Nano Energy (2015) 12, 258–267

Available online at www.sciencedirect.com

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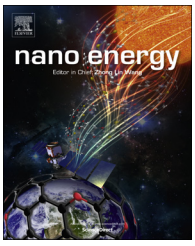

SHORT COMMUNICATION

Electrochromo-supercapacitor based on direct growth of NiO nanoparticles

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Received 8 November 2014; received in revised form 9 December 2014; accepted 22 December 2014
Available online 31 December 2014

KEYWORDS
Nickel oxide;
Energy storage;
Electrochromism;
Nanoparticle;
Electrochromo-supercapacitor

Abstract
In this paper, uniform NiO nanoparticles on different substrates were successfully synthesized by a simple and low-cost solvothermal method. The high capacitance (1386 F g^{-1} at 1 A g^{-1}) and excellent rate capability were achieved for NiO nanoparticle film as supercapacitor electrode. A large optical modulation (63.6% at 550 nm), high coloration efficiency (42.8 cm^2 C^{-1} at 550 nm) and good cycling stability can be achieved when the same NiO nanoparticles are used for electrochromic application. The excellent electrochemical performance is attributed to the uniform nanoparticles morphology and stable chemical bonding of the NiO nanoparticle on the substrates, which shorten the ion diffusion length and greatly facilitated the charge transfer both at the contact interfaces and within the electrode materials during the electrochemical process. In addition, we present a smart supercapacitor which function as a regular energy storage device and simultaneously monitor the level stored energy by visual changes. The findings present great promise for NiO nanoparticle film as practical electrode materials as chromo-supercapacitor.

Introduction

The escalating problems of energy and environment require society to move towards sustainable and renewable resources. Harvesting, converting, storing and saving renewable energy are the most important energy solution strategies [1–5]. Supercapacitors also known as electrochemical capacitors are gaining increasing attention due to their high power density, rapid charging/discharging rate, superior rate capability, long cycle life and the ability to balance the need of high energy density of battery and fast power delivery of capacitor. However, while major progress has been achieved in the theoretical and practical aspect of supercapacitors recent years, supercapacitors still suffer from high production cost, compromised rate capacitance and reversibility [6–10].

On the energy conservation spectrum, smart glass based on electrochromics potentially reduce 16% of peak electricity load through modulation of transmitted light and solar

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http://dx.doi.org/10.1016/j.nanoen.2014.12.031
2211-2855/

heat, providing indoor comfort and energy efficiency simultaneously [11–13]. The optical modulation of electrochromics such as transmittance, reflectance and absorptance is achieved by an electric field assisted insertion and extraction of cations and electrons. Unfortunately, short life time, low chromatic contrast, long switching time and low coloration efficiency limit its widespread deployment. To overcome the drawbacks of the supercapacitor and smart glass, tremendous research effort on the development of nanostructure materials for electrochemical active electrodes has been pursued.

Recently, nickel oxide (NiO) as a typical electrode material has been intensively researched because of its superior electrochemical performances in both supercapacitors [14,15] and electrochromic devices [16]. Synthesis of high surface area NiO nanoparticles film obtained from sol-gel [17], electrodeposition [18] and spray pyrolysis [19] has facilitated a reduced ion diffusion length and improved electrolyte penetration within the NiO nanoparticle layer. However, most of the pure NiO films suffer from poor cycling stability due to the poor adhesion with the transparent conducting substrate such as indium tin oxide (ITO). For example, Zayim et al. [17] fabricated NiO films by the spin-coating technique, the films gradually degraded after 500 cycles. Xia et al. [20] prepared highly porous NiO thin films on ITO glass by a simple chemical bath deposition method in combination with a heat-treatment process. Although the films exhibit large optical modulation up to 82% and the high coloration efficiency (*CE*) of 42 $cm^2\,C^{-1}$, parts of the film detached from the substrate after 300 cycles and the film electrode started to break down. Recently, Cai et al. [21] synthesized nanostructured NiO thin films by simple and efficient electrodeposition in a choline chloride-based ionic liquid. The films exhibit fast switching speed and high *CE*, but the film started to fall off the ITO substrate after 600 cycles. In addition, the synthesis of the uniform NiO nanoparticles is not easy due to the existing approaches plagued by complex procedures, unwanted side-reaction, small yield, large particle size distribution, and required a subsequent thermal treatment. For instance, Jahromi et al. [22] synthesized NiO nanoparticles by a sol-gel method in a gelatinous medium. The reaction process required a subsequent thermal treatment, and the NiO nanoparticles exhibited a broad particle size distribution. Li et al. [23] found that the reaction between hexadecylamine and nickel acetylacetonate was rapid and hard to control, resulting in the formation of a black Ni precipitate exclusively. Recently, Liang et al. [24] synthesized the NiO based on ligand protection method, but the yield of the product was small. Furthermore, the experiment process is complex due to the NiO powder need to be precipitated out and further purify by adding some solvents. In addition, the NiO films were prepared by a two-step fabrication procedure. We have previously introduced the use of linear polyethylenimine treatment to provide bonding that proves to enhance the cycling stability of V_2O_5 and WO_3 sol-gel films on ITO [25,26]. Therefore, it is of great importance to design and fabricate high-quality electrode materials with chemical compatibility to the surface of the ITO substrates.

Herein, we report direct growth of uniform NiO nanoparticles on different substrates using a simple and low-cost solvothermal method. The uniform NiO nanoparticle films were fabricated without further thermal treatment. We evaluate the electrochemical properties of the NiO nanoparticles in the applications of supercapacitor and electrochromics. The uniform NiO nanoparticle films exhibit excellent electrochemical performance, including excellent rate capability, high capacitance, large optical modulation, high coloration efficiency and super-long cycle life. We demonstrate an electrochromo-supercapacitor that changes color to reflect the state of charging based on the NiO nanoparticles electrode.

Experimental section

Tert-butanol (anhydrous, $\geq$99.5%), nickel acetylacetonate (95% purity), nickel nitrate hexahydrate and Triton™ X-100 were purchased from Sigma-Aldrich. Isopropyl alcohol (95% purity) was purchased from Aik Moh Paints & Chemicals Pte Ltd. (95% purity). Polyethylene glycol 200 and ammonia solution (29%) were obtained from Merck. All chemicals were used without further purification.

Preparation of uniform NiO nanoparticles film

Firstly, nickel foam and ITO-coated glass were washed with acetone, de-ionized water, and finally with ethanol in an ultrasonic bath for 10 min. For ITO-coated glass substrate, a NiO seed layer needs to be prepared before growth of uniform NiO nanoparticles. The NiO seed layer was prepared on ITO-coated glass through a spin coating method. The coating solution was prepared according to the literature [27]. Briefly, 1.7 g nickel nitrate hexahydrate was dissolved into 60 ml of equal amounts of isopropanol alcohol and polyethylene glycol 200. Then 2 ml ammonia solution (29%) and 1 ml Triton™ X-100 were added to the above solution under stirring to form nickel hydroxide colloid solution. The solution was further stirred for 30 min and the final solution was used to coat on the ITO substrates by a spin-coater. The spin coating processes were performed at 3000 rpm for 60 s and repeated for 2 times. The coated substrates were heated at 350 °C for 20 min during each coating process. For growth of uniform NiO nanoparticles on different substrates, the reaction solution was prepared through a modified approach on a previously reported method [28]. Briefly, 0.39 g nickel acetylacetonate was added into 42 ml tert-butanol under magnetic stirring forming a light green suspension. Afterwards, the suspension obtained was transferred into a Teflon lined stainless autoclave. The nickel foam and ITO-coated glass with the NiO seed layer were placed vertically in the autoclave, and then the autoclave was sealed and heated at 200 °C for 24 h. After synthesis, the autoclave was cooled to room temperature under natural cooling. The substrates were taken out, rinsed extensively with deionized water and allowed to dry in ambient air. The precipitates in the solution were also collected and treated the same way for Fourier transform infrared spectra (FTIR) characterization.

Sample characteristics

X-ray diffraction (XRD, Shimadzu discover diffractometer with CuKα-radiation (λ=1.5406 Å)), scanning electron microscopy (SEM, JEOL 7600F), and transmission electron microscopy