (i.e., sword-shaped petals; Figure 2b) and new flowers made of many nanosheets (i.e., sheet-shaped petals; Figure 2c). Figure 1d displays XRD patterns of the abovementioned three products, in which the typical peaks were well-indexed to standard hexagonal (wurtzite) structure (JCPDS No.36-1451) for ZnO film with minor Zn(OH)$_2$ phase. The amorphous structure was, however, presented in 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 success in transforming TiO$_2$ into SrTiO$_3$. We note that there is a small quantity of SrCO$_3$ impurity in the product. Moreover, the EDS analysis further showed that only Zn and O elements in ZnO template had an atomic ratio of Zn:O = 1:1 (Figure S1a and S1d); for TiO$_2$, in addition to Ti and O elements, a little of residual Zn...
patterns of ZnO flowers, TiO$_2$ (pH = 11.00) containing 0.025 M Zn(NO$_3$)$_2$ for 4 h (the close-up of one ZnO flower in shown as the inset); (b) TiO$_2$ flowers produced by converting ZnO flowers in aqueous solution (pH = 11.00) containing 0.1 M (NH$_4$)$_2$TiF$_6$ and 0.1 M H$_2$BO$_3$ 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 (CH$_3$COO)$_2$Sr at 180 °C for 24 h. (d) XRD patterns of ZnO flowers, TiO$_2$ flowers and SrTiO$_3$ garden.

Figure 1. SEM images of (a) ZnO flowers prepared in aqueous solution (pH = 11.00) containing 0.025 M Zn(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 into TiO$_2$ without any other visible superstructures; however, the atomic ratio of Sr:Ti:O was approximately 1:1:3, corresponding well to the molecular formula of strontium titanate (Figure S1c and S1d).

The detailed features of the SrTiO$_3$ garden were shown in Figure 2 (SEM images) and Figure 3 (TEM images). A full view of the garden is shown in Figure 2a, indicating the coexistence of various structures in the garden. Figure 2b presents the original flower composed of several nanorods with a diameter of nanorod in the range of 300-500 nm and a length within 1-2 µm. However, these rod-shaped petals possessed considerably rough surface (Figure 2b) in comparison to the translucent hollow TiO$_2$ nanorods (inset in Figure 1b). The mesoporous SrTiO$_3$ nanorod is hollow as evidenced by the TEM imaging (Figure 3a, where the center of the nanorod appeared relatively bright. In addition, other flower-like structure with a diameter of approximately 5 µm, assembled by many thin nanosheets as petals was also developed (Figure 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-looking flower (Figure 2c).

More interestingly, uniformly shaped bouquet-like structure with a size ranging from 3–5 µm is seen in Figure 2d. The further scrutiny of SrTiO$_3$ bouquet revealed that such 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 (Figure S2a). Furthermore, 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 (Figure 2c). 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 Figure 2f) can intercalate into the bouquet-like structure (red cycle in Figure 2f), while some larger sheet-shaped petals (red square in Figure 2d) implanted into the bouquet-like structure that was made of numerous smaller flake-shaped petals (red cycle in Figure 2d). Figures 3a-3d display the TEM images for the fragments of four representative building blocks, that is, a hollow nanorod (Figure 3a, corresponding to Figure 2b), several nanosheets (Figure 3b, corresponding to Figure 2c), a part of bouquet (Figure 3c, corresponding to Figure 2d) and a nanoblade (Figure 3d, corresponding to Figure 2e), respectively. The corresponding high resolution TEM (HRTEM) images of the four building blocks are shown in Figures 3a-3d. All of them possessed 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 (Figure 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 Figures 4a-4e. As evidenced in Figure 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 (Figure 4f) revealed that these flowers were cubic SrTiO$_3$, suggesting the rapid transformation of amorphous...
Figure 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 Figure S2a for a better view where nanoflakes are clearly evident), (e) SrTiO$_3$ grass containing long blades, and (f) hierarchical structure SrTiO$_3$ showing the coexistence of bouquet and grass.

The formation of SrTiO$_3$ is a crystal SrTiO$_3$. As the hydrothermal reaction time increased to 6 h, some scattered bud-like protuberances (red cycle in Figure 4b) for bouquets were created and situated on the flower surface (Figure 4b). Quite interestingly, the sheet-like building blocks (red cycle in Figure 4c) for the new flower-like structure (Figure 2c) emerged as the reaction progressed (Figure 4c). The prolonged reaction to 24 h yielded dense and ripe superstructures comprising diverse morphologies (Figure 2a and Figure 4d) due to the crystal growth. However, when the growth time was extended up to 40 h, several flowers were aggregated together, forming a bulky wreath-like morphology. In addition, Figure S3 showed the photoluminescence (PL) emission of SrTiO$_3$ samples, which can be characterized as 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 material due to intrinsic defects of material. 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 SrTiO$_3$ samples. Remarkably, the corresponding XRD (Figure 4f) and PL (Figure S3) results implied that the appearance of this luxuriant garden may probably be ascribed to the transformation from unstable structures (i.e., original flowers in Figure 2b) to stable structures with reduced defects (i.e., sheet-shaped flowers in Figure 2c).

These flower-like structures undergo the dissolution-recrystallization process, namely, the well-known Ostwald ripening process, 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 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 (Figures S4a and S4b), which loosely interacted with their adjacent nanosheets. In contrast, higher temperature synthesis (200 °C) introduced 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 randomly

Figure 3. TEM images of (a) a SrTiO$_3$ hollow nanorod; (b) several SrTiO$_3$ nanosheets; (c) part of SrTiO$_3$ bouquet; (d) SrTiO$_3$ blade fragment. (a’-d’) HRTEM images, corresponding to TEM images in (a-d).
connected with their neighbors (Figures S4c and S4d). Subsequently, the study of the precursor concentration effect showed that lower concentration of (CH$_3$COO)$_2$Sr (0.05 M) resulted in the formation of a small quantity of rounded nanosheets with 3 µm in size (Figures S5a and S5b), while many bougainvillea3like architectures built by 2 µm wide fine sheet3shaped petals (Figures S5c and S5d) were developed for higher concentration (0.2 M). Finally, it is found that OH$^-$ played an important role in the generation of SrTiO$_3$ since it was impossible to obtain any crystalline SrTiO$_3$ when the pH was lower than 12.00 (Figures 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 presented (Figure S6c and S6d).

Due to their unique dielectric, piezoelectric, and ferroelectric properties, in addition to SrTiO$_3$, other perovskite structures, such as BaTiO$_3$, CaTiO$_3$, and PbTiO$_3$ 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 MTiO$_3$ (M = Ba, Ca, and Pb) noted above by adjusting the reaction parameters used in the hydrothermal reaction. Under optimized conditions, the creation of well-defined superstructures can be readily realized for these three perovskite structures, that is, dendritic BaTiO$_3$ (Figures 5a and 5b), nest-like CaTiO$_3$ (Figure 6a), and plate-like pyrochlore Pb$_2$Ti$_2$O$_6$ (Figure 6b) were observed. The XRD measurement revealed that BaTiO$_3$ possessed high crystallinity (Figure 5c, JCPDS No. 83-1880). Moreover, Figure 5d showed the Raman spectrum of BaTiO$_3$ sample where the Raman peaks located at 186, 261 and 509 cm$^{-1}$ are related to the transverse optical (TO) modes of A1 symmetry.

![Figure 5](image-url)

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

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 Raman peak at 304 cm$^{-1}$ suggests the asymmetry within the TiO$_6$ octahedra of BaTiO$_3$ on a local scale, indicating the presence of tetragonal BaTiO$_3$ phase. However, for CaTiO$_3$, XRD pattern showed that the as-prepared product can be indexed to an orthorhombic lattice (Figure 6c; JCPDS No. 82-0229). Quite interestingly, cubic pyrochlore Pb$_2$Ti$_2$O$_6$ (Figure 6d; JCPDS No. 26-0142) was formed, which is often observed as an intermediate phase during the preparation of perovskite PbTiO$_3$ material. It is difficult to obtain the single-phase of Pb$_2$Ti$_2$O$_6$ because of the close stoichiometry to perovskite (Pb:Ti:O = 1:1:3) and metastable nature of Pb$_2$Ti$_2$O$_6$ at high temperature. However, under hydrothermal condition, well-crystallized cubic pyrochlore Pb$_2$Ti$_2$O$_6$ kept rather stable although a trace of impurities existed (Figure 6d, additional peaks in XRD pattern were from impurities, e.g., Pb$_3$O$_2$CO$_3$ and Ti$_6$O$_7$). After thermal annealing at 600 °C for
2 h, cubic pyrochlore Pb2Ti2O7 was transferred into cubic PbTiO3 (Figure S7a, JCPDS NO. 40-0099). Notably, this observation is totally different from a recent report where cubic pyrochlore Pb2Ti2O7 was converted to tetragonal phase by calcination,31 due partially to the morphological difference between the present study and that reported in literature as the change of crystal size can affect on both lattice structure and polarization.32 In addition, Figure 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 in the reduced intensity of PL spectra.

Figure 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) Pb2Ti2O7 hydrothermally synthesized in 0.05 M (CH3COO)2Pb solution at pH=7.00 at 200 °C for 24 h. (c-d) XRD patterns of (c) CaTiO3 and (d) Pb2Ti2O7, respectively.

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 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 H3BO3.25 This conversion facilitated the subsequent hydrothermal synthesis of perovskite structures. To date, there have been two possible mechanisms to account for the formation of MTiO3 under hydrothermal conditions:4,33 (1) heterogeneous nucleation by which in-situ transformation of TiO2 into MTiO3 occurs due to inward diffusion of dissolved M2+,33 (2) homogeneous nucleation in which dissolution–precipitation process takes place via the dissolution of some soluble TiO2 as hydroxyl–titanium complexes (i.e.,[Ti(OH)6]2+) and subsequent precipitation of MTiO3 crystals as a result of the reaction between [Ti(OH)6]2+ and M2+, either homogeneously in solution or heterogeneously on TiO2.4 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 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]2+) 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 MTiO3 nuclei predominantly on the TiO2 surface; then the nuclei grow into small nanoparticles.34 The dissolution of TiO2 and precipitation of MTiO3 occur 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.34 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 grew at the expense of small and less crystalline particles. According to 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 disappeared due to the dissolution (e.g., CaTiO3 formed at 180 °C for 40 h (Figure S2c); SrTiO3 prepared at 200 °C for 24 h (Figures S4c and S4d)). Notably, due
to different crystal growth nature, different MTiO3 have their preferred growth orientations, which accounts for diverse final structures,27, 28 including nanosheets for SrTiO3(Figure S2a), nanoneedles for BaTiO3(Figure S2b), nanospheres for CaTiO3 (Figure S2c), and microplates for Pb5Ti4O12 (Figure S2d). These structures interacted with one another and self-organize into elaborate hierarchical superstructures (Schemes 1d-1g). In particular, garden-like SrTiO3 feature 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, 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.

Figure S8a shows the UV–vis absorption spectra of as-prepared MTiO3 materials, from which the absorption coefficient can be calculated based on Lambert-Beer law,38

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

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

\[
\alpha = 2.303A / l \quad (3)
\]

where \( I_0 \) is the intensity of incident light, \( I \) is the intensity of transmitted light, \( \alpha \) is the optical absorbance (Figure S8a), \( \alpha \) is the absorption coefficient, and \( l \) is the film thickness, respectively. Subsequently, the optical band gap energy \( E_g \) can be analyzed by the Tauc formula:39, 40

\[
(\alpha h\nu)^n = \beta (h\nu-E_g)^m \quad (4)
\]

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

where \( n \) depends on the characteristics of the transition in a semiconductor, which is either 1/2 for direct inter-band transition (e.g., PbTiO3) or 2 for 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 absorption constant, respectively.40, 42, 43 Accordingly, \( E_g \) of as-prepared MTiO3 materials can thus be determined from the plot of \((\alpha h\nu)^n \) vs. \( h\nu \) by extrapolating the intercept of the tangent of plot to \((\alpha h\nu)^n \) = 0 (Figures S8b and S8c), as shown in Figure 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 PbTiO3, respectively, signifying that their photocatalytic activities exist under UV-light irradiation.

It is worth noting that SrTiO3 possesses 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 (used SCE as reference electrode) than that of anatase TiO2 (i.e., -1.2 V vs SCE), suggesting that SrTiO3 has a stronger reduction ability.12, 42, 43 In the present study, the photocatalytic activity of these hierarchically structured MTiO3 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 Figure 7a. It is not surprising that 7% of MB was degradable after 120 min in the absence of catalyst because of its self-degradation characteristic under UV light illumination. Enhanced photocatalytic performance was obtained in the presence of all as-prepared materials. The order of photocatalytic activities followed SrTiO3>ZnO> TiO2>PbTiO3> 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 \( \ln(C/C_0) = kt \), 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 Figure 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 Figures 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 to 40 h led to reduced photocatalytic activity (6.31 × 10⁻³ min⁻¹). Obviously, this was due possibly to the crystal and morphological differences of samples, namely, amorphous TiO₂ flowers at 0 h (Figure 1b), pure flower-like SrTiO₃ structure after 3 h (Figure 4a), peculiar garden-like hierarchical architecture after 24 h (Figures 2a and 4d), and large agglomerates after 40 h (Figure 4e). It is well accepted that dark adsorption is a prerequisite for good photocatalytic activity. In general, large surface area and a well diffusion state from the nanosheet shape facilitate the dye loading. Accordingly, Figure S9c reveals that after 1 h dark adsorption the order of adsorption capacity for 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 possessed the best adsorption capacity, which may be considered as additional major reason for its highest photocatalytic activity. Alternatively, SrTiO₃ garden-like feature 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 sheets-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 (i.e., BaTiO₃ and CaTiO₃) and pyrochlore (Pb₂Ti₂O₇) 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), due primarily to their hierarchical architectures with enhanced diffusion and improved dye adsorption capacity.

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### Notes and references

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23. G. Xu, W. He, Y. Zhao, Y. Liu, Z. Ren, G. Shen and G. Han, *CrystEngComm*, 2011, **13**, 1498-1503.
The table of contents entry

Garden-Like Perovskite Superstructure with Enhanced Photocatalytic Activity
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Keywords: garden-like perovskite superstructures, hydrothermal process, photocatalysis

One sentence, of maximum 20 words, highlighting the novelty of the work:

Garden-like perovskite superstructures directly grown on transparent conducting substrates exhibited superior photocatalytic performance in photodegradation of MB dyes.