



Hydrogenated TiO₂@reduced graphene oxide sandwich-like nanosheets for high voltage supercapacitor applications



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ABSTRACT

Hydrogenated TiO₂ has recently attracted considerable attention as potential electrode materials for supercapacitors due to its abundance, low cost, high conductivity, remarkable rate capability, and outstanding long-term cycling stability. Herein, we demonstrate the synthesis of hydrogenated TiO₂ nanoparticles anchored on reduced graphene oxide nanosheets (HTG) in the form of sandwich-like nanosheet composites. Further, we explored their implementation as electrode materials for high voltage, symmetric supercapacitors, operating in the voltage window of 0–1.8 V. The HTGs were prepared by a sol-gel method, followed by hydrogenation in the temperature range 300–500 °C. Of the prepared composites, HTG prepared at 400 °C exhibited the largest specific capacitance of 51 F g⁻¹ at the current density of 1.0 A g⁻¹ and excellent rate capability with 82.5% capacitance retention as the current density increased 40-fold, from 0.5 to 20.0 A g⁻¹. HTG's excellent rate capability was attributed to its sandwich-like nanostructure, in which ultrasmall hydrogenated TiO₂ nanoparticles densely anchored onto both surfaces of the two-dimensional reduced graphene oxide sheets. Moreover, HTG-based supercapacitors also exhibited long-term cycling stability with the retention over 80% of its initial capacitance after 10,000 cycles. These properties suggest that HTG is a promising electrode material for the scalable manufacture of high-performance supercapacitors.

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1. Introduction

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted significant attention in recent years due to their high power density, superior rate capability, rapid charging/discharging rate, long cycle life, simple principles, fast dynamics of charge propagation and low maintenance cost [1–3]. Supercapacitors have a wide range of applications that require high power density, such as energy back-up systems, consumer portable devices, electric vehicles and hybrid electric vehicles [2,3]. Unfortunately, the energy density of supercapacitors is quite low, usually less than 10 Wh kg⁻¹, which is significantly lower than those of batteries, potentially limiting their applications [2]. Most studies on supercapacitors focus on improving their energy density by increasing the specific capacitance (C) of the electrode materials

and widening the working voltage (V) of the cell in accordance with the equation of $E = \frac{1}{2}CV^2$ [2,3]. Since the energy density is proportional to the square of the cell working voltage, improvement of the energy density would be more efficient by increasing the cell working voltage rather than increasing the specific capacitance of the electrode materials [3].

The electrolyte is the most important factor determining the cell working voltage [3,4]. Organic electrolytes based on acetonitrile and ionic liquids facilitate the operation of supercapacitors working in the voltage range 0.0–4.0 V. However, organic electrolytes and ionic liquids are characterized by poor conductivity and high viscosity, which significantly hinders their penetration into an electrode's structure and aggravates charge propagation, resulting in low specific capacitance and poor rate performance [4]. In contrast, aqueous electrolytes have high conductivity and low viscosity, but their working voltage is thermodynamically limited by the decomposition voltage of water at ~1.23 V [3–5]. Aqueous acidic and alkaline electrolytes generally work at lower voltage, around 1.0 V [3,4]. However, the aqueous neutral electrolytes, which have

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high overpotential for hydrogen and oxygen evolution reactions due to their low H^+ and OH^- concentration, produce supercapacitors that operate at much higher voltages, especially with carbon-based electrode materials (1.6–2.2 V) [3–9]. Fic et al. [4] reported that the activated carbon symmetric supercapacitors using Li_2SO_4 electrolytes could operate at 2.2 V without any significant capacitance fade over 15,000 cycles of charging/discharging.

Although carbon-based electrode materials have great capacitive properties over a wide range of working voltages, their low specific capacitance, especially volumetric specific capacitance, significantly limiting their volumetric energy densities. In contrast, pseudocapacitive electrode materials generally have high specific capacitance, but their working voltages are usually quite narrow, resulting in limited energy density [2,10]. Therefore, a search for novel electrode materials that have a wide working voltage is of great importance for the continued development of aqueous supercapacitors.

Among various pseudocapacitive materials, titanium dioxide (TiO_2) has been received less attention as a potential electrode materials for supercapacitor applications due to its low electrical conductivity and poor electrochemical activity, originating from its wide band gap semiconductor characteristic [11,12]. TiO_2 is typically used in combination with reduced graphene oxide (RGO) as spacer to prevent the restack of RGO sheets [13–15]. In 2011, Chen et al. [16] found that the hydrogenation of TiO_2 nanocrystals induced disorder of the surface layer of TiO_2 nanocrystals with simultaneous dopant incorporation, leading to significant reduction of the band gap, which greatly improves electrical conductivity of TiO_2 . Moreover, the hydroxyl groups introduced on TiO_2 surface during hydrogenation could alter the electrochemical activity of TiO_2 and therefore increase its pseudocapacitance. Lu et al. [17] first reported hydrogenated TiO_2 nanotube arrays as electrode materials for supercapacitors. They found that the hydrogenated TiO_2 nanotube arrays annealed in hydrogen at 400 °C possessed greatly enhanced specific capacitance, ~40 times higher than TiO_2 nanotube arrays annealed in air [17]. Hydrogenated TiO_2 also showed remarkable rate capability and outstanding long-term cycling stability. The prominent improvement of electrochemical capacitive performance of hydrogenated TiO_2 was attributed to enhanced electrode conductivity and electrochemical activity associated with the effective hydrogen-induced Ti^{3+} sites in TiO_2 lattices [17]. Thereafter, several investigations attempted to use hydrogenated and electrochemically self-doped TiO_2 nanotube arrays and nanowires grown on titanium foils and carbon cloths as electrode materials for supercapacitors. These showed decent electrochemical capacitive behaviors with areal specific capacitances of 1.0–20 $mF\ cm^{-2}$ [18–25]. Recently, Yang et al. [26] reported that hydrogenated TiO_2 /reduced graphene oxide, prepared by a hydrothermal method followed by hydrogenation, exhibited a gravimetric specific capacitance of 62.8 $F\ g^{-1}$ in aqueous KOH electrolyte, characterized by a three-electrode configuration within a window potential of –0.05–0.45 V (vs. Ag/AgCl). In this article, we report the synthesis of hydrogenated TiO_2 /reduced graphene oxide (HTG) sandwich-like nanosheets, whose structure and composition function as an excellent electrode material for high voltage, symmetric supercapacitors. These materials, which can operate within a voltage window up to 1.8 V, exhibited a specific capacitance of 51 $F\ g^{-1}$ at the current density of 1.0 $A\ g^{-1}$ and excellent rate capability with 82.5% capacitance retention when the current density increases 40 times, from 0.5 to 20.0 $A\ g^{-1}$. Moreover, HTG also exhibited long-term cycling stability with a retention over 80% of its initial capacitance after 10,000 cycles. HTGs' excellent capacitive performance was attributed to their sandwich-like nanosheet structure, in which ultrafine hydrogenated TiO_2 nanoparticles densely decorated both sides of reduced graphene

oxide sheets.

2. Experimental

2.1. Synthesis of HTG

Graphene oxide (GO) was prepared by the modified Hummers method using microwave-assisted expanded graphite as the starting material, as reported elsewhere [27]. Ethanol was exchanged as the solvent of the as-synthesized aqueous GO solution (10.0 $mg\ mL^{-1}$); the new ethanolic solution was set at a concentration of 1.0 $mg\ mL^{-1}$. The composite comprising TiO_2 nanoparticles, decorating the surface of graphene oxide, ($TiO_2@GO$) was prepared by a sol-gel method [28,29]. 0.5 mL ammonia solution (28 wt %) was added in the 100 mL of GO solution in ethanol (1.0 $mg\ mL^{-1}$). Then, 1.27 mL of tetrabutyl titanate (TBOT) was slowly added under mixing. The mixture was stirred for 24 h at room temperature, allowing TBOT hydrolysis and creating amorphous TiO_2 nanoparticles attached onto the GO sheets. The resulting $TiO_2@GO$ was collected by centrifugation, repeatedly washed with deionized water, and freeze-dried. The $TiO_2@GO$ was finally hydrogenated in a 99.99% hydrogen atmosphere at the temperature of 300–500 °C for 2 h. The obtained hydrogenated TiO_2 /reduced graphene oxide hybrids were denoted as HTG_x where x is the hydrogenation temperature.

2.2. Characterizations

The morphologies of the $TiO_2@GO$ and HTGs were characterized by scanning electron microscopy (SEM, Hitachi 4800), transmission electron microscopy (TEM, JEOL 1400), and atomic force microscope (AFM, VEECO multimode V). Structural analysis was carried out on a Rigaku Ultima III X-ray diffractometer with CuK_{α} radiation ($\lambda_{\alpha} = 0.15418\ nm$), operating at 40 kV and 44 mA. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (Perkin Elmer) in air atmosphere at a heating rate of 10 °C min^{-1} . Raman spectroscopy was performed on a WiTec Alpha 300 micro-Raman confocal microscope at room temperature with 532 nm laser as an excitation source. X-ray photoelectron spectroscopy (XPS) was recorded on a RHK-XPS/STM/AFM system using Mg- K_{α} source and a hemispherical analyzer (PHOIBOS HSA-3500,100). Brunauer–Emmett–Teller (BET) specific surface areas were determined by N_2 adsorption/desorption at 77 K using a Micromeritics ASAP 2020 instrument.

2.3. Electrode preparation and electrochemical measurements

The HTG electrodes were prepared by: a) mixing HTGs with carbon black and polytetrafluoroethylene (PTFE) in a mass ratio of 85:10:5 in ethanol; and b) sonicating the mixture for 5 min to make a slurry. The slurry was partially dried, yielding a solid paste, which was subsequently casted and pressed onto nickel foam ($1.5 \times 1.5\ cm^2$) current collector. The obtained electrode was dried at 100 °C for 3 h. The mass of the HTGs were about 3.0–3.5 $mg\ cm^{-2}$. Prior to the electrochemical measurement, the electrodes were soaked in 1 M Na_2SO_4 electrolyte for 12 h.

The capacitive properties of HTGs were characterized using a symmetrical two-electrode electrochemical cell. Two identical HTG electrodes were assembled into a sandwiched structure, separated by a cellulose filter paper separator (Fisherbrand™ grade P8) that was soaked with 1 M Na_2SO_4 electrolyte. All the components were tightly sealed within a supercapacitor test cell (EQ-STC split flat cell, MTI Corp.). Cyclic voltammetry measurements were performed on a potentiostat/galvanostat PARSTAT 2273 (Princeton Applied Research); galvanostatic charge–discharge tests were conducted

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