



Template-free synthesis of two-dimensional titania/titanate nanosheets as electrodes for high-performance supercapacitor applications



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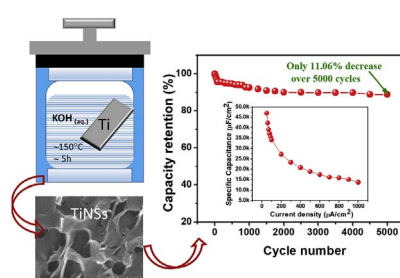
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HIGHLIGHTS

- The 2D TiNS-based electrodes were firstly prepared by a template-free method.
- The Morphology of TiNS was significantly varied with KOH concentrations.
- The TiNS were a mixture of rutile phase TiO₂ and K-titanate (K₂Ti₃O₇ and K₂Ti₂O₅).
- It shows high specific capacitance & excellent cycling stability upto 5000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Template-free two-dimensional (2D) titania/titanate nanosheets on Ti metal foil (TiNS/Ti) is prepared by a hydrothermal method at 150 °C assisted by KOH_(aq.), followed by sintering at 500 °C. A single thin layer of TiNS is grown with 2D morphology when using low concentrations of KOH_(aq.) (0.25 and 0.5 M). However, the morphology is transformed to 1D when using a high concentration of KOH_(aq.). The TiNS is a mixture of rutile TiO₂ and K-titanate (K₂Ti₃O₇ and K₂Ti₂O₅) with the formation of Ti³⁺ interstitials. The optimized TiNS/Ti electrode exhibits quasi-rectangular cyclic voltammograms (CVs) in a wide potential range. The specific capacitance (C_s) are 6.8 × 10³ and 4.7 × 10³ μF/cm² according to the CV (scan rate, 5 mV/s) and charge-discharge measurements (CD, current density, 50 μA/cm²), respectively. These values are much higher than those reported for pure 0D and 1D TiO₂ nanostructures. The higher C_s for the TiNS/Ti electrode can be ascribed to the increased rate of K⁺ intercalation and de-intercalation during charging and discharging, as well as enhanced conductivity enable by the K in the crystal lattice (10.30%) and Ti³⁺ interstitials (5.2%), respectively. The TiNS/Ti electrode shows excellent stability with the C_s retention of 89% even after 5000 CD cycles.

1. Introduction

Two-dimensional (2D) layered nanomaterials have attracted significant interest since the isolation of graphene from graphite by mechanical exfoliation in 2004 [1,2]. Such materials have excellent conducting or semiconducting properties that arise from the confinement

of electrons in 2D. Other features include nanoscale thickness effects, as well as physical, chemical, and mechanical properties that depend on the infinite lateral dimension, such as ultra-high surface-to-volume ratios, high catalytic activity, magnetic properties, and dielectric properties [3-6]. Many inherently 2D layered materials have been developed, such as graphene [1], transition metal di-chalcogenides (e.g.,

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WS₂, MoS₂, SnS₂, MoSe₂, VS₂) [7–10], hexagonal boron nitride (h-BN) [11–13], and graphitic carbon nitride (g-C₃N₄) [14,15]. The most popular method for the synthesis of such materials is based on the exfoliation of their corresponding natural or artificial layered compounds by mechanical, chemical, electrochemical, and intercalation methods [16,17]. However, such methods are not suitable for the synthesis of 2D layered metal-oxides (MOs) or hydroxides due to a lack of layered lattice structures [16,18,19].

Consequently, graphene-oxide (GO) template-assisted methods and molecular self-assembly methods have been applied using lamellar reverse micelles. These methods have been successfully demonstrated to synthesize 2D layered MOs nanostructures of TiO₂, ZnO, Fe₂O₃, MnO₂, WO₃, Co₃O₄, and SiO₂ [16,18,20]. Nevertheless, the methods still need to be simplified and adapted to overcome the size limitation resulting from the fixed size of templates. A facile and low-cost method is crucial for use in various nano technological applications, including photocatalysts, solar cells, biosensors, lithium-ion batteries, and electrochemical supercapacitors (ESs) [21–27]. Particularly, the development of ESs with high energy density and power density is promising for a broad range of applications, such as micromechanical systems (MEMS), portable electronics, electric vehicles, and energy harvesters.

Based on their mechanisms of energy storage and delivery, ESs can be classified as electrochemical double layer capacitors (EDLCs) and pseudocapacitors [28,29]. EDLCs are based on charge separation at the electrode|electrolyte interface by a non-faradaic process. EDLCs widely use carbon-based materials with large surface area, such as activated carbon, carbon nanotubes, and graphene [29]. Pseudocapacitive ESs are based on reversible redox reactions that occur at electrode surfaces and frequently use conducting polymers and transition MOs, such as RuO₂, MnO₂, ZnO, and TiO₂ [28–30].

Among the transition MOs, TiO₂ nanostructures have attracted significant interest as a potential electrode material for the development of pseudocapacitive ESs. This is due to their high surface area, environmental friendliness, natural abundance, low cost, and high stability [25]. Furthermore, nanostructured TiO₂ exhibits low volume change (< 4%) during the intercalation and de-intercalation processes of metal ions (e.g., Li), as well as large surface area for enhanced intercalation channels and short diffusion-path lengths [31]. Accordingly, many different electrodes have been fabricated for the development of ESs based on TiO₂ nanostructures, such as TiO₂ nanoparticles [32], one-dimensional (1D) TiO₂ nanotubes [32–37], nanorods [38], nanofibers [39], nanoparticles/nanotube arrays [40]. However, the specific capacitance (C_s) is significantly lower in ESs based on TiO₂ nanostructures than other MOs (e.g., MnO₂ and RuO₂). This is due to their high electrical resistivity and slow ion diffusion capacity [41–43].

To improve the capacitive performance, various TiO₂ composites have been developed, including doped TiO₂ [44–46], polymer/TiO₂ [47], carbon nanotube/TiO₂ [48], and TiO₂/graphene [49] composites. These composites have better capacitive performance than pure TiO₂ nanostructures. Furthermore, the phase transition of TiO₂ nanostructures from anatase to rutile contributes to improving the conductivity due to the conversion of Ti⁴⁺ to Ti³⁺ and creation of oxygen vacancies by the breakage and rearrangement of Ti–O bonds [32,50,51], which is beneficial for obtaining high capacitance [43]. To the best of our knowledge there is no report on the synthesis of phase controlled and template-free synthesis of 2D layered TiO₂ nanostructures or its composites by simple hydrothermal method assisted by alkali for ESs applications.

Herein, we developed a simple, template-free, and low-cost hydrothermal method for the synthesis of 2D layered titania (TiO₂)/titanate nanosheets (TiNS) on Ti foil. This was achieved by using a low concentration KOH_(aq.) at 150 °C and subsequent annealing at 500 °C. The concentrations of KOH_(aq.) were varied to control the size and shape of the TiNS. The as-synthesized TiNS exhibited high crystallinity and purity with improved interconnectivity between the nanosheets (NSs) and their electrochemical performance were tested to develop ESs,

which exhibited greatly enhanced C_s with high stability.

2. Experimental

2.1. Chemicals and reagents

Titanium foil (99% purity) with a thickness of 2.0 mm, NaOH (95%), and acetone (95%) were obtained from Sigma-Aldrich (St Louis, MO, USA). Waterproof and electro-coated silicon carbide (SiC) abrasive paper with grit sizes of 800 and 2000 was obtained from O-Shung Abrasive, Korea. Deionized (DI) water was obtained from a Millipore Milli-Q Biocell A10 water-purifying system (18 MΩ cm) and used throughout the experiments unless otherwise noted.

2.2. Synthesis of titania/titanate nanosheets

Prior to the synthesis of TiNS, Ti foil was cut into a square shape (40 × 40 mm²) and polished using SiC abrasive paper. Then, the foils were sequentially cleaned in acetone and DI water for 30 min each using an ultrasonic bath and dried in an oven at 50 °C for 1 h. The cleaned Ti foils were dipped individually into a stainless-steel autoclave lined with poly(tetrafluoroethylene) and containing two different concentrations of KOH_(aq.) (0.25 and 0.5 M). The foils were then hydrothermally treated in an oven at 150 °C for 5 h. The samples were removed, rinsed with DI water, and air dried. The samples were then annealed at 500 °C for 12 h in ambient conditions using an electric muffle furnace and were designated as TiNS_{KOH(0.25M)} and TiNS_{KOH(0.5M)}.

2.3. Instrumentation

The surface morphology of the samples was characterized using a field-emission scanning electron microscope (FE-SEM, S-4200, Hitachi, Japan). The surface topography was investigated by atomic force microscopy (AFM, XE100, PSIA, Korea) in non-contact mode. An energy-dispersive X-ray spectroscope (EDX) with an FE-SEM instrument was used to obtain the elemental compositions and atomic mapping of the samples. The crystallographic phase of TiNS was analyzed by an X-ray diffractometer (D8 Advance, Bruker Germany) using CuK_α radiation (λ = 0.15406 nm) with an accelerating voltage of 40 kV and cathode current of 30 mA. Raman scattering spectra were obtained at room temperature on a Raman spectrometer (LabRAMHR, Horiba JobinYvon SAS using a 632.8 nm laser). X-ray photoelectron spectroscopy (XPS) spectra were obtained via a Thermo Scientific™ K_αXPS system (Thermo Fisher scientific, UK) with a monochromatic AlK_α source. All the electrochemical measurements were performed using a CHI660C electrochemical workstation (CH Instruments Inc., USA), including cyclic voltammograms (CVs), galvanostatic charge-discharge plots (CD), and electrochemical impedance spectroscopy (EIS). The as-synthesized TiNS was used as the working electrode (active area ca. 0.77 cm²). Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively. All electrochemical experiments were performed in ambient conditions in 1 M KOH_(aq.) solution. The potential of the electrochemical experiments was referred to the reference electrode. The EIS spectra were fitted with a Randles equivalent circuit model using Z-view software.

3. Results and discussion

3.1. Morphological and elemental composition analysis

The structure, surface morphology, and topography of the as-synthesized TiNS were observed by FE-SEM and AFM analysis. Fig. 1a and b shows the FE-SEM images of TiNS_{KOH(0.25M)} and TiNS_{KOH(0.5 M)}, respectively. At a low concentration of KOH_(aq.) (0.25 M), the TiNS_{KOH(0.25M)} started to grow on the Ti foil by opening up one of the

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