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Short Communication

Virus-templated visible spectrum active perovskite photocatalyst

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ABSTRACT

In this study, photocatalytically active perovskite strontium titanate ($SrTiO_3$) nanowires are fabricated for the first time using genetically engineered AEEE-M13 phage and metal alkoxide precursors. One newly developed doping approach with an ammonia gas treatment efficiently produced strontium titanate nanowires, which split water and produce hydrogen under visible-light irradiation. The optical absorption of nitrogen-doped strontium titanate can be tuned by varying the processing conditions and lies in the visible spectrum range when treated at 625 °C–650 °C. The excellent hydrogen evolution rate of these nanomaterials is correlated with both optical absorption and nitrogen doping level.

1. Introduction

In recent years, there have been significant advances in applying biological systems for the synthesis of natural minerals with control of morphology and crystal structure [1–3] as well as the preparation of non-natural materials [4,5]. M13 bacteriophage is a widely studied and versatile template for the synthesis of nanomaterials and manufacture of nanodevices [6–8] since it can be genetically engineered and has a unique morphology. Furthermore, genetically engineered M13 virus has been successfully exploited as a bio-scaffold to fabricate metal, metal alloy, and semiconductor nanowires [8]. Perovskite materials including strontium titanate and bismuth ferrite have photocatalytic properties. In our recent work [9], M13-virus-templated perovskite nanowires have been fabricated and demonstrated to show hydrogen production and photovoltaic behavior under solar irradiation. Although virus-templated strontium titanate nanowires show a hydrogen evolution rate ten times higher than free strontium titanate and titania nanoparticles under UV irradiation, its performance under visible-light irradiation is lacking due to a large band gap.

To utilize strontium titanate for water splitting under visible-light irradiation, band gap engineering approaches including metal ion doping have been applied [10]. Sayama et al. [11,12] and other groups [13–15] studied the H_2 evolution using a $SrTiO_3$ (Cr–Ta-doped) photocatalyst and an I^- electron donor. In this study, the authors considered that the Cr^{3+} and Ta^{5+} ions were applied to substitute Ti^{4+} atom rather than Sr^{2+} atom (radii of Sr^{2+}: 1.32 Å) since the ionic radii of both Cr^{3+} (0.76 Å) and Ta^{5+} (0.78 Å) are close to that of Ti^{4+} (0.75 Å) in the strontium titanate. Konta et al. [16] explored the photocatalytic activity of $SrTiO_3$ doped with metal ions including Mn, Ru, Rh, and Ir. The doped strontium titanate demonstrated photocatalytic activities for O_2 evolution from an aqueous silver nitrate solution, and Ru-, Rh-, and Ir-doped $SrTiO_3$ loaded with Pt-cocatalysts produced H_2 from an aqueous methanol solution under visible-light irradiation ($\lambda > 440$ nm). In addition, nitrogen, carbon, sulfur, fluorine, and boron anions are applied to dope the metal oxide photocatalysts, including TiO_2, TaON, etc., and create a visible-light active photocatalyst. Furthermore, in this doping, nitrogen replaces the oxygen atom in the TiO_2 lattice and creates a new intermittent level. Since nitrogen doping leads to fewer recombination centers and no significant *d* state formation within the band gap, it efficiently enhances the photocatalytic activity of titania [17].

Therefore, in our research, strontium titanium precursor prepared with n-butanol and isopropanol was applied for growth of strontium titanate nanowires for the first time using AEEE-engineered M13 virus as a bio-scaffold. We further investigated the doping of strontium titanate nanowires with ammonia and evaluated the photocatalytic performance of these nanowires under visible-light irradiation. This communication discusses the biotemplated synthesis of ternary perovskite minerals as well as the characterization of these perovskite for solar energy applications.

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2. Experimental

2.1. Materials

Strontium titanium alkoxide ($SrTi(OR)_6$) was purchased from Gelest, Inc.. The ammonia-gas tank was purchased from Air Gas.

2.2. Virus template-assisted synthesis of $SrTiO_3$

$SrTiO_3$ nanowires were synthesized by the addition of $SrTi(OR)_6$ precursor to genetically engineered M13 viruses in aqueous solutions(Fig. 1a). In the synthesis, 0.2 ml of the precursors was first mixed with 10^{11} pfu/ml of E3 virus solution, which in following was adjusted to pH neutral by titrating with sodium hydroxide. Then the sodium hydroxide was further added to the pH neutral solution to keep a 2:1 molar ratio of sodium hydroxide to titanium ions. It was then heated at 80 °C for 4 h.

2.3. Ammonia treatment of $SrTiO_3$

As shown in Fig. 2c, the samples were sintered at 600 °C, 625 °C, 650 °C, and 700 °C in a tube furnace under an ammonia gas atmosphere. The ramp rate was 5 °C/min, and the flow rate of ammonia was 200 ml/min. The hold time was 4 h, and the temperature was varied between trials.

2.4. Characterization

The absorption of these powders was measured by a Cary 5000 Scan UV-Vis-diffusive reflectance spectrophotometer in the wavelength (λ) range of 190–2000 nm.

X-ray photon spectroscopy (XPS) was utilized to investigate the nitrogen doping level of the strontium titanate nanomaterials. The crystalline structure was confirmed by X-ray powder diffractometer (XRD) (a Rigaku (50 kV, 200 mA)) (Fig. 2d). The nanowire microstructure was studied with transmission electron microscopy (TEM) (JEOL 200CX). The Zeta-potential measurement was performed as described in [9].

2.5. Photoelectrochemistry measurements

Hydrogen evolution test: the experimental procedure was described in [9]. All tests were conducted under visible-light irradiation using a 400-nm UV cutoff filter. Briefly, 60 ml of a mixture of methanol and water (volume ratio 1:1.4) containing 0.05 g of strontium titanate was purged with Argon, then 250 μl of gas was tested using Gas chromatography before and after irradiation

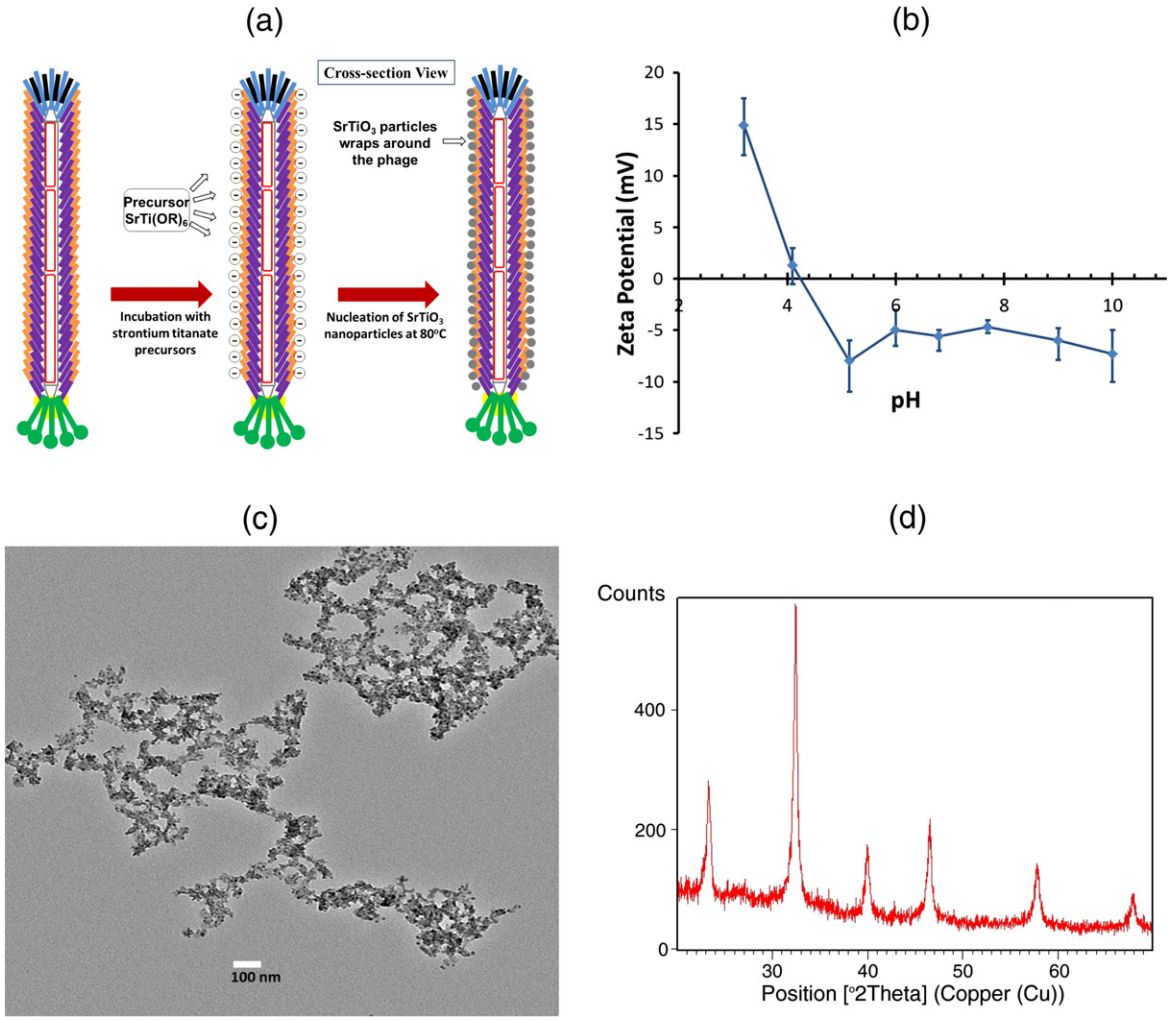

Fig. 1. (a) Schematic description of M13 virus-assisted synthesis of strontium titanate nanowires. Carboxyl acid groups on the surface of virus electrostatically interact with $SrTi(OR)_6$. At 80 °C, $SrTiO_3$ was formed on the viruses. (b) Zeta potential curve of AEEE-M13 virus. (c) TEM micrograph of strontium titanate template M13 virus (scale bar: 100 nm). (d) XRD spectrum of M13 virus template strontium titanate nanowires.