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One-step hydrothermal preparation of $TiO_2/RGO/Ni(OH)_2/NF$ electrode with high performance for supercapacitors

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ABSTRACT

A facile one-step hydrothermal process is employed to synthesize a $TiO_2/RGO/Ni(OH)_2$ (reduced graphene oxide, RGO) composite on nickel foam (NF) by means of an in-situ growth route. In this case, NF acts as support, nickel source of $Ni(OH)_2$, and supplement reductant of GO. For comparison, RGO nanosheets serve as nano-sized flexible support for connecting TiO_2 and $Ni(OH)_2$ blocks, which improves the electron transfer and alleviates the volume changes during the repeated charge/discharge process thanks to its high conductivity and mechanical properties. Besides, P25 (commercial TiO_2 consisting of 80% anatase and 20% rutile) serves as TiO_2 source, at different GO/P25 ratio of 1%, 2%, 5%, 10% and 20%. Electrochemical performances of $TiO_2/RGO/Ni(OH)_2/NF$ electrode were evaluated by using cyclic voltammetry (CV), galvanostatic charge/discharge tests (GCD) and electrochemical impedance spectroscopy (EIS) in 1 M KOH electrolyte. The $TiO_2/RGO/Ni(OH)_2/NF$ electrode exhibited significantly enhanced capacitive performance when the weight ratio of GO/P25 was 10%. It delivered high capability of 4342 $mF\,cm^{-2}$ at a current density of 5 $mA\,cm^{-2}$ (374.3 $F\,g^{-1}$ at 0.43 $A\,g^{-1}$), and excellent charge-discharge cycling stability with 93.75% capacitance retention after 2000 cycles. An asymmetric supercapacitor (ASC) device consisting of this $TiO_2/RGO/Ni(OH)_2/NF$ and an AC negative electrode was assembled.

1. Introduction

With the dramatic development of economy, we cannot ignore the increasingly terrible energy issue. Although there are numbers of new energy resource, it is very disheartening for world to make little use of them. In contemporary society, it is a necessary and extra-urgent task to call for a novel high-efficient energy storage device acquiring rapid storage and stable delivery of electrical energy [1].

Supercapacitor enjoys the unrivaled prestige in terms of electrochemical energy storage, due to its ability to fill the gap between the battery and the conventional capacitor according to high power density, as well as ultralong cycle life [2,3]. Pseudocapacitor is different from the electric double-layer capacitor on the basis of charge storage mechanisms, which provides rapidly reversible Faradic reactions based on electrode materials [4,5]. Among the electrode materials, transition metal oxides attract significant attention because of their ideal pseudocapacitance, such as RuO_2, NiO, TiO_2, Co_3O_4 and MnO_2 [2].

TiO_2 is a rising star of electrode materials for energy conversion and storage, ascribing to its advantages of low cost, relative nontoxicity, abundance in nature, and outstanding chemical stability [3,6–10]. Unfortunately, pure TiO_2 has unsatisfactory capacitance due to its high electric resistance [9]. However, the recent decades have witnessed the development of composites being in its heyday, and many TiO_2-based composites loaded with other materials have been designed and synthesized. Ramadoss et al. [11] reported the hierarchical TiO_2 nanorod (NR)/porous Co $(OH)_2$ electrodes with areal specific capacitance of 274.3 $mF\,cm^{-2}$ at a scan rate of 5 $mV\,s^{-1}$, and 82.5% retention after 4000 cycles. Zhou and coworkers [12] proposed the deposition of MnO_2 spheres on a TiO_2 nanotube arrays substrate by using a sequential chemical bath deposition (SCBD) method, which delivered an areal specific capacitance of 175 $mF\,cm^{-2}$ at a scan rate of 10 $mV\,s^{-1}$. From the capacitance point of view, these data can still not meet the requirements of supercapacitor. On the other hand, NiO or $Ni(OH)_2$ is also a promising candidate of electrode materials owing to its

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high theoretical capacitance and stability in alkaline electrolyte [13]. Thus, the TiO_2/NiO composite maybe be an inspirational option. Wu et al. [14] fabricated the TiO_2/NiO core/shell nanorod arrays through composing of hydrothermal synthesis and electrodeposition method, which displayed excellent electrochemical performance with both high specific capacitance of 611 F g^{-1} at 2 A g^{-1}, and a retention of 89% after 5000 cycles. What a pity is that the fabrication process is complicated.

There is no doubt that most metal oxides suffer from the characteristic shortcoming of poor conductivity and remarkable resistance, this deficiency is pretty much the same for TiO_2 and $Ni(OH)_2$. Combination of carbon materials is a legitimate solution to break through this obstacle, and the first choice is graphene. To the best of our knowledge, graphene has a maximum specific area (2630 $m^2 g^{-1}$), extraordinary conductivity and a high charge carrier mobility (20 $m^2 V^{-1} s^{-1}$), which enable it to be qualified as a potential candidate of an electrode material or support in the future energy storage [15,16]. Zhu et al. [17] presented the fabrication of nanostructured titanium nitrides on graphene nanosheets substrate via atomic layer deposition process. Yang et al. [18] synthesized hybrid materials of ultrafine H-TiO_2 nanocrystals/nitrogen-doped graphene via a two-step method including a hydrothermal route and then hydrogenation. However, TiO_2 decorated graphene with $Ni(OH)_2$, i.e., composite of TiO_2, graphene and $Ni(OH)_2$ has been hitherto unexplored.

Herein, a cost-efficient and facile hydrothermal approach to fabricate a hybrid material of TiO_2/RGO/$Ni(OH)_2$ is reported. Especially, a NF is chosen as Ni source of $Ni(OH)_2$ and support for loading active materials, so an in-situ growth route of TiO_2/RGO/$Ni(OH)_2$/NF electrode is developed. The introduction of nanoscale graphene, could relegate the size of composites, and offer the promise of shortening the ion diffusion distance, increasing the utilization of active materials. Regarding as TiO_2, P25 (commercial TiO_2 consisting of 80% anatase and 20% rutile) is more convenient and homogenous, which can effectively facilitate controllable regulation. As-synthesized TiO_2/RGO/$Ni(OH)_2$/NF directly serves as supercapacitor electrode by using NF as current collector, exhibits ultrahigh areal capacitance of 4342 mF cm^{-2} at a current density of 5 mA cm^{-2}, i.e., 374.3 F g^{-1} at 0.43 A g^{-1} and superior charge-discharge cycling stability of 93.75% capacitance retention after 2000 cycles.

2. Experimental

2.1. Synthesis of TiO_2/RGO/$Ni(OH)_2$ composites on NF

Graphene oxide (GO) was prepared from pristine graphite powder (315 mesh) referred to a modified Hummer's method [19]. Pretreatment of Nickel foam (NF) was completed by an ultrasonic treatment with ethanol, acetone, and DI water, respectively in the bath, and then dried at 80 °C in vacuum oven.

In a typical synthesis procedure, 30 mg GO was added into the DI water with stirring and sonication for 1 hour to form homogeneous dispersion at room temperature. Afterwards, a certain amount of P25 was suspended into the DI water under stirring for 30 minutes, the resulted P25 suspension was added into the above-mentioned GO dispersion. Subsequently, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave. The cleaned NF (1×2 cm^2) was immersed in the mixture solution, and then suffered from hydrothermal treatment at 180 °C for 24 h. Eventually, when the autoclave was naturally cooled in air, the as-prepared product was washed by DI and ethanol water several times and dried at 80 °C for 8 h in a vacuum oven. According to different weight addition ratio of GO/P25 (1%, 2%, 5%, 10%, 20%), made TiO_2/RGO/$Ni(OH)_2$ composites named as P1GN, P2GN, P5GN, P10GN, P20GN at the same experimental conditions.

In order to further verify the necessary for the formation of TiO_2/RGO/$Ni(OH)_2$ composites, various blank experiments were supplied at the same hydrothermal conditions, which respectively named them as NF (bare NF), DI-NF (NF after hydrothermal treatment), P25-NF (Composites through hydrothermal process in the absence of GO), GO-NF (Composites through hydrothermal process without P25).

2.2. Characterization of TiO_2/RGO/$Ni(OH)_2$ composites

X-ray diffraction (XRD) patterns of the samples were detected by the X-ray diffractometer with Cu Kα radiation (λ=0.15406 nm). Raman spectra were collected using an INVIA Raman microprobe (Renishaw Instruments, England) with a 514 nm laser excitation. X-ray photoelectron spectroscopy (XPS) spectra were examined by an ESCALAB 250 Xi (ThermoFisher, U.S.A.) instrument. The morphology and microstructure of the as-synthesized products were monitored by using a field-emission scanning electron microscope (FESEM, JEOL, JSM-7800F) assisted with energy dispersive X-ray spectroscopy (EDS, Oxford instrument, England) and a transmission electron microscopy (TEM, JEOL JEM-2100) equipped with energy dispersive X-ray spectroscopy. N_2 adsorption-desorption was determined by the Brunauer–Emmett–Teller (BET) measurements using the 3H-2000PS1 surface area analyzer.

2.3. Electrochemical measurements of TiO_2/RGO/$Ni(OH)_2$ composites

The electrochemical performances of obtained composite electrodes were investigated by a standard three-electrode configuration in 1 M KOH solution using an electrochemical workstation (CHI660e, Shanghai). The mass loading of active materials (TiO_2/RGO/$Ni(OH)_2$) on NF for P10GN was determined to be 11.6 mg. The as-prepared samples were directly used as working electrodes, platinum foil (2×3 cm^2) acted as the counter electrodes, and a saturated calomel electrode (SCE) served as the reference electrodes. The cyclic voltammograms (CV), galvanostatic charge/discharge (GCD) curves were recorded within a potential window of −0.1 V to 0.55 V and −0.1 V to 0.5 V respectively, and electrochemical impedance spectroscopy (EIS) was measured at the open circuit potential, with a sinusoidal signal of 5 mV in the frequency range of 100 kHz to 0.01 Hz.

2.4. Fabrication of asymmetric supercapacitors devices

Activated carbon (AC) was purchased from Fuzhou Yihuan Carbon Company (YEC-8A), with a particle size of 10 μm and a specific surface area of 2100 $m^2 g^{-1}$. The negative electrode was fabricated by mixing AC, acetylene black and poly(tetrafluoroethylene) at a mass ratio of 8:1:1, and the resulted mixture was coated onto a NF substrate (1×1 cm^2). The electrode was then dried at 60 °C for 12 h in a vacuum oven.

Asymmetric supercapacitors (ASC) were assembled by directly employing as-prepared TiO_2/RGO/$Ni(OH)_2$ composites on NF as positive electrode and AC as negative electrode, and the weight of active materials for the two electrodes were about 11.6 mg and 10.5 mg, respectively. The electrochemical performance of ASC devices were tested in a two-electrode system at room temperature in 1 M KOH electrolyte.

3. Results and discussion

3.1. XRD patterns, Raman spectra and XPS of TiO_2/RGO/$Ni(OH)_2$ composites

XRD patterns of TiO_2/RGO/$Ni(OH)_2$ composites and pure RGO are given in Fig. 1. It can be seen that, in Fig. 1a, there are three