Hydrothermal synthesis of perovskite-type MTiO₃ (M = Zn, Co, Ni)/TiO₂ nanotube arrays from an amorphous TiO₂ template†

Xuming Zhang,a Biao Gao,b Liangsheng Hu,a Limin Li,a Weihong Jin,a Kaifu Huo*b and Paul K. Chu*a

Ordered perovskite-type MTiO₃/TiO₂ nanotube arrays (NTAs) (M = Zn, Co, Ni) are prepared by a general hydrothermal route based on amorphous TiO₂ NTAs via electrochemical anodization of Ti foil. The as-anodized amorphous TiO₂ is not stable and can react with H₂O in solution producing soluble Ti(OH)₆²⁻ to form anatase nanoparticles (NPs) via water-induced dissolution and recrystallization. The pH and salt content in the solution play important roles in the morphology and composition of the hydrothermal products. In the presence of a metal acetate, the reaction between Ti(OH)₆²⁻ and H⁺ is dramatically restricted and the reaction proceeds preferentially between Ti(OH)₆²⁻ and M²⁺ (M = Zn, Co, Ni) to produce insoluble MTiO₃ NPs which adhere onto the original architecture in situ to form perovskite-type MTiO₃/TiO₂ NTAs. This study elucidates the role of the amorphous structure in the formation of MTiO₃ and provides a general means of synthesizing nanostructured MTiO₃.

Introduction

One-dimensional perovskite-type titanates composed of titanium and alkaline earth or transition metals with a common formula of MTiO₃ (M = Ba, Sr, Ca, Co, Zn, Ni, etc.) have attracted much attention and found many applications in the nanoscale electronics and biomedical industry due to their excellent inherent chemical and physical properties such as photoelectricity, ferroelectricity, piezoelectricity, high dielectric constant, photorefractivity, as well as good biocompatibility.¹⁻⁷ Various techniques including sol–gel,⁸⁻¹⁰ molten-salt synthesis,¹¹ and solid-state reactions¹² have been proposed to fabricate nanostructured perovskite-type titanates. In addition, the hydrothermal route¹³–¹⁶ in the presence of an alkaline mineralizer and a template composed of nanostructured TiO₂ is a facile approach to synthesize nanostructured perovskite-type titanates with the original TiO₂ shape.¹³,¹⁷,¹⁸

Recently, vertically ordered TiO₂ NTAs prepared by anodization of Ti or Ti alloy foil have attracted increasing attention due to their high photocatalytic activity and excellent biological properties.⁵,¹⁹⁻²² The as-anodized TiO₂ NTAs are also good templates for the fabrication of perovskite-type titanate NTAs with excellent physicochemical properties.²³,²⁴ The morphological and structural parameters of the TiO₂ NTAs such as the tube diameter, length, and wall thickness can be controlled by adjusting the anodic voltage, temperature, processing time, and electrolyte composition.²² BaTiO₃, SrTiO₃, and CaTiO₃ nanostructures have been fabricated by hydrothermal treatment of crystalline TiO₂ NTAs in alkaline hydroxide solutions.⁵,¹⁴,²⁰ The principle of the hydrothermal reaction involves breaking the Ti–O bonds to form soluble Ti[OH]₆⁵⁻ species by hydroxy radicals (OH⁻) and then combining with metal ions to form the perovskite-type titanate. Unfortunately, since most of the transition metal hydroxides such as Zn(OH)₂, Co(OH)₂, and Ni(OH)₂ are insoluble, the amounts of Zn²⁺, Co²⁺ and Ni²⁺ are very small while the concentration of OH⁻ is high. It has been demonstrated that amorphous TiO₂ NTAs have higher chemical reactivity than crystalline TiO₂ NTAs.²⁵⁻²⁷ In our previous study,²⁸ the amorphous TiO₂ NTAs could gradually and spontaneously transform into anatase NPs and finally TiO₂ nanorod arrays (NRAs) composed of compact anatase NPs via water-induced dissolution and recrystallization at relative low hydrothermal temperature. Compared with crystalline TiO₂ NTAs, the amorphous TiO₂ NTAs are not stable in water and the unstable TiO₆²⁻ octahedra in amorphous TiO₂ first absorb water molecules via the surface hydroxyl groups to form soluble species of Ti(OH)₆²⁻, which can be further dehydrated and precipitated by bridging together and sharing faces to form crystal anatase TiO₂ NPs.²⁸,²⁹ This self-transformation process provides a novel method to fabricate perovskite-type titanate NTAs in neutral
solutions by inserting foreign metal ions into the octahedral TiO$_6$$^\text{−}$ group during dehydration.

Herein, we describe a novel means and investigate the mechanism to fabricate aligned transition metal (Zn, Co, Ni, etc.) perovskite-type titanate NTAs by hydrothermal treatment of amorphous TiO$_2$ NTAs with the corresponding metal acetate. The pH and salt content in the solution play important roles in the morphology and composition of the hydrothermal products. This promising route has great potential for producing different kinds of aligned MTiO$_3$ NTAs or other perovskite-type materials in the presence of a self-transforming amorphous template and suitable salts without surfactants under neutral conditions.

Experimental procedure

All chemicals and solvents used in this study were of analytical reagent grade and used as received without purification, and deionized (DI) water was used throughout the experiments.

Firstly, Ti foil (99.6% purchased from Aldrich) was cut into dimensions of 10 × 10 × 1 mm$^3$, polished with SiC paper, and ultrasonically cleaned in acetone, ethanol, and distilled water sequentially. A conventional two-electrode cell with a direct current (DC) power supply (IT6834, ITECH, China) was employed. Graphite foil and Ti foil served as the cathode and the anode, respectively. The highly ordered amorphous TiO$_2$ NTAs were fabricated at a constant voltage of 60 V for 1 h in an ethylene glycol solution containing 0.5 wt% ammonium fluoride (NH$_4$F) and 5 vol% DI water at room temperature. After anodization, the samples were rinsed with distilled water and dried in air. The as-anodized samples were first annealed at 200 °C and then ultrasonically cleaned for 10 min in water to remove residues from the Ti surface formed during anodization. The clean samples were immersed in 40 mL of aqueous solutions (containing different metal acetates) in a 60 mL Teflon-lined autoclave. The autoclave was sealed and heated in an oven to different temperatures for various time durations at a heating rate of 10 °C min$^{-1}$. After the hydrothermal reaction, the system was cooled to room temperature naturally. The foil was removed from the vessel, ultrasonically washed with DI water for 5 min, and dried in air. The samples were subsequently annealed at different temperatures for 3 h in air at a heating rate of 10 °C min$^{-1}$.

The samples were characterized using an X-ray diffractometer with Cu K$_\alpha$ radiation (λ = 1.5418 Å) (XRD, Philips X’Pert Pro), a field-emission scanning electron microscope (FE-SEM, FEI Nova 400 Nano) equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford INCA 200 attached to the FE-SEM instrument), a transmission electron microscope (TEM) as well as a high-resolution TEM (JEM-2010 F). The micro-Raman spectra were acquired on a Raman spectrometer (LabRam HR) at room temperature with a 514.5 nm argon laser in the range of 1000–150 cm$^{-1}$ with a resolution of 1 cm$^{-1}$.

Results and discussion

The ordered TiO$_2$ NTAs were fabricated by electrochemical anodization of Ti foil in an NH$_4$F-ethylene glycol solution. Fig. 1a–b depict the top-view and side-view field-emission scanning electron microscopy (FE-SEM) pictures of the as-anodized TiO$_2$ NTAs prepared at 60 V for 1 h, revealing uniform NTAs with an average inner diameter of 120 nm, a wall thickness of about 15 nm, and a length up to 6.8 μm. The transmission electron microscopy (TEM) image in Fig. 1c further reveals a tubular structure. The diffuse ring of the selected-area electron diffraction (SAED) pattern in the inset of Fig. 1c indicates the amorphous nature of the as-anodized NTAs. The glancing angle XRD pattern (GAXRD, glancing angle of 1°) acquired from the as-anodized NTAs shows no diffraction peaks of any TiO$_2$ phases, further confirming the amorphous nature of the as-anodized NTAs (Curve 1, Fig. 1d). The as-anodized amorphous NTAs can be crystallized into anatase TiO$_2$ NTAs (JPDCS no. 21-1271) by thermal treatment in air at 450 °C for 3 h (curve 2, Fig. 1d).

The as-anodized amorphous TiO$_2$ NTAs on Ti foil are not stable under hydrothermal conditions and gradually self-transform into the anatase phase spontaneously. During the self-transformation, the pH of the solution affects the recrystallization behaviour and morphology of TiO$_2$. Fig. 2 shows the FE-SEM images of the amorphous TiO$_2$ NTAs after hydrothermal treatment at 200 °C for 6 h at different pH values. In the HCl solution (pH = 3, Fig. 2a), NRAs composed of compact NPs with a large diameter of 80 nm are observed. In DI water (pH = 6.5, Fig. 2b), NRAs have geometrical dimensions similar to those of NTAs but some small NPs are formed. The corresponding XRD pattern of the NRAs in Fig. 2d shows sharp anatase TiO$_2$ diffraction peaks. The representative TEM image of a single NR suggests that NPs with a diameter of about 40 nm aggregate to form the NR. The high-resolution TEM image in Fig. 2f reveals single-
crystalline anatase TiO₂ consistent with the XRD results in Fig. 2d. By further increasing the pH to 11 (Fig. 2c), smaller NPs of 20–30 nm in diameter are observed on the surface and sections of the hydrothermal samples. These NPs are more compact and have a uniform shape compared to the product obtained at low pH. At higher pH (pH = 12.2, 0.02 M NaOH), the NRs are dissolved and nanosheets begin to form (Fig. S1†). The hydrothermal reaction can be visualized as a water-assisted dissolution and precipitation process between water molecules and amorphous TiO₂ NTA s. Initially, water molecules react with the amorphous TiO₂ to form soluble TiO₆²⁻ octahedra and then precipitation proceeds with the assistance of H⁺ forming anatase TiO₂. The overall reaction is described as follows:28

\[
\text{TiO}_x + 4\text{H}_2\text{O} + (1 - x/2)\text{O}_2 \rightarrow \text{Ti(OH)}_6^{2-} + 2\text{H}^+ (1 < x < 2) \quad (1)
\]

\[
\text{Ti(OH)}_6^{2-} + 2\text{H}^+ \rightarrow \text{TiO}_2\downarrow + 3\text{H}_2\text{O} \quad (2)
\]

As the hydrothermal reaction proceeds, the amorphous TiO₂ NRAs can be fully converted to anatase TiO₂ NRAs composed of anatase TiO₂ NPs. In this self-transformation process, the concentration of H⁺ plays a crucial role in controlling the growth of anatase TiO₂ NPs. Based on chemical eqn (1), the formation of Ti(OH)_6^{2-} can be promoted at high pH due to the combination of H⁺ and OH⁻. However, reaction (2) forming anatase TiO₂ from Ti(OH)_6^{2-} is prevented at a high pH value. Conversely, at low pH, the growth of anatase TiO₂ NPs is improved as a result of acceleration of reaction (2), thus forming larger TiO₂ NPs as shown in Fig. 2.

In an alkali solution, the perovskite-type titanate NTAs (Ba, Sr and Ca) can also be fabricated in the presence of amorphous TiO₂ NTAs and the corresponding alkaline mineralizer. (Fig. S2†) However, the amorphous TiO₂ NTAs collapse completely after the hydrothermal treatment in a neutral salt solution even at a high concentration, suggesting that reaction (2) is the dominant reaction in the recrystallization process. Thus, in order to precipitate perovskite-type titanate NTAs, reaction (2) should be controlled. A salt containing a transition metal and weak acid radicals, such as acetate, can be used. The weak acid radicals can combine with H⁺ to restrict the formation of TiO₂ NPs. On the other hand, the acetate salt provides various metal ion sources to promote the formation of different kinds of perovskite-type titanates. The hydrothermal reactions in the presence of amorphous TiO₂ NTAs and acetate can be described as follows:

\[
\text{M(Ac)}_2 \rightarrow \text{M}^{2+} + 2\text{Ac}^- \quad (3)
\]

\[
\text{Ac}^- + \text{H}^+ \rightarrow \text{HAc} \quad (4)
\]

\[
\text{Ti(OH)}_6^{2-} + \text{M}^{2+} \rightarrow \text{MTiO}_3\downarrow + 3\text{H}_2\text{O} \quad (5)
\]

where M is the metal source and Ac is the acid radical of acetate (CH₃COO⁻).

To fathom the role of acetate in the formation of perovskite-type titanates on the amorphous TiO₂ NTAs, the growth mechanism is investigated. Here, the acetates of Zn, Co and Ni were used to fabricate the corresponding perovskite-type titanates because of their excellent properties and, more importantly, there have been no reports about the fabrication of ZnTiO₃, CoTiO₃ and NiTiO₃ NTAs by hydrothermal treatment. Fig. 3a–c depict the morphological evolution...
of the samples hydrothermally treated at 200 °C for 6 h with
Zn(Ac)$_2$ solutions at different concentrations. In a 0.05 M
Zn(Ac)$_2$ solution (pH = 6.78), the FE-SEM image in Fig. 3a
indicates that the double layered NTAs consist of an inner
granular tube and an outer continuous skeleton. When the
concentration of Zn(Ac)$_2$ is increased to 0.2 M (pH = 6.41),
the NPs on the inner wall of the tube aggregate forming a
smooth tube with a thickness of about 16 nm. Eventually,
nanoporous arrays without boundaries are produced in 0.5 M
Zn(Ac)$_2$ (pH = 6.30), as shown in Fig 3b–c. The FE-SEM image
of the as-hydrothermal sample (Fig. 3b) indicates that the
length of the NTAs is about 7.0 μm without shrinkage
compared to the original amorphous TiO$_2$ NTAs, as shown in
Fig. 3d. After annealing at 450 °C for 3 h in air, the XRD
patterns of these samples in Fig. 3e exhibit the characteristic
diffraction peaks of ZnTiO$_3$ (JCPDS, 39-0190) at 2θ = 30.0°,
35.4°, and 62.4° (ref. 30 and 31) and the relative intensities of
the ZnTiO$_3$ peaks increase with Zn(Ac)$_2$ concentrations in the
hydrothermal solutions, but those of the anatase TiO$_2$ phase
peaks decrease significantly. The surface Raman spectra in
Fig. 3f reveal no significant structural change at 450 °C
except for anatase TiO$_2$ vibration bands at 198, 398, 516 and
638 cm$^{-1}$ (ref. 32) but at 750 °C, Raman shifts at 708, 611,
343, 446, 266, 231 and 176 cm$^{-1}$, assigned to the vibration
modes of ZnTiO$_3$, are observed.\(^{10,32}\) Despite the high
annealing temperature (750 °C), the tubular arrays are
preserved (Fig. S3†). However, the crystalline TiO$_2$ NTAs
hydrothermally treated with 0.2 M Zn(Al)$_2$ and amorphous
TiO$_2$ NTAs hydrothermally treated with 0.2 M ZnCl$_2$
cannot produce ZnTiO$_3$ NTAs as shown in Fig. S3,\(^{†}\)
suggesting that both the self-dissolved amorphous
structure and the weak acid radicals are important to the fab-
rication of MTiO$_3$ by producing soluble Ti(OH)$_6^{2+}$ and
controlling the deposited product.

Fig. 4 shows the morphological and structural evolution of
the amorphous TiO$_2$ NTAs hydrothermally treated with
Co(Al)$_2$ solutions at different concentrations. After the hydro-
thermal process in 0.05 M Co(Al)$_2$ (pH = 7.53), a rough tubu-
lar surface with many NPs up to 6.5 μm long can be observed
in Fig. 4a–b. In the 0.1 M Co(Al)$_2$ (pH = 7.43) solution, the
tubular structure is preserved. The average wall thickness is
about 40 nm and the length is 6.6 μm (Fig. 4c–d). When the
Co(Al)$_2$ concentration is increased to 0.2 M (pH = 7.30),
porous NTAs with a smooth surface and well-aligned tubular
structures from mouth to bottom are still observed (Fig. 4e–f).

The XRD patterns of these samples acquired after annealing
at 450 °C for 3 h in air show characteristic peaks of CoTiO$_3$
(JCPDS, 77-1373) and the relative intensities of the CoTiO$_3$
peaks are enhanced by increasing the Co(Al)$_2$ concentration
(Fig. 4g). The Raman spectra in Fig. 4h indicate that the surface structure is unstable until at a high annealing tem-
perature of 600 °C. The strong Raman peaks at about 705,
612, 463, 396, 344, 290, 245, and 192 cm$^{-1}$ correspond to vibrations of CoTiO$_3$ and the characteristic peak at 705 cm$^{-1}$
 stems from the high-frequency vibration mode (A$_{1g}$) of octahe-
dral CoO$_6$ (ref. 33) further confirming that the product is
CoTiO$_3$ in lieu of a mixture of CoO and anatase TiO$_2$. The
Raman results are in agreement with the XRD patterns.
However, when the hydrothermal reaction is carried out in
0.2 M Co(NO$_3$)$_2$ instead of in Co(Al)$_2$, a collapsed morphology
with a nanorod array shape is again observed (Fig. S4†).

Fig. 5 shows the morphological and structural evolution of
as-anodized amorphous TiO$_2$ NTAs produced by hydrother-
mal treatment at different temperatures in 0.2 M Ni(Al)$_2$
 (pH = 6.91) for 6 h. A higher or lower concentration of Ni(Al)$_2$
does not induce the formation of NTAs (Fig. S5†). After
hydrothermal treatment at 200 °C for 6 h, the tube diameter
shrinks as shown in Fig. 5a. By lowering the hydrothermal
temperature to 175 °C, a uniform NT structure (Fig. 5b) with
tube lengths up to 6.8 μm can be observed (Fig. 5d). When the
temperature is reduced to 150 °C, the NTAs are preserved,
as shown in Fig. 5c. The XRD pattern in Fig. 5e suggests that a minimum temperature of 175 °C is needed to form NiTiO$_3$.
The diffraction peaks are in good agreement with a rhombohedral lattice for NiTiO$_3$ (JCPDS no. 33-0960).\(^{3}\) In the range of
150–1000 cm$^{-1}$, the surface Raman spectra in Fig. 5f reveal
an unstable structure unless the annealing temperature is
over 600 °C. The strong broad band at 770 cm\(^{-1}\) can be assigned to the stretching vibrations of TiO\(_6\) in NiTiO\(_3\) and several bands at around 705, 347, 290, and 240 cm\(^{-1}\) correspond to the rhombic structure of NiTiO\(_3\). Similarly, the NTAs collapse when the acetate is replaced by neutral salts after the hydrothermal treatment (Fig. S5†).

Based on the above experimental results, the mechanism pertaining to the formation of the MTiO\(_3\) nanostructures on the amorphous TiO\(_2\) NTAs is illustrated in Scheme 1. Under non-alkaline hydrothermal conditions, the water molecules or salts with weak acid radicals cannot react with the crystalline TiO\(_2\) NTAs due to the stable chemical bonds in anatase TiO\(_2\). Thus, a metal hydroxide solution is needed during the hydrothermal process in order to form MTiO\(_3\). However, using the as-anodized amorphous TiO\(_2\) NTAs, water molecules can react with the amorphous TiO\(_2\) to form soluble Ti(OH)\(_6\)^{2−}. Then, Ti(OH)\(_6\)^{2−} reacts with H\(^+\) swiftly leading to the precipitation of anatase TiO\(_2\) NPs. To control the behaviour of H\(^+\) by using the salt containing weak acid radicals, the reaction between Ti(OH)\(_6\)^{2−} and H\(^+\) is restricted due to the consumption of H\(^+\) by the weak acid radicals. Therefore, the reaction between Ti(OH)\(_6\)^{2−} and M\(^{2+}\) is promoted resulting in the production of insoluble MTiO\(_3\) NPs on the wall of the tubular structure.

**Conclusion**

Ordered perovskite-type MTiO\(_3\)/TiO\(_2\) (M = Co, Zn, Ni) NTAs are fabricated hydrothermally using highly oriented amorphous TiO\(_2\) NTAs as the template and metal acetates as the metal source. During the hydrothermal process, the amorphous TiO\(_2\) NTAs easily self-transform into crystalline TiO\(_2\) by water-assisted dissolution and precipitation and the size of the TiO\(_2\) NPs decreases with increasing pH (<12.2). By introducing the acetate to combine with H\(^+\) preferentially depending on the weak acid radicals, perovskite-type MTiO\(_3\) NPs are precipitated on the original tubular wall and form MTiO\(_3\)/TiO\(_2\) NTAs. The result provides a new method to fabricate perovskite-type MTiO\(_3\) without an alkaline mineralizer and insight into the role of the amorphous structure in the fabrication of perovskite-type materials in the hydrothermal process.

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**Notes and references**


**Fig. 5** Low- and high-resolution FE-SEM images of samples hydrothermally treated at different temperatures for 6 h with 0.2 M Ni(AC)\(_2\): (a) 200 °C, (b) 175 °C, and (c) 150 °C. (d) The corresponding SEM image of (b). (e) XRD patterns of the samples (1-c, 2-b and 3-a) after annealing at 450 °C for 3 h in air. (f) Raman spectra of (b) at different annealing temperatures.