Materials Letters 200 (2017) 113–117

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Buckypaper templating Ni-Co hydroxide nanosheets film with stimuli-responsive properties

Xinxue Wang [a,b], Tianshu Song [a,*]

[a] School of Aerospace and Civil Engineering, Harbin Engineering University, Harbin, PR China
[b] Mudanjiang Normal University, Mudanjiang, PR China

ARTICLE INFO

Article history:
Received 14 March 2017
Received in revised form 20 April 2017
Accepted 22 April 2017
Available online 24 April 2017

Keywords:
Ni-Co hydroxide nanosheets
Buckypaper
Stimuli-responsive sensors

ABSTRACT

Ni-Co hydroxide nanosheets (NCHs) deposition on as-oxidized Buckypaper (BP) were fabricated by a one-step electrodeposition method for sensitive stimuli-responsive sensors (temperature, mechanical deformation etc.). This NCHs/BP film exhibits a near linear relationship between normalized electrical resistance (R/R_0) responses with different external conditions, such as large coefficient of linear thermal expansion (CLTE) α of 235.0 in 10^{-6}/K under temperature stimuli, and linear electro-mechanical relationship with ultimate strain of 2.1% and ultimate stress of 21.0 MPa under mechanical deformation stimuli (stretching, bending and torsion), suggesting its promising applications as thermal sensors and mechanical-stimulated devices.

1. Introduction

Stimuli-responsive materials with decent mechanical and electrical properties are increasingly demanded for developing electrochemical sensors, biomedical devices and actuators [1–8]. The characteristic responses to different stimuli inputs, including temperature variation, stress distributions, and pH change, to name a few, make them feasible to prepare smart materials with special functions. Among this, thin paper-like materials have been widely studied due to their excellent flexibility, good processability and high efficiency [9,10]. In the present work, Buckypaper (BP) was chosen as a fabrication precursor attributed to its excellent mechanical robustness and electrical conductivity [11,12]. After the electrochemical oxidization process with Ni-Co hydroxide electrodeposited, the as-formed NCHs/BP films exhibit a high capacitance (1.5 F·cm^{-2}) and long term cycle life (capacitance retention of 92% over 10,000 cycles) for flexible supercapacitors in our earlier report [13]. And we are gratified to find that this NCHs decorated Buckypaper film demonstrated interesting responses to temperature variation and mechanical stimuli types (stretching, bending and torsion) with high sensitivity, suggesting its great potentials as sensitive thermal sensor and mechanical-stimulated device.

2. Materials and method

The thin NCHs/BP film was prepared by a facial one-step electrodeposition method as reported in earlier work [13]. The BP was purchase from Nanolab Inc (USA), and sulfuric acid, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2\ {\cdot}6H_2O$ and polyethylene terephthalate film were purchased from local supplier, respectively. In detail, the BP was electrochemically oxidized in H_2SO_4 solution (1 M) to make it hydrophilic firstly. After that, the electrodeposition was conducted using a conventional three-electrode system consisting of the as-treated BP as the working electrode, a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A constant potential of −1.0 V vs. SCE was adopted to deposit the NCHs upon the BP in an aqueous solution containing 0.1 M $Ni(NO_3)_2$ and 0.03 M $Co(NO_3)_2$. After electrodeposition for 2 min, the final NCHs/BP film was obtained after rinsing several times with deionized water. For electromechanical test, the as-prepared NCHs/BP film was firstly cut into small pieces by a size of 10 × 20 × 0.075 mm, and was electrically insulated and packaged at two sides by 0.5 mm thick polyethylene terephthalate film after the setting up of copper tape for conductive electrodes.

The surface morphologies of the NCHs/BP were characterized by scanning electron microscope (SEM, ZEISS Merlin) with an operating voltage of 10 kW. X-ray diffraction (XRD) analysis was carried out by an X-ray diffractometer (Rigaku Smartlab) using Cu-Kα source (1.54 Å). X-ray photoelectron spectroscopy (XPS) was obtained on an SSI SProbe XPS spectrometer (PHI 5700 ESCA System) with an Al(Kα) source. And polyethylene terephthalate

* Corresponding author.
E-mail address: xiwang_hit@126.com (T. Song).

http://dx.doi.org/10.1016/j.matlet.2017.04.108
0167-577X/© 2017 Published by Elsevier B.V.

film packaged NCHs/BP film was employed to test the electromechanical responses using a typical two electrode method.

3. Results and discussion

The XRD patterns of the bare BP and NCHs/BP film are comparatively shown in Fig. 1a. The highly intense (002) peak at 26.4° confirms the graphite structure from the BP precursor. Both diffraction peaks at 36.8° and 42.8° are ascribed to the typical crystal components of $NiCoO_2$. Meanwhile, the four sharp peaks at 34.9°, 39.5°, 53.1° and 60.9° is attributed from the crystal structures of comblainite ($Ni_{6.10}Co_{2.90}(OH)_{18.27}(CO_3)_{1.315}\cdot 6.7H_2O$) according to the JCPDS no. 33-0429. And the peaks located at 31.1° and 44.6° correspond to the (220) and (400) plane reflections of the Co_2NiO_4 sample. From the XRD patterns, the formation of the NCHs during the electrodepositing process can be proved. The chemical composition of NCHs/BP film was further studied by XPS analysis, as shown in Fig. 1b and d. The peaks located at 284.90, 530.91, 780.91 and 855.91 eV are corresponding to C_{1s}, O_{1s}, Co_{2p} and Ni_{2p}, and the deconvoluted peaks of C_{1s} spectrum of Fig. 1c corresponds to non-functionalized graphic structures (C–C, 286.4 eV), C-O functional groups (286.4 and 288.7 eV), respectively. Due to the electrochemically oxidized process of the BP, a considerable portion of oxygen-containing groups is derived. The peak centered at 530.5 eV indicates a typical characteristic of metal-oxygen bonds, while the peaks at 531.6 and 533.2 eV are related to C-O functional groups.

Fig. 2a and c are the SEM images of NCHs at different magnifications. A porous surface of BP is formed by the continuous connections among carbon nanotubes with diameters ranged from 20 nm to 30 nm (Fig. 2a). The combination of the mechanical robustness and excellent conductivity of the BP film provide a flexible template for NCHs deposition. As shown Fig. 2b and c, the NCHs is uniformly decorated on the as-treated BP film after the electrodeposition. The high-resolution SEM image in Fig. 2c reveals a 'star-shaped' pattern of NCHSs with a lateral size of approx. 100 nm.

The obtained NCHs/BP film was cut into strip with a size of 10×20 mm for mechanical test. The tensile test is conducted by a universal material testing machine (Instron-5569, UK) using quasi static loading by a loading rate of 0.5 mm/min. As shown in Fig. 3(a), The resultant strain-stress curve reveals a superior ultimate tensile strength and strain of 21.0 MPa and 2.1%, respectively. And a sharp crack of the films has been observed by SEM in Fig. 3b,c.

As demonstrated in Fig. 4, the sensing performance of NCHs/BP was evaluated responding to temperature variation. The normalized electrical resistance (R/R_0, where $R_0 = 8.2\ \Omega$) decreases almost linearly with the temperature elevation ranged from −60 °C to 80 °C , and about a 2.79% of electrical resistance variation ($\Delta R/R$) per 5 °C is observed, indicating a high sensitivity to such temperature fluctuations. After that, the influence of the temperature to the resistance variation becomes unobvious, and the electrical resistance remains the same even the temperature rises to 150 °C, showing an interesting dependent relationship between normalized electrical resistance and temperature curve as shown in Fig. 4a. Meanwhile, a near linear expansion is detected with a coefficient of linear thermal expansion (CLTE) α of 235.0 in 10^{-6}/K by laser thermal expansion test in Fig. 4b. In less than 45 min, the

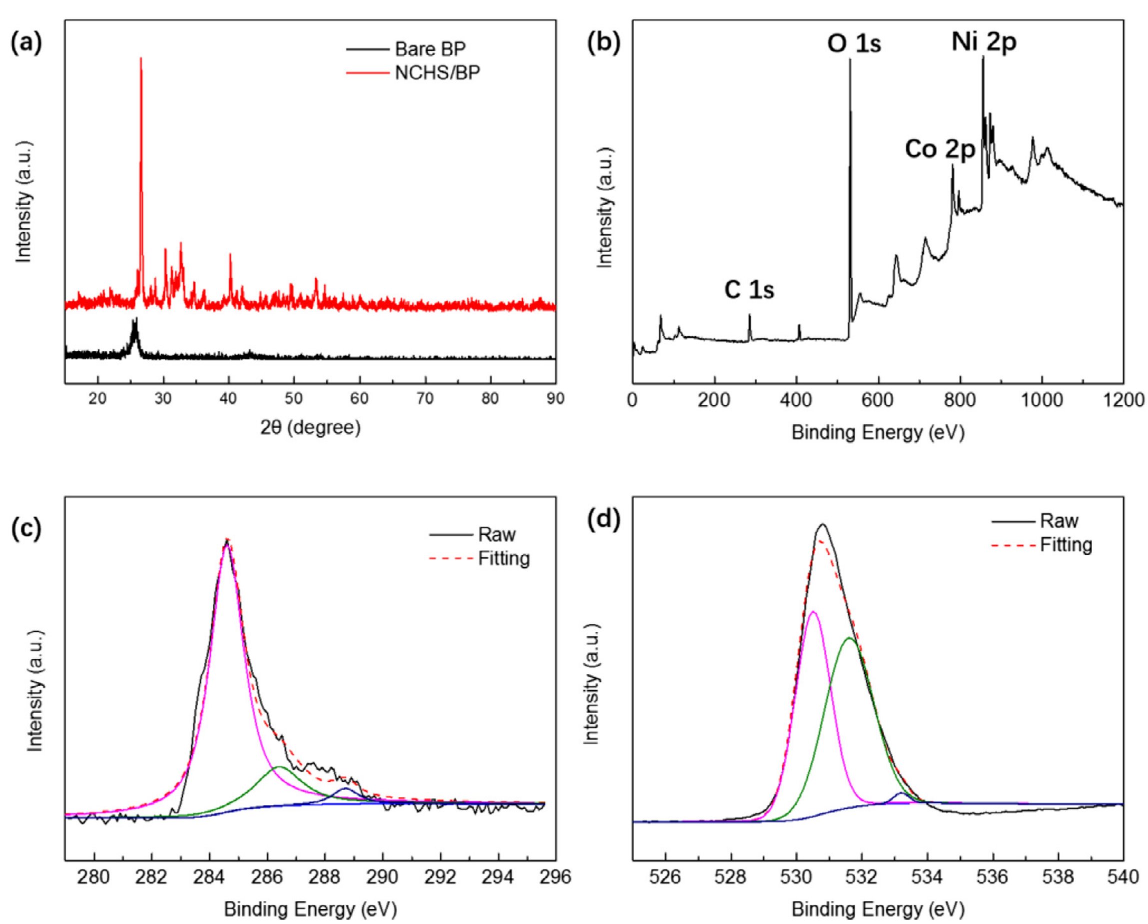

Fig. 1. (a) XRD patterns of bare BP and NCHs/BP; (b) Wide-scan of XPS spectrum of NCHs/BP; XPS spectrum of NCHs/BP: (c) C_{1s}; (d) O_{1s}.