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In-situ evolution of the NiO nanosheets on 3D-Ni-foam as a self-supported electrode for energy storage device applications

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ABSTRACT

This report shows the inexpensive synthesis of *in-situ* evolution of NiO nanosheets on 3D-Ni-foam as an outstanding binder-free and self-supported electrode for supercapacitors. The NiO//NiO supercapacitor shows a high specific capacitance (159.3F g^{-1}) at 6.7 A g^{-1}, energy density (22.1 W h kg^{-1}), and excellent power density (15250 W kg^{-1}). It unfolds superb stability (93.9%) after 10,000 GCD cycles and (95.4%) after 14 h voltage holding tests (VHTs). Also, it shows a low leakage current of 0.09 mA during 2 h VHTs.

1. Introduction

The depleting fossil fuels-based energy has recently encouraged researchers to develop alternative and new energy storage technologies [1]. Supercapacitors with two charge storage mechanisms such as Faraday reactions and electrostatic attractions have appealed much attention to energy storage devices, among various other energy storage systems due to their high power density, inexpensive, quick charging, and outstanding cycling stability, having advantages over fuel cell and batteries [2–4]. The numerous claims in electric transportation and handy electronic gadgets have previously been discussed with supercapacitors [4–6]. Significant developments have been made towards preparing different electrode materials-based supercapacitors; however, the lack of study of stability using voltage holding tests (VHTs) and leakage current needs more attention from researchers. Therefore, exploring the VHTs and leakage current of novel morphology electrode materials with excellent electrochemical properties of supercapacitors is a reliable opportunity to solve these concerns.

The NiO is an exciting nanomaterial due to its high electrical conductivity, inexpensive, excellent theoretical capacitance (2584F g^{-1}), high thermal and chemical stability, and wide bandgap (3.6–4.0 eV) [7–9]. It has exclusive eight-electron distribution in 3D orbital, which leads to the reengineering of electronic properties for various applications [10]. The binder-free and self-supported electrodes lead to a decrease in ohmic resistance. Extensive research has been performed on NiO-based supercapacitor, as discussed in the literature [11–15]. However, these reports have not discussed stability using voltage holding tests and leakage current of the supercapacitors, which is extremely important for their commercial applications.

This work studied the electrochemical properties of the NiO nanosheets grown on 3D-Ni-foam synthesized by the hydrothermal method. The NiO//NiO supercapacitor shows high specific capacitance, high energy, and power density. The outstanding stability and low leakage current were observed during voltage holding tests (VHTs). It also justified that the stability result was observed during 10,000 galvanostatic charging-discharging (GCD) cycles.

2. Experimental method

The 1 mmol nickel nitrate hexahydrate, 2 mmol urea, and 2 mmol ammonium fluoride were dissolved in 60 ml de-ionized water under stirring. After that, the above-prepared Ni precursor solution was transferred in a 100 ml autoclave. A cleaned Ni-foam (2 × 3 cm) was immersed into the above solution, and it was kept in the oven at 120 °C for 5 h. Finally, the as-grown precipitate on 3D-Ni-foam was washed, dried at 80 °C for 8 h, and annealed at 400 °C for 2 h to obtain the NiO nanosheets grown on 3D-Ni-foam as a self-supported electrode for supercapacitors.

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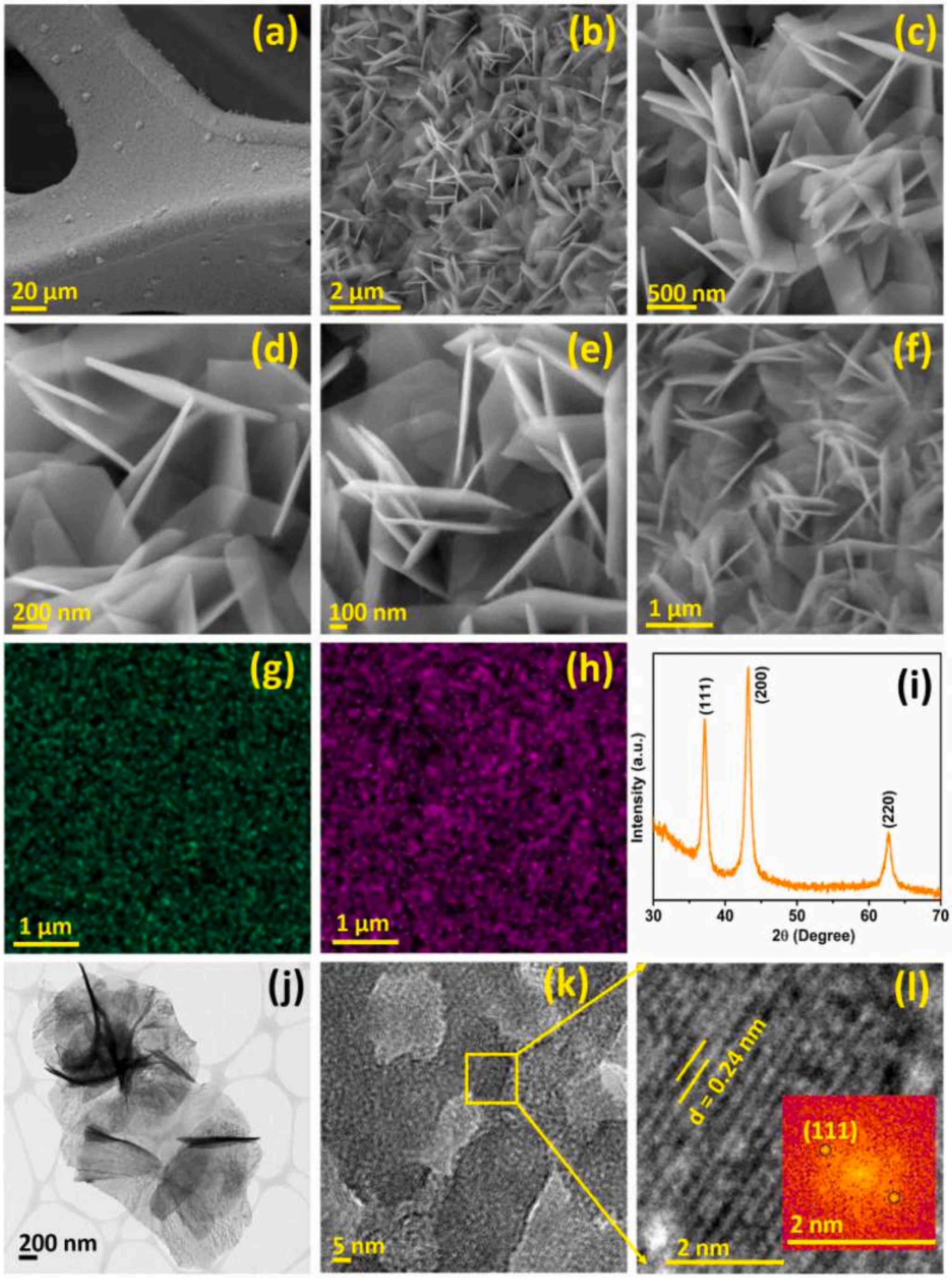

Fig. 1. (a–e) FESEM images, (f) area for mapping, (g) Ni, and (h) O elements; (i) XRD spectrum; (j) TEM, (k) HETEM, and (l) enlarged portion of HRTEM image (inset: FFT) of NiO nanosheets.

The morphology and color mapping studies were investigated using field emission scanning electron microscopy (FESEM) [JEOL, JSM-7800F] and transmission electron microscopy (TEM) [JEOL, JEM-2100F]. The structure was investigated using the X-ray diffraction (XRD, Smart Lab 3 kW, Rigaku) technique. The NiO//NiO supercapacitor was made up using two NiO electrodes, a separator (Whatman paper), and electrolyte gel (PVA/Na_2SO_4). The deposited NiO nanosheets mass on both electrodes is ~ 1.23 mg. The electrolyte gel was prepared by mixing 1.5 g PVA and 1.5 g Na_2SO_4 in 25 ml DI water at 95 °C for 5 h stirring. The electrochemical properties of supercapacitors were studied using an electrochemical workstation of IVIUM Technologies (Compactstat.h). The stability [using 14 h voltage holding tests (VHTs)] and leakage current (2 h) of the supercapacitor were studied using constant potential at 1.0 V for 2 h + 10 GCD cycles (at 14.2 A g^{-1}) and repeated 7 times.

3. Results and discussion

The NiO nanosheets [Fig. 1(a–e)] stand at different angles, parallel to each other, and coincided, exploring quick electronic transport, more and fast interactions between electrons and electrolyte ions, resulting in high electrochemical properties. The Ni and O elements are homogeneously dispersed entirely over the region, vindicating the flourishing development of the NiO nanosheets, as shown in Fig. 1(f–h). Fig. 1i

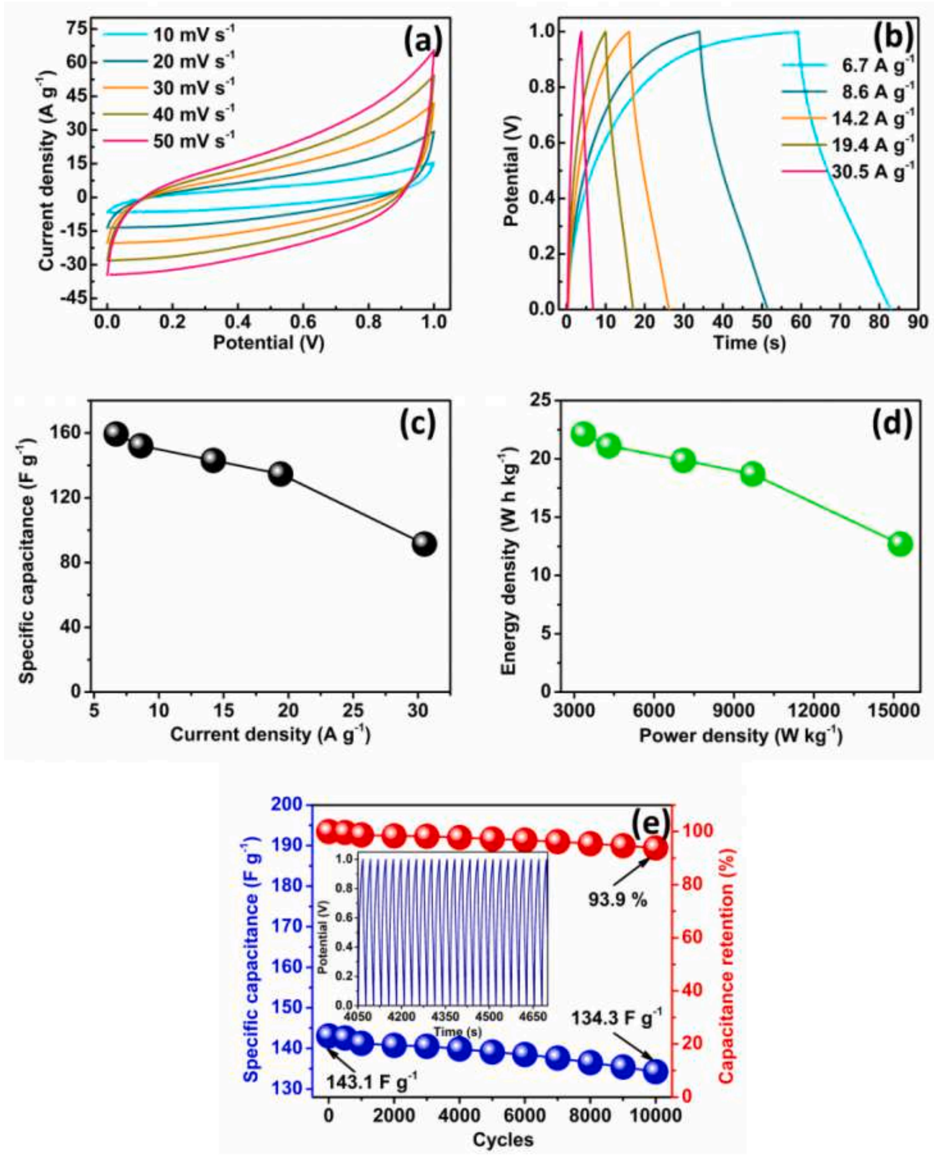

Fig. 2. (a) CV plots, (b) charge-discharge, (c) specific capacitance, (d) energy density plot, and (e) stability during 10,000 GCD cycles at 14.2 A g^{-1} (inset: in-between GCD cycles) of the supercapacitor.

displays the XRD spectrum with observed Bragg's diffraction peaks of (1 1 1), (2 0 0), and (2 2 0) of the NiO nanosheets, which corresponds to cubic NiO structure (JCPDS 47–1049) [10]. Fig. 1j depicts the TEM image of the NiO nanosheets overlapped with different orientations. Fig. 1(k and l) shows the HRTEM image and its enlarged portion with a lattice spacing of 0.24 nm and FFT pattern with (1 1 1) lattice plane of the NiO nanosheets.

Fig. 2a reveals CV plots of the NiO//NiO supercapacitor at various scan rates. It is observed that the CV curves are nearly rectangular forms, which represent the characteristics of the pseudocapacitance and electrical double layer capacitance [5]. The CV curves of NiO//NiO supercapacitor show high current at different scan rates due to the thin nanosheets of NiO, which enables sufficient interaction (electrodes and electrolyte ions) and executes the fast electron-ion charge transport [11,12]. However, there are no redox peaks in the CV curves due to the lack of hydrogen ions in the electrolyte [6]. Further, the symmetrical charge-discharge behavior at 14.2, 19.4, and 30.5 A g^{-1} revealed capacitive nature; however, the asymmetrical charge-discharge behavior at 6.7 and 8.6 A g^{-1} depicted Faradaic reactions, as exposed in Fig. 2b [5]. Fig. 2c shows specific capacitance (calculated using Eq. S1) ranges from 159.3 to 91.4F g^{-1} at various current densities. It may be due to the following reasons; (i) high ionic diffusivity, (ii) both the surface of the NiO nanosheets interacts with electrolyte ions, and (ii) no delamination due to the binder-free Ni foam substrate. In Fig. 2d, energy density varies from 22.1 to 12.7 W h kg^{-1} at different power densities from 3350 to 15250 W kg^{-1} [calculated using Eq. S2 and S3]. Fig. 2e shows excellent retention of 93.9% after 10,000 cycles at 14.2 A g^{-1}. The outstanding stability, power, and energy density may be due to the excellent conductivity of the NiO, and better interface ability between electrode and electrolyte ions reduces ionic charge transfer resistance.

Furthermore, Fig. 3a shows 14 h voltage holding tests (VHTs) [10 charging-discharging cycles at 14.2 A g^{-1} + 2 h VHTs] of the NiO//NiO supercapacitor to justify the stability results discussed in Fig. 2e. Fig. 3b depicts GCD cycles in-between VHTs at 14.2 A g^{-1}. Fig. 3c manifests the stability of the supercapacitor using 14 h VHTs. It is observed that the specific capacitance decreases from 143.1 to 136.5F g^{-1} after 14 h VHTs. The supercapacitor exhibits excellent specific capacitance retention of 95.4% after 14 h VHTs. Fig. 3d reveals a low leakage current (0.09 mA) during 2 h VHTs (inset: zoomed area). It may be due to the double-layer structure of the supercapacitor with a diffusion layer, where electrolyte

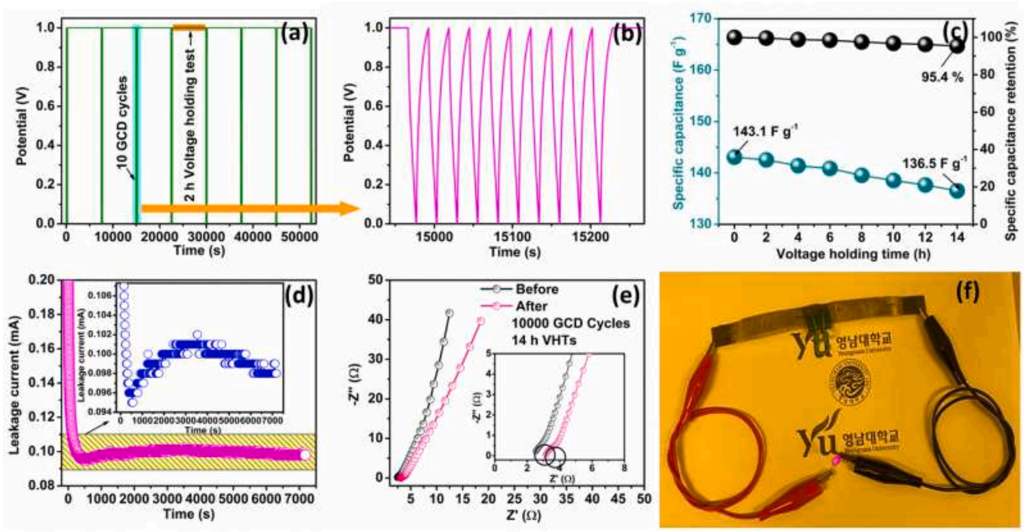

Fig. 3. (a) GCD cycles + VHTs, (b) GCD cycles in-between VHTs, (c) stability during 14 h VHTs, (d) leakage current (inset: enlarged portion), (e) impedance, and (f) red LED illumination of the supercapacitor.

ions have different interactions with NiO nanosheets [16]. Fig. 3e shows the impedance spectra of the supercapacitor before and after 10,000 GCD cycles & 14 h VHTs. The internal resistances are 2.52 Ω and 3.12 Ω before and after 10,000 cycles & 14 h VHTs. The charge transfer resistances are 1.11 Ω and 1.23 Ω after 10,000 cycles & 14 h VHTs (inset shows the enlarged area of the EIS spectrum). Fig. 3f demonstrates the illumination of a red LED using two supercapacitors in series. Fig. S1 (a–e) shows the TEM, HAADF, color mapping and EDX of the NiO nanosheets after electrochemical characterizations. It illustrates a stable phase structure of the NiO nanosheets with no deformation. Table S1 shows the comparative performance of the present work with the other reports on NiO nanomaterials/composite electrodes based supercapacitors.

4. Conclusion

In conclusion, the NiO//NiO supercapacitor illustrates high electrochemical parameters with outstanding stability (93.9%) after 10,000 cycles and 95.4% after 14 h VHTs. The supercapacitor shows a low leakage current of 0.09 mA during 2 h VHTs. Therefore, the NiO nanosheets can be suitable nanomaterials grown on 3D-Ni-foam as a self-supported electrode in supercapacitors for futuristic device applications.

CRediT authorship contribution statement

Rajneesh Kumar Mishra: Conceptualization, Methodology, Investigation, Writing – review & editing. **Gyu Jin Choi:** Formal analysis, Data curation, Investigation. **Hyeon Jong Choi:** Formal analysis, Data curation. **Huisu Shin:** Software, Data curation. **Youngku Sohn:** Supervision, Writing – review & editing. **Seung Hee Lee:** Supervision, Resources, Writing – review & editing. **Jin Seog Gwag:** Supervision, Resources, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2021.131052.

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