

Fabrication of TiO₂ Microrod with Desired Shapes from Rod-like Titanium Glycolate

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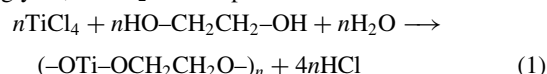
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Rod-like titanium glycolate was prepared by poly-condensation of TiCl₄, ethylene glycol, and water. Focusing electronic beam on one side of a titanium glycolate microrod led to bending of the micro-rod at the irradiation part. Calcination of the polymer results in formation of rod-like titania. By controlling irradiation time and changing focus position of electronic beam, we realized controllable processing of titania microrod with desired shapes, which may be find application in nano or microdevices.

One-dimensional (1D) nanoscale materials, such as, nanotube, nanorod, nanowire, and nanobelt, have stimulated great interests recently because of their unique electronic, optical, and mechanic properties.¹⁻⁴ For their application in nano electronic and optical device, such as, constructing nano circuit or optical waveguide,⁵ it is desirable and of great challenge to process nanowire or nanorod to desired shape. However, it is very difficult to achieve such target for inorganic nanowires or nanorods due to their fragility. Titania (TiO₂) has been received much attention because of its unique physicochemical properties in wide-ranging applications.⁶⁻¹⁰ Here, we developed a novel strategy to fabricate titania microrod with desired shape. The strategy included three steps as follows: first, we prepared rod-like polymer of titanium glycolate. Then, a polymer rod was processed to certain shape by electronic beam. Finally, rod-like titania with desired shape was obtained by calcination of the polymer.

Microscale rod-like titanium glycolate was prepared according to the following procedure. 1 mL of TiCl₄ was added to 25 mL of ethylene glycol (contained 0.5% H₂O) in a flask. The obtained mixture was heated to 176 °C under magnetic stirring, and kept at this temperature until a large amount of white precipitate was formed. After cooling to ambient temperature, the white precipitate was filtered, washed by acetone for several times, and finally dried at 80 °C for 12 h. The obtained white powder can not dissolve in conventional organic solvents, such as, ethylene glycol, acetone, *N,N*-dimethylformamide, dimethyle sulfoxide, etc. TG-DSC analysis shows that the powder keep stable below 200 °C except for releasing of 8.9% adsorbed H₂O (Figure S1).¹¹ When temperature increased to 286 °C, it was oxidized by air with a weight loss of 26.9%, accompanying by a very strong exothermic peak. Further increasing of temperature to 600 °C, residue carbons are completely burned, accompanying by a weight loss of 8.6%. The elemental analysis shows that the powder contains 19.0 wt % C and 4.2 wt % H. After deducting the contribution of the adsorbed H₂O, the atomic ratio

of C and H is 1:2 in the polymer. XPS results show that the powder has an atomic ratio of 1:2:3 among Ti, C, and O after the adsorbed water was removed by high vacuum desorption followed by Ar⁺ sputtering. Therefore, it was deduced that the polymer itself has an atomic composition of TiC₂H₄O₃, which is in agreement to results by thermal analysis. FT-IR experiment (Figure S2)¹¹ shows that the powder has several absorption peaks in the range of 632–497 cm⁻¹, and a strong absorption at 917 cm⁻¹, which are probably assigned to Ti–O bonds and Ti=O bond, respectively.¹² As compared to the FT-IR spectra of ethylene glycol, the reaction between TiCl₄ and ethylene glycol leads to greatly decreasing of the intensity of stretching vibration of –OH bond (3320 cm⁻¹), but the symmetric and asymmetric –CH₂– stretching vibrations (2879 and 2946 cm⁻¹), and stretching vibrations of the O–C bond (1086 cm⁻¹) remain unchanged after the reaction except for a red-shift of 19 and 29 nm for the former and the latter bonds, respectively. The red-shifts are most probably contributed to electronic effect because of the lower electronic negativity of Ti atom than H atom. In addition, HCl is detected during the reaction. These results indicate that a polycondensation reaction between TiCl₄, ethylene glycol, and H₂O takes place as follows:



Xia et al. prepared titanium glycolate nanowire by heating a solution of titanium tetrabutoxide in ethylene glycol. It has a chain-like complex structure of [–Ti(OCH₂CH₂OH)₂–OCH₂–CH₂O–]_n, in which two ethylene glycol molecules chelate with each Ti atom in the polymeric chain of [–Ti–OCH₂CH₂O–]_n.¹³ In this paper, using TiCl₄ together with a small amount of water instead of titanium tetrabutoxide results in the formation of new titanium glycolate compound with polymeric chain of [–OTi–OCH₂CH₂O–]_n.

Figure 1 shows SEM and TEM images of the titanium glycolate. It has rod-like morphology with sizes of 1–3 μm by 10–30 μm (Figure 1a). It can be seen from the TEM image of the axial edge of a single polymer microrod that it is built up of 2–4 nm nanoparticles (Figure 1b). The result of XRD (Figure S3)¹¹ shows that the polymer has a crystalline structure. The polymer exhibits a UV–vis spectrum pattern similar to the rod-like titania, but it shows stronger absorption with a blue shift of absorption edge (Figure S4a).¹¹ The plot of transformed Kubelka–Munk function vs. the energy of light affords band gap of 3.34 eV for the polymer (Figure S4b).¹¹ The polymer may be directly used as a new UV absorbent instead of titania,

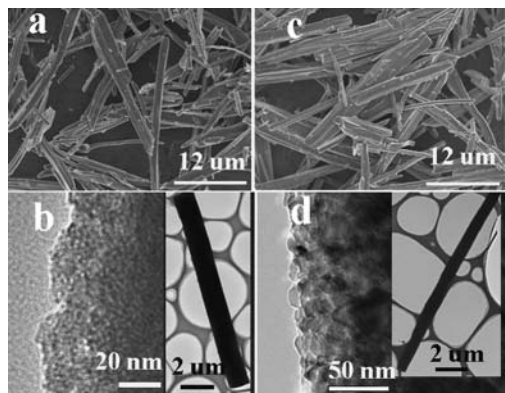


Figure 1. SEM and TEM images of titanium glycolate: (a), (b), inset: single polymer rod, and titania: (c), (d), inset: single titania rod.

one of best UV absorbent, due to its high UV absorption, thermal stability, low photocatalytic activity (Figure S5),¹¹ and compatibility to organic compound.

We used the polymer as starting material to prepare titania by temperature-programmed calcination in air, which is similar to the procedure reported by Wang et al.¹⁴ FT-IR confirms that organic moieties were completely removed after the polymer was heated to 480 °C at a rate of 1 °C/min, and kept at the temperature for 2 h. The result of XRD shows that the obtained titania has a crystalline structure of pure anatase (Figure S3).¹¹ N₂ adsorption experiment shows that it has BET surface area of 33 m²/g. As shown in Figure 1c, the rod-like morphology of the polymer keeps unchanged after calcination. The obtained rod-like titania has sizes of 1–3 μm by 10–25 μm. TEM image of the axial edge of a single titania rod (Figure 1d) shows that it is built up of 6–20 nm nanoparticles stacked closely together. The nanoparticles have preferential orientation (100) with interplanar spacing of 0.352 nm (Figure S6),¹¹ which matches very well to the value calculated by XRD.

It is well known that polymer could be easily processed by different methods (e.g. thermal, mechanic, etc.) to desired shapes because of its rheology and flexibility. As the morphology of the glycolate polymer remained unchanged after calcination, we could obtain rod-like titania with different shapes if we firstly process the rod-like polymer to desired shapes. To do so, we covered a SEM stage with aluminum foil, and then dispersed the polymer on the foil. After that, the stage was put into the chamber of a SEM instrument. Electronic beam was focused on the one side of a polymer rod. The thermal effect caused by electronic beam led to bending of the polymer rod at the irradiation part. After irradiating for known time, the SEM stage was transferred to a muffle furnace for calcination (480 °C, 2 h). After cooling to ambient temperature, the SEM stage was transferred to the chamber of a SEM instrument for another observation. As shown in Figure 2a, golf pole-like titania was obtained by this procedure. By controlling irradiation time and changing focus position of electronic beam followed by calcination at 480 °C, we obtained titania with desired shape, such as; arch, “L” shape, and “U” shape (Figures 2b–2d). It should be noted that the SEM image of the sample after calcination may not be the same

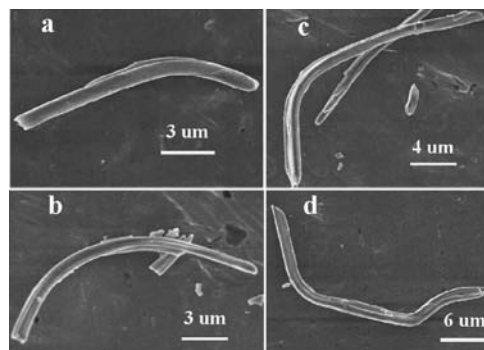


Figure 2. SEM images of titania rod with different shapes.

portion of irradiation, but titania microrod with desired shapes could be feasibly fabricated by our novel procedure.

In summary, we realized controllable processing of titania microrod, which maybe find application in nano or microdevices. It is expected that the present method can be easily extended to other oxide materials, which is currently underway.

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