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Exfoliation of titanium oxide powder into nanosheets using hydrothermal reaction and its reassembly into flexible papers for thin-film capacitors

Sangkyu Lee [a], Hun Park [b], Ungyu Paik [c], Tae Hee Han [b,*]

[a] Department of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea
[b] Department of Organic and Nano Engineering, Hanyang University, Seoul, 133-791, Korea
[c] Department of Energy Engineering, Hanyang University, Seoul, 133-791, Korea

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ABSTRACT

We have discovered a methodology to realize the fabrication of flexible metal oxide film using two-dimensional (2D) nanosheets. Atomic scale titanium oxide (TiO_x) nanosheets were exfoliated from bulk TiO_x powder that had a layered structure via the modified Sasaki's method. The vacuum-assisted filtration generates films with laterally aligned TiO_x nanosheets. The 2D sheet-like structure and hydrophilic nature of TiO_x nanosheets enables the film consisting of TiO_x nanosheets to be bendable. Also, we demonstrate the fabrication of electrochemical capacitors using this film. The mechanically flexible metal oxide film is expected to open up the possibility of fabricating flexible energy storage devices from 2D metal oxide nanosheets.

1. Introduction

The development of exfoliation technologies to make graphene and graphene-derivatives has opened up a new scientific area in the field of two-dimensional (2D) nanomaterials [1–3]. Motivated by the advent of graphene, a variety of 2D materials have been widely investigated for many applications including electrical and optical devices, electrochemical energy storage devices, and catalysts [4–7]. To date, several attempts at material modification, such as mechanical cleavage [1], introduction of chemical functionalities [8], or sonication-aided separation [9], have been applied to prepare individually isolated layers from their mother layered materials. The exfoliated 2D atomic crystals including hexagonal boron nitride (*h*BN), chalcogenides, and layered oxides, exhibit unique electronic, optical, magnetic, thermal, and mechanical properties that originated from the properties of the bulk materials; these materials also manifest certain newly emergent properties of 2D atomic crystals such as large surface area [7,10]. Despite of these advantageous properties, however, it has been difficult to achieve practical applications using 2D nanomaterials because of the complicated and laborious preparation process, including poor-quality, time-consuming, and low-yield production.

Titanium oxide (TiO_x) is a versatile material that has attracted much attention for use in a wide variety of applications including energy harvesting and storage devices [11–13], optical displays [14], catalysts [15], and sensors [16]. TiO_x materials have typically been prepared via a wet process of sol–gel transition [17] and thin film deposition, such as atomic layer deposition (ALD) [18] or chemical vapor deposition (CVD) [19]. Layered TiO_x materials were synthesized by the introduction of structure stabilizing ions to tightly hold the TiO_x single layer [20]. Recently, Sasaki et al. reported that single layer TiO_x sheets are successfully exfoliated from the bulk TiO_x powders by exchange of those ions with bulk ammonium ions [20–23]. Bulk layered TiO_x particles are soaked in an HCl solution for 24 h and refreshed with a new solution for a week to introduce hydrogen ions to replace structure stabilizing ions, such as magnesium, potassium, and lithium ion. Then, hydrogen ions are additionally substituted for bulky ions by vigorous mixing in ammonium cation solution for 5–10 days.

Here, we propose a modified ion exchange approach for preparing TiO_x sheets. In our modification, acid exchange was simplified by applying hydrothermal reaction, enabling to reduce the production time of TiO_x nanosheets. Furthermore, vacuum-assisted filtration results in free standing films consisting of self-assembled nanosheets along the film normal direction. We also discovered that the resulting TiO_x film is mechanically flexible similar to GO film and unlike bulk TiO_x materials. The flexibility of

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* Corresponding author. Tel.: +82 2 2220 0493.
E-mail address: than@hanyang.ac.kr (T.H. Han).

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this film allows us to expect a significant number of practical applications.

2. Experimental

2.1. Preparation of TiO_x sheets

Magnesium, potassium, and lithium-stabilized TiO_x were purchased from Otsuka Chemical Co., Ltd. Delamination of bulk TiO_x power was achieved by the ion-exchange manner, as reported by Sasaki et al. at elsewhere [20]. 0.75 g of the TiO_x was dispersed in 50 mL of 1 M hydrochloric acid solution. The mixture solution was directly transferred to a Teflon-lined stainless steel container with a capacity of 100 mL and was then maintained at 100 °C for 1 h. After cooling to room temperature, the sediments were collected using a filtration process with a 0.45 μm mixed cellulose ester membrane filter. The resulting particles were re-dispersed in a fresh 1 M hydrochloric acid solution. This acid exchange process was repeated 3 times. Then, the particles were washed with excessive de-ionized water and dried in an oven at 80 °C overnight. Tetramethylammonium hydroxide (TMAH) was selected as the source of quaternary ammonium cations in this experiment. 0.4 g of protonated TiO_x was dispersed in a 100 mL of 2.5–3.7 mM TMAH solution. The solution was magnetically stirred for one week to substitute the hydrogen ions for bulky tetrammonium (TMA) cations in the gallery between TiO_x nanosheet layers. In addition, the Tyndall effect was observed using a red laser (632 nm).

2.2. Fabrication of TiO_x papers

To produce a freestanding film consisting of TiO_x nanosheets, a vacuum filtration process was employed. The colloidal suspension containing 20 mg of TiO_x nanosheets was poured to the filtration system. The concentration of the solution was 3.98 mg/mL. A single film of TiO_x nanosheets was obtained within 3 min. The film was washed with de-ionized water and dried at room temperature. The resulting film easily detached from the membrane leading to a flexible and freestanding film. The thickness of the film was ~350 nm.

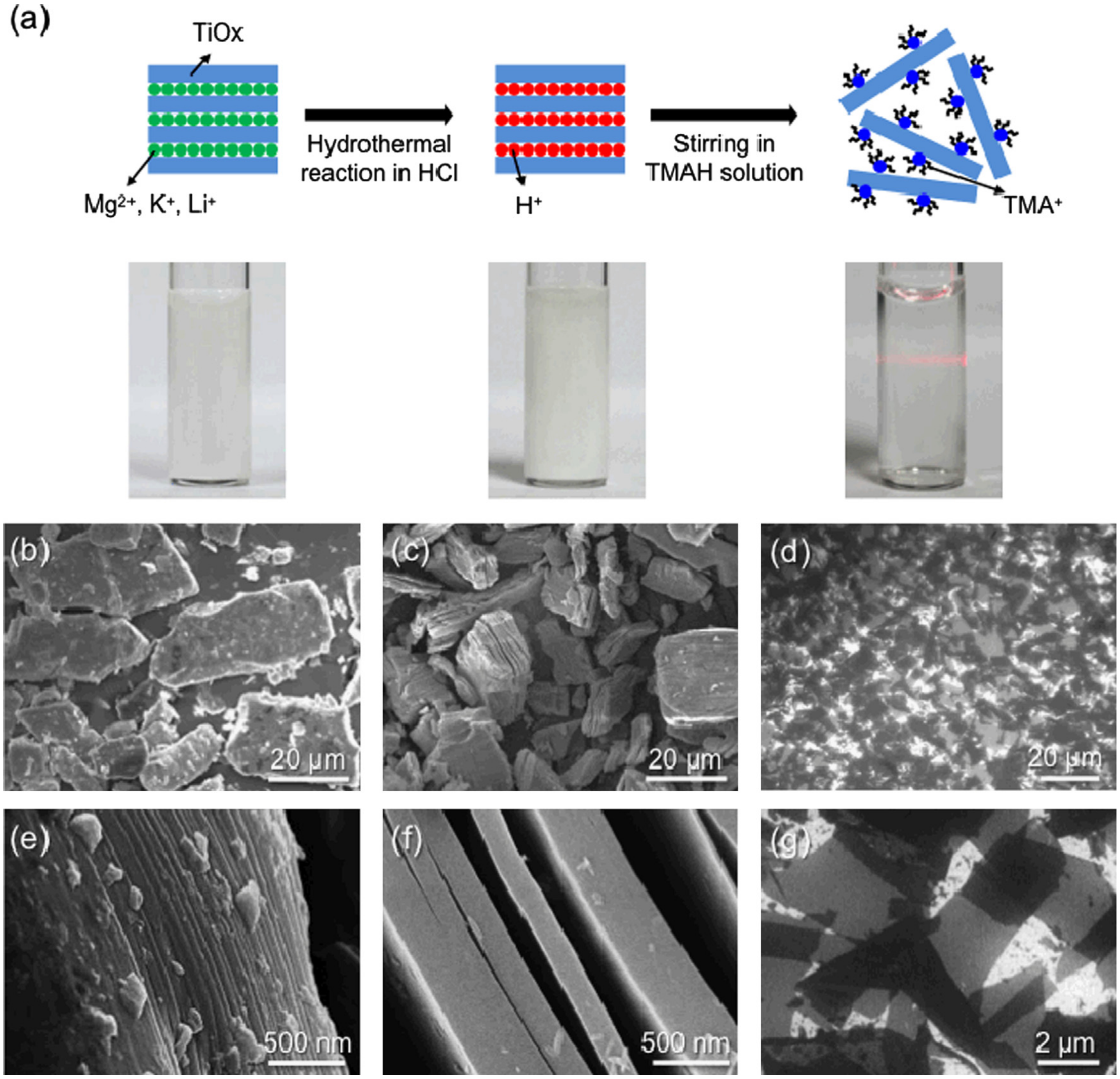

Fig. 1. (a) Schematic illustration of TiO_x nanosheet fabrication process and photographs of the experimental vials of each step. Solutions of as-received TiO_x powders, TiO_x powders stabilized with hydrogen atoms, and exfoliated TiO_x sheets (from left to right). The Tyndall effect confirms the stable colloidal characteristic of TiO_x dispersion. SEM images of as-received cation-stabilized TiO_x (b), TiO_x particles after hydrogen ion exchange (c), and fully exfoliated TiO_x nanosheets ((d) and (g)). Enlarged SEM images showing the edge of TiO_x particles (e) and TiO_x stabilized with hydrogen ions (f).