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One-pot synthesis of high aspect ratio titanium dioxide nanorods using oxalic acid as a complexing agent

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ABSTRACT

We report the novel one-pot synthesis of high aspect ratio titanium dioxide (TiO_2) nanorods using a simple hydrothermal technique. Specifically, oxalic acid and sodium hydroxide (NaOH) were used as additives to promote the conversion of titanium tetraisopropoxide (TTIP) into a one-dimensional TiO_2 morphology. All resultant products were characterized by X-ray powder diffraction and scanning electron microscopy. Influential factors on the growth mechanisms of TiO_2 nanorods are discussed. This approach contrasts the typical approach of using spherical TiO_2 as a starting material in the fabrication of one-dimensional TiO_2 structures, and instead allows for the direct synthesis of TiO_2 nanorods from TTIP precursors.

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1. Introduction

Titanium dioxide (TiO_2), or titania, is a wide bandgap semiconductor material that is inexpensive, chemically stable, and has negligible absorption in the visible region [1]. A particularly intriguing property of this material is its tendency to generate electron–hole pairs upon irradiation with UV light. This process provides a means of inducing chemical reactions at the surface of the material. Hence, TiO_2 is often utilized as a photocatalyst, an electrode in dye-sensitized solar cells, as a gas sensor, and as a decontamination agent [2–7].

The generation of electron–hole pairs and the subsequent transport of charge through the particle network are significant factors in determining whether or not TiO_2 is an efficient catalyst or electrode [8]. The efficiency of titania as a catalyst or electrode is maximized when charge transport is significantly faster than hole–charge recombination. For example, when TiO_2 is used as an electrode in dye sensitized solar cells, charge transport has been found to be highly dependent on the morphology associated with the particle network, *i.e.* the number of inter-particle connections, or the lack thereof, can lead to hole–charge recombination [9]. One approach to mitigating insufficient inter-particle connections has been the use of one-dimensional TiO_2 nanostructures, which maximize charge transport along the major dimension. Typical approaches used to synthesize TiO_2 nanorods include electrochemical anodization [10–13], hydrothermal synthesis [14,15], and template-assisted synthesis [16,17].

Hydrothermal synthesis, in particular, has been found to be a highly versatile approach to fabricating various types of nanocrystals. This technique is scalable and provides experimental control of temperature within the pressurized vessel. Numerous attempts to fabricate TiO_2 nanorods and nanotubes have been reported using this technique. These approaches primarily involve the treatment of pre-synthesized TiO_2 nanoparticles with sodium hydroxide (NaOH), resulting in the formation of lamellar sheets via the rupture of Ti–O–Ti bonds [18]. Subsequent washing steps with water and acid, which remove the electrostatic charge within the sheets, were found to lead to the formation of nanotubes and nanorods. For example, Zhang et al. previously demonstrated a simple chemical/hydrothermal approach to fabricating TiO_2 nanowires with diameters from 30 to 45 nm and lengths of several micrometers [19].

In conjunction with the hydrothermal approach, several additives have also been explored as a means of inducing the formation and elongation of TiO_2 nanotubes, nanorods, and nanowires during the hydrothermal process. These additives include oleic acids, oleylamine, and tetraalkylammonium cations [20–22]. Recently, oxalic acid has been explored as a means of complexing with metal cations while also promoting the formation of linear

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crystal structures in other metal oxides, including MgO and WO_3[23–24]. Specifically, in the work by Mastuli et al., it was postulated that the formation of a metal cation–oxalate complex precedes the subsequent formation of a linear polymer network of $Mg–C_2O_4$, before forming the eventual MgO nanowires. Dambournet et al. also exploited this fact and demonstrated the use of oxalate anions to complex with titanium atoms, which yielded titanium oxalate hydrate, Ti_2O_3 $(H_2O)_2$ $(C_2O_4)\cdot H_2O$ [25]. Upon annealing at 300 °C, egg shaped TiO_2 particles were obtained. A metal:oxalate ratio of 1:2, was determined to be optimal for the formation of rutile crystals in this study. To our knowledge, the use of oxalic acid has not been explored in the formation of TiO_2 nanorods via the complexation of Ti^{4+} with C_2O_4. Hence, in this manuscript, we describe our attempts and results in utilizing oxalic acid as a means of forming linear crystals of TiO_2 during a one-pot hydrothermal synthesis.

2. Experimental section

Oxalic acid, titanium tetraisopropoxide (TTIP), and sodium hydroxide pellets (NaOH) were obtained from Sigma Aldrich, Alfa Aesar, and Fisher Scientific, respectively. Additionally, 18.2 MΩ deionized water, obtained from a Millipore Direct-Q 5 system, was used in all experiments.

In a typical synthesis, titanium oxalate was first prepared by reacting TTIP with 0.364 M oxalic acid (aq) in a 1:2 M ratio. Next, while magnetically stirring, 16 g of NaOH pellets were slowly added to a 125 mL Teflon-lined stainless steel autoclave containing 40 mL of the titanium oxalate solution. After ten minutes of continuous stirring, the NaOH was fully dissolved and a gel-like consistency was observed. Next, the reaction vessel was tightly sealed and placed in an oven for 48 h at 150 °C. Upon cooling, the product was sequentially rinsed with 1.0 L of 0.1 M HCl and 1.0 L of H_2O. Finally, the washed product was dried at 100 °C for 12 h yielding TiO_2 nanorods. All products were placed in a porcelain crucible and annealed in air, in a muffle furnace at temperatures ranging from 300 to 1100 °C.

Powder X-ray diffraction (XRD) patterns of the products were recorded on a Panalytical X'Pert Pro diffractometer with Xcelerator, using Cu Kα radiation ($\lambda = 1.5406$Å) at 45 kV and 40 mA. Scanning electron microscopy (SEM) images of the products were obtained using a JEOL JCM-5700 Scanning Electron Microscope. Samples were supported on double-sided carbon tape and sputter coated with gold prior to analysis. The instrument was operated in high vacuum mode using accelerating voltages of 2–15 kV at nominal working distances of 7–12 mm. Elemental analysis was also performed using energy-dispersive X-ray spectroscopy (EDX), which was an accessory to the JEOL JCM-5700 SEM.

3. Results and discussion

High-aspect ratio nanorods with an average diameter of 160 nm and a major dimension ranging from 5 to 40 μm were formed using a one-pot synthesis containing TTIP, oxalic acid, and sodium hydroxide, as shown in Fig. 1A. Numerous experimental controls were subsequently conducted. First, NaOH was omitted from the reaction vessel, while keeping all other experimental parameters the same. This experiment yielded spiked spherical particles as demonstrated in the SEM image shown in Fig. 1B. A second experimental control involved the omission of oxalic acid from the reaction vessel, while keeping all other experimental parameters the same (*i.e.* NaOH was present). This experiment yielded shorter nanorods as demonstrated in Fig. 1C. Inspection of the experimental parameters used to generate Figs. 1A–C indicate that NaOH is a prerequisite for the formation of rod shape morphologies, while oxalic acid in conjunction with NaOH is required to further elongate the rods. As an additional control, we explored the omission of both oxalic acid and NaOH from the reaction vessel. This experiment yielded spherical and largely amorphous particle morphologies, as demonstrated in the SEM image shown in Fig. 1D. This result confirmed the impact of both NaOH and oxalic acid on inducing non-spherical geometries. Finally, as additional controls, we explored the impact of reaction vessel temperature, both in the presence and absence of both oxalic acid and NaOH. When oxalic acid and NaOH were present, an ambient reaction temperature interestingly yielded

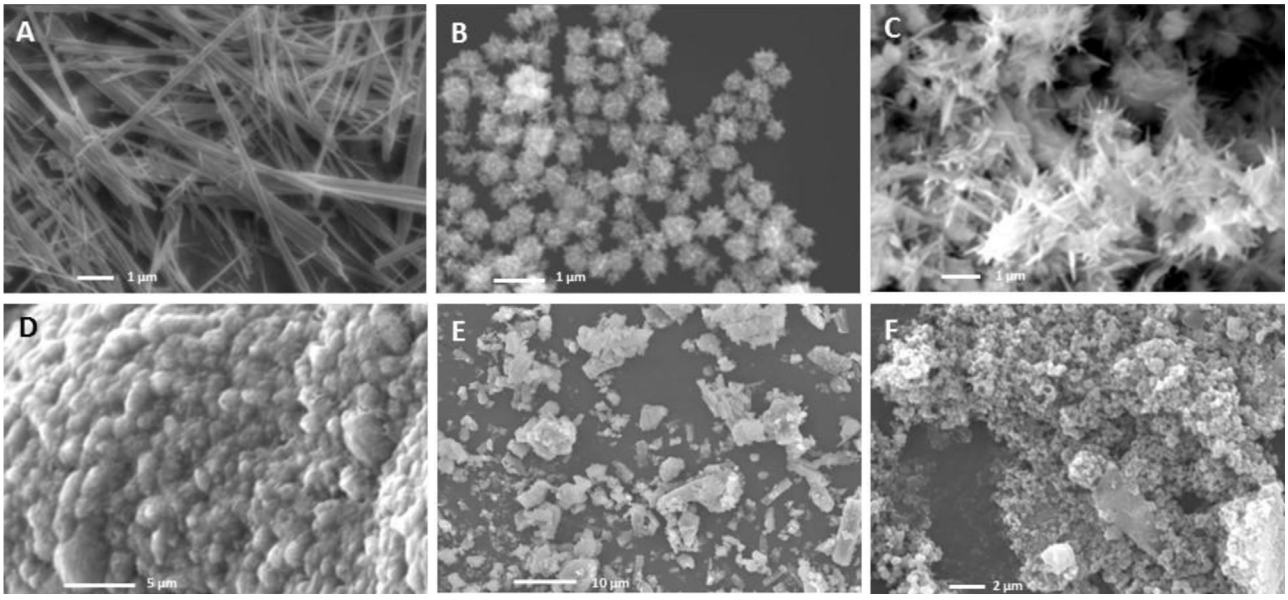

Fig. 1. SEM images of TiO_2 particles obtained in various experiments at 150 °C (unless otherwise stated) for 48 h. (A) High aspect ratio TiO_2 nanorods were obtained when oxalic acid, NaOH, TTIP, and H_2O were present; (B) TiO_2 spiked spheres were obtained when oxalic acid, TTIP, and H_2O were present; (C) Short TiO_2 nanorods were obtained when NaOH, TTIP, and H_2O were present; (D) Amorphous TiO_2 was obtained when only TTIP and H_2O were present; (E) TiO_2 flakes/plates were obtained when oxalic acid, NaOH, TTIP, and H_2O were present and when the reaction was performed at RT; and (F) TiO_2 porous matrix was obtained when TTIP and H_2O were present, when the reaction was performed at RT.