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Application of binder-free TiO_xN_{1-x} nanogrid film as a high-power supercapacitor electrode



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HIGHLIGHTS

- \bullet TiO_xN_{1-x} nanogrid electrode showed high specific surface area and low impedance.
- \bullet TiO_xN_{1-x} electrode showed high specific capacitance and electrochemical stability.
- \bullet TiO_xN_{1-x} nanogrid supercapacitor showed high operating frequency (398 Hz).
- TiO_xN_{1-x} nanogrid supercapacitor showed high energy density (15.0 Wh kg⁻¹).
- \bullet TiO_xN_{1-x} nanogrid supercapacitor exhibited high power density (166.1 kW kg^{-1}).

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ABSTRACT

Binder-free TiO_xN_{1-x} nanogrid films with high conductance, high specific surface area, and high electrochemical stability can meet the demand for high-performance supercapacitor materials. A metal-phase TiO_xN_{1-x} nanogrid film was prepared by a simple hydrothermal-nitrification method. The TiO_xN_{1-x} nanogrid film showed higher specific surface area (75.9 m² g⁻¹) and lower impedance than nanosheet, nanowire, and nanoribbon films. As a result, the TiO_xN_{1-x} nanogrid electrode showed the highest specific capacitance (8.28 mF cm⁻²), the highest capacitance retention (95.8%) after 10,000 galvanostatic charge/discharge cycles, and the highest operating frequency (398 Hz). To improve the power density and energy density of the supercapacitor, an organic electrolyte (1 mol L⁻¹ tetraethy-lammonium tetrafluoroborate in acetonitrile, TEA-BF₄/AN) and a room temperature ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, EMIM-TFSI) were applied to enlarge the voltage range to 0–2.5 V and 0–3.5 V, respectively, compared with the 0–0.8 V of a KCl aqueous electrolyte. The EMIM-TFSI supercapacitor reached the highest energy density, 15.0 Wh kg⁻¹, while the highest power density with the TiO_xN_{1-x} nanogrid electrode, 166.1 kW kg⁻¹ determined in 1 mol L⁻¹ KCl aqueous electrolyte but also the 144.1 kW kg⁻¹ measured in EMIM-TFSI.

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1. Introduction

Supercapacitors are different from other electrochemical energy storage devices because they exhibit high power uptake and delivery abilities [1]. These abilities originate from ion adsorption/ desorption on solid/liquid interfaces [2]. To meet the ever-growing demand for high power ability in practical applications, the power

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density of supercapacitors needs to be extensively expanded. The energy density (E) and power density (P) can be expressed as [3]

$$E = \frac{C\Delta V^2}{2} \tag{1}$$

$$P = \frac{C\Delta V^2}{4R} \tag{2}$$

Obviously, both the energy and power density are proportional to the square of the voltage range (ΔV). Improvements to the



energy and power density can be achieved by maximizing the voltage range and the specific capacitance (C). In practice, this can be achieved by applying non-aqueous electrolytes and by enlarging the specific surface area of the active materials, respectively. In addition, the improvement of the power density can be also achieved by minimizing the equivalent series resistance (R) of the supercapacitor. That is, electrode materials with higher conductivity bring on higher power density or better rate capability.

Traditional electrochemical double-layer capacitors (EDLCs) are based on carbon materials because of their high surface area and conductivity (for high energy and power density) and electrochemical stability (for long charge/discharge cycling life). Activated carbon, carbon nanotubes, and graphene have been applied in supercapacitor electrodes [3-6]. However, the fabrication of high-quality carbon materials with high conductivity requires expensive equipment (e.g., chemical vapor deposition) and complex procedures, while low-cost and effective synthesis routes always compromise the conductance and quality of the product [7–10]. Other materials such as titanium oxynitride (TiO_xN_{1-x}) are good candidates for EDLC electrode materials that can achieve high power uptake and delivery abilities. TiO_xN_{1-x} is a metalphase material reported to have a conductivity of 30,000–35,000 S cm⁻¹ [11,12], which is much higher than chemically converted graphene (210–1000 S cm⁻¹) [5], or carbon nanotubes (60–170 S cm⁻¹) [13].

Nanostructured TiO_xN_{1-x} has been applied in the field of supercapacitors, and excellent capacitive performance has been exhibited [14-16]. Various methods have been used to fabricate nanostructured TiO_xN_{1-x} for application in supercapacitor electrodes. TiN-VN core-shell fibers, prepared by the electrospinning method, achieved improved rate capability by virtue of the high electronic conducting properties of TiN [17]. MnO₂/TiN or MnO₂/ TiO_xN_{1-x} nanotubes and coaxial structures have been fabricated by anodization or atomic layer deposition methods [18–20]. Lu et al. reported that free-standing titanium nitride nanowires were grown on a carbon substrate by a hydrothermal and ammonia atmosphere annealing process, achieving excellent performance as a supercapacitor electrode [21]. Unfortunately, the limited power density of TiO_xN_{1-x}-based supercapacitors has been reported in the literature because of the low operating voltage of aqueous electrolytes. Previous research concerning titanium oxynitride-based supercapacitors with high operating voltage and long cycling life stretching to 10,000 cycles has not been reported. Generally speaking, by applying a proper organic electrolyte or room temperature ionic liquid (RTIL) with a high decomposition voltage, the power density and energy density can be enhanced, according to Equations (1) and (2).

Because of their exceptionally wide electrochemical window, excellent thermal stability, nonvolatility, and relatively inert nature, RTILs have become candidates for electrolytes used in supercapacitors [22]. As far as we know, there is no report of TiO_xN_{1-x}-based supercapacitors with high energy density fabricated using room temperature ionic liquid electrolytes or organic electrolytes. In this study, a room temperature ionic liquid (1ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was used as an electrolyte for TiO_xN_{1-x}-based supercapacitors, in which TiO_xN_{1-x} was fabricated by nitrification of the titania precursor, forming a nanostructured binder-free TiO_xN_{1-x} film with an interconnected topological structure and a high specific surface area. The TiO_xN_{1-x} nanogrid electrode exhibits a very high power density of 166.1 kW kg^{-1} in TEA-BF₄/AN electrolyte and 144.1 kW kg⁻¹ in EMIM-TFSI, which is promising for practical applications. These results may open up new opportunities to develop high-power supercapacitors in the field of energy storage.

2. Experimental

2.1. Synthesis of nanostructured $TiO_x N_{1-x}$ electrodes

Titanate hydrate nanostructured films with large specific surface areas were prepared by a hydrothermal method. Titanium foil (99.8%, 50 μ m) was submerged in 40 mL of NaOH aqueous solution with various concentrations in a Teflon-lined autoclave with a volume of 60 mL. The autoclave was then sealed and heated in an electronic oven at 200 °C for various amounts of time (detail hydrothermal conditions are shown in Table 1). The obtained samples were immersed in 1 mol L⁻¹ HCl solution for 10 min to exchange Na⁺ with H⁺. The titanate hydrate films were further nitrificated in a quartz tube oven to prepare TiO_xN_{1-x}. After rinsing with 1000 sccm (standard-state cubic centimeter per minute) NH₃ gas for 30 min, the titanate hydrate was heated to 700 °C at a heating rate of 5 °C min⁻¹ under an NH₃ flow of 500 sccm, and kept for 5 h, thus obtaining the TiO_xN_{1-x} samples.

2.2. Material characterization and instruments

XRD patterns of the samples were recorded on a powder X-ray diffractometer (XRD, Ultima III, Rigaku, Japan) equipped with graphite monochromatized Cu-K α radiation ($\lambda = 1.54178$ Å). Scanning electron microscopy (SEM) images were recorded with a field-emission scanning electron microscope (FESEM, Nova nano-SEM 230, FEI, USA). The average thickness of the nanostructured films was measured by SEM. Samples for transmission electron microscopy (TEM, IEM-200CX, IEOL, Japan) analysis were prepared by drying a drop of scraped powder dispersion in absolute ethanol on amorphous carbon-coated copper grids. Surface element compositions of the samples were examined using X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe, ULVAC-PHI, Japan). The active materials on every electrode were carefully scraped by a blade, and then the powders scraped from the electrodes were weighed by a microbalance (METTLER TOLEDO, MX5, Switzerland). The specific surface areas and pore size distributions of the samples were determined by Brunauer-Emmett-Teller and Barrett-Joyner-Halenda measurements via nitrogen adsorption at -196 °C by an automatic surface area analyzer (Tristar-3000, Micromeritics). The samples were scraped from the corresponding film and degassed under a nitrogen flow at 150 °C for 4 h before the measurements. The viscosity of the electrolyte was tested by a Vibro Viscometer (SV-1A, A&D Company Ltd., Japan).

2.3. Electrochemical testing of the electrodes and supercapacitor devices

The electrodes were tested in a three-electrode configuration. employing a saturated calomel electrode (SCE) and platinum foil as the reference and counter electrode, respectively, conducted in 1.0 mol L⁻¹ KCl aqueous solution, by an electrochemical workstation (CHI 633C, CH Instruments). To investigate the actual performance of the supercapacitor devices, symmetric electrode devices were fabricated and tested. Electrochemical impedance spectroscopy (EIS) measurements were performed with a sinusoidal signal of 10 mV over the frequency range of 0.1 Hz–100 kHz, conducted in a Solartron electrochemical analyzer system (1260 + 1287, Solartron, USA). Prototype supercapacitors using the TiO_xN_{1-x} films as electrodes were assembled in a symmetrical two-electrode configuration with a separator (glass fiber paper). Finally, they were infiltrated and sealed with an aqueous (1 mol L^{-1} KCl aqueous electrolyte, KCl/aqueous) or organic electrolyte (1 mol L^{-1} tetraethylammonium tetrafluoroborate in acetonitrile, TEA-BF₄/AN) and a RTIL (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) Download English Version:

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