



Short communication

# Citric acid as complexing agent in synthesis of mesoporous strontium titanate via neutral-templated self-assembly sol–gel combustion method

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## ABSTRACT

In the present work, mesoporous SrTiO<sub>3</sub> (MST) nanoparticles were synthesized via a self-assembly sol–gel combustion method using a commercial non-ionic triblock copolymer (Pluronic P123) as a structure-directing agent. The effect of adding citric acid as a metal-ion complexing agent on the formation of crystalline SrTiO<sub>3</sub> with enhanced surface area and mesoporosity was investigated. Simultaneous thermal analysis and powder X-ray diffraction indicated that the citric acid added to the synthesis mixture enhances the formation of high-purity perovskite SrTiO<sub>3</sub> crystallites. The MST synthesized in the presence of both Pluronic P123 and citric acid (MST-C) possessed higher surface area (41.5 m<sup>2</sup> g<sup>-1</sup>) and larger pore volume (0.20 cm<sup>3</sup> g<sup>-1</sup>) than materials synthesized without the addition of either citric acid or the templating agent. The SrTiO<sub>3</sub> crystals of MST-C shared edges and corners to form globular agglomerates with accessible mesopores revealed by electron microscopy. Results suggest that the mesoporous structure is generated via a hard template route.

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## 1. Introduction

Strontium titanate (SrTiO<sub>3</sub>) is a well-known cubic-perovskite-type multimetal oxide that has been used in various photocatalysis applications [1,2] because of its high activity [2] and high chemical, structural, and thermal stability [3]. The conventional SrTiO<sub>3</sub> synthesis method involves a solid-state reaction wherein SrCO<sub>3</sub> and TiO<sub>2</sub> powders are mixed and calcined at 1200 °C [4]. This method not only consumes a massive amount of energy but also results in particle-size non-uniformity and compositional inhomogeneity [4]. Several synthesis methods such as the hydrothermal technique [2], sol–gel method [5], combustion method [6], and sol–gel combustion method [7] have been studied in an attempt to improve the physicochemical properties of SrTiO<sub>3</sub>. The sol–gel combustion method appears promising as a route to prepare a high-purity

mixed oxide [7]. Citric acid as a reducing agent and fuel was added to a mixed-metal precursor solution to induce the redox reaction with nitrate anions. Then, the generated exothermic heat facilitated the formation of SrTiO<sub>3</sub> nanoparticles at relatively low calcination temperatures [7]. However, the SrTiO<sub>3</sub> attained by all of these methods exhibited low specific surface area (<5 m<sup>2</sup> g<sup>-1</sup>) [2,5] and porosity [5–7].

In the past few decades, mesoporous materials have attracted considerable attention because of their large surface area and high porosity, which are advantageous in various applications [8,9]. Assembled mesoporous SrTiO<sub>3</sub> materials with a specific surface area of 9–28 m<sup>2</sup> g<sup>-1</sup> were synthesized via a sol–gel method with the aid of low-molecular-weight ionic surfactants as structure-directing agents [1]. Grosso et al. successfully synthesized a mesostructured crystalline SrTiO<sub>3</sub> thin film via an evaporation-induced self-assembly method using a specially designed non-ionic block-polymer (PBH<sub>79</sub>-*b*-PEO<sub>89</sub>; PBH = hydrogenated polybutadiene, PEO = poly[ethylene oxide]; KLE3739) as a molecular self-assembly template [10]. The KLE polymer possessed relatively high thermal stability that maintained the nanoarchitecture of the mesophase during SrTiO<sub>3</sub> crystallization

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at high temperatures [10]. However, the use of commercial non-ionic block copolymers as structure-directing agents in the fabrication of mesostructured mixed oxides is more attractive because of their availability and low cost. Yang et al. used a triblock copolymer Pluronic P123 ( $\text{PEO}_{20}\text{-}b\text{-PPO}_{70}\text{-}b\text{-PEO}_{20}$ ; PPO = poly[propylene oxide]) as a neutral template in the synthesis of various mesoporous mixed oxides via a sol–gel method in a non-aqueous solution [11]. Nevertheless, the mesoporous materials attained only had amorphous frameworks, which collapsed during the thermal crystallization process due to mesostructures assembled by weak interactions [11].

In this work, we synthesized mesoporous  $\text{SrTiO}_3$  nanoparticles via a self-assembly sol–gel combustion method using Pluronic P123 for neutral-templating molecules. The effect of adding citric acid as the metal-ion complexing agent and fuel in the combustion step during the formation of crystalline  $\text{SrTiO}_3$  with enhanced surface area and mesoporosity was investigated. The synthesis of mesoporous Sr and Ti mixed oxides, with the aid of both Pluronic P123 and citric acid, via the sol–gel combustion route has never been reported to the best of our knowledge.

## 2. Experimental

### 2.1. Chemical reagents

Tetrabutyl titanate (TBT; AR grade, 97%), strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ; AR grade, 99%), citric acid (AR grade, 99%), and super-dehydrated ethanol (AR grade, 99%) were purchased from Wako. Pluronic P123 (AR grade) and hydrochloric acid (HCl; AR grade, 37%) were purchased from Sigma–Aldrich. All reagents were used without prior purification.

### 2.2. Synthesis of mesoporous $\text{SrTiO}_3$ (MST) materials

Typically, 1 g of Pluronic P123 was completely dissolved in 12 g of super-dehydrated ethanol. A mixture of TBT (10 mmol) and HCl (16 mmol) was then added to this solution under vigorous stirring at room temperature. The resulting yellowish solution was mixed with an aqueous solution containing  $\text{Sr}(\text{NO}_3)_2$  (10 mmol) and citric acid (20 mmol). A clear solution was attained after vigorous stirring for 3 h. The solution was aged in an oven at 100 °C overnight to obtain a yellow dry gel, followed by calcination in a muffle furnace at 600 °C for 4 h. The white powder obtained is denoted as MST-C. To compare the effect of citric acid addition on the physicochemical properties of resulting materials, the synthesis of MST in the absence of citric acid was carried out using the same procedure and molar composition, similar to the case of MST-C but without adding citric acid. The material obtained is designated MST-N.

### 2.3. Materials characterization

Thermal decomposition of as-synthesized MST materials was investigated with a NETZSCH STA 449 F3 simultaneous thermal analyzer (STA) operating from room temperature to 1000 °C at a heating rate of 8 °C  $\text{min}^{-1}$  under a dry air flow of 50  $\text{mL min}^{-1}$ . Powder X-ray diffraction (XRD) determined the crystalline structure of MST materials before and after the calcination. The XRD patterns were recorded at room temperature on a Rigaku Ultima III X-ray diffractometer equipped with  $\text{Cu K}\alpha$  radiation at 40 kV voltage and 40 mA current. Textural properties of MST materials were determined by physisorption of nitrogen ( $\text{N}_2$ ) at  $-196$  °C using a BEL Japan BELSORP-mini II instrument. The calcined sample was precisely weighed after pretreatment at 300 °C for 2 h in a vacuum. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation, and the relative pressure

( $P/P_0$ ) ranged from 0.05 to 0.1. Pore size distribution was calculated from the adsorption branch of physisorption isotherms using the Barrett–Joyner–Halenda (BJH) method. Morphology of MST nanoparticles was studied by scanning transmission electron microscopy (STEM) using a Hitachi S-5200 electron microscope. Transmission electron microscopy (TEM) images were recorded on a JEOL 2010 transmission electron microscope operating at a 200 kV accelerating voltage. The powder samples for STEM and TEM were examined without a metal coating.

## 3. Results and discussion

Thermal decomposition profiles of MST-N and MST-C are shown in Fig. 1. Weight loss of MST-N and MST-C occurred in multiple stages. The first endothermic peak below 120 °C corresponded to loss of moisture. MST-N exhibited a second weight loss centered at 164 °C. This endothermic change was ascribed to the loss of water from  $\text{Sr}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , as a crystalline phase was observed for the as-synthesized MST-N (Supplementary information S1: Figure S1). Combustion of template molecules occurred in the range of 320 °C–360 °C [12]. The next weight loss with large exothermic changes between 380 °C and 580 °C could be divided into 2 steps. The exothermic change in the range of 380 °C–500 °C was attributed to the formation of crystalline phases, such as  $\text{SrCl}_2$ ,  $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ , and  $\text{SrTiO}_3$ , as evidenced by the XRD analysis of MST-N calcined at

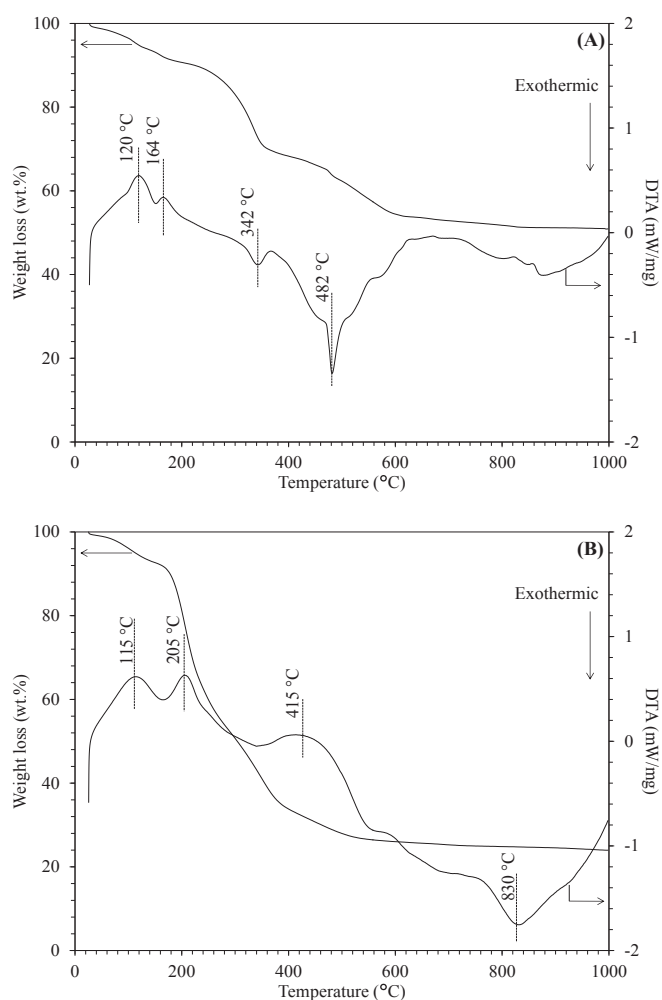


Fig. 1. Weight loss and DTA curves of as-synthesized (A) MST-N and (B) MST-C.

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