High-performance solid state asymmetric supercapacitor based on electrochemically decorated 3D network-like Co$_3$O$_4$ architecture on NiO nanoworms

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ABSTRACT
The unique 3D network-like cobalt oxide architecture was electrochemically deposited on nickel oxide nanoworms (NiONWs) with nickel foil (NF) substrate. After the anodic polarization of NF and its activation, a very thin film of NiO nanoworms with the average diameter of 30 nm and the length of 100 nm was successfully grown on anodized Ni foil (a-NF) by using a facile hydrothermal method under the mild conditions including a saturated alkaline solution of Ni$^{2+}$ at 65 °C to prepare a-NF/NiONWs. Then, 3D network-like Co$_3$O$_4$ nanosheets with the average thickness of 25 nm were directly electrodeposited on a-NF/NiONWs by using cyclic voltammetry under the optimized experimental conditions. The morphologies and detailed geometrical structures of the electrodes were conducted by FE-SEM. The fabricated a-NF/NiONWs/Co$_3$O$_4$ electrode provides a high areal specific capacitance of 1320 mF cm$^{-2}$ at a current density of 4 mA cm$^{-2}$ and high mass specific capacitance of 2000 F g$^{-1}$ at the current density of 6 A g$^{-1}$. By using a-NF/NiONWs/Co$_3$O$_4$ as a positive electrode and reduced graphene oxide-deposited NF (RGO/NF) as a negative electrode, a solid-state asymmetric a-NF/NiONWs/Co$_3$O$_4$/RGO/NF supercapacitor was assembled and it exhibited a high specific capacitance of 471.4 mF cm$^{-2}$ at a current density of 3 mA cm$^{-2}$. The fabricated solid-state supercapacitor also showed good rate capacity and long-term cycling performance of 2000 cycles.

Keywords: Supercapacitor; NiO nanoworms; 3D network-like; Co$_3$O$_4$ nanosheets; Reduced graphene oxide
1. Introduction
To address the rapid depletion of fossil fuels and the environmental pollution issues, there is a clear urgent need to develop green and renewable energy storage technologies to achieve a secure and reliable energy supply. Among the energy storage devices such as batteries, supercapacitors (SCs) have drawn intensive research attention mainly due to their high specific power densities, fast recharge capability and excellent cycling life. Besides, SCs can be used in hybrid energy storage systems (HESS) in combination with batteries and solar panels to minimize the battery stress.

Electrode materials are considered to play an important role in the performance of SCs. So far, there are mainly three kinds of electrode materials for their SC applications including carbon-based high surface area materials, conductive polymers and transition metal oxides. Although carbon-based SCs are the most widely used materials for commercially available SCs due to their long cycle life in the order of $10^5$, transition metal oxides can provide higher specific capacitances than carbonaceous materials and conducting polymers because of their multiple oxidation states for reversible Faradaic reactions and unique redox properties.

Among metal oxides available for SCs, cobalt oxides/hydroxides are favorable candidates due to their low cost, natural abundance, environmental compatibility, high theoretical specific capacitance of $3560 \text{ F g}^{-1}$, and high cycle life of about 20,000 cycles. Well-defined electrochemical redox activity and facilitated Co(OH)$_2$/CoOOH redox processes are all the benefits of Co-based SCs. As reported very recently, the lattice structural similarity between Co(OH)$_2$ and CoOOH redox couple enables a battery-mimic mechanism, resulting in high specific pseudocapacitance and long cycling life of Co-based SCs. Similar to pseudocapacitive mechanism of Co-based SCs, Ni(OH)$_2$ and NiOOH as a redox couple of Ni-based SCs have similar lattice structures which can result in the facilitated redox processes in Ni-based SCs.

Surface structure and size of these nano-architectures for charge storage in few nanometers of the electrode surface seriously affects the specific capacitance of SCs. Actually, the limited ion diffusion within the dense nanostructure and the slow electron transport between the electrolyte and electroactive species at the electrode surface will result in low specific capacitances for Co and Ni-based SCs far from their theoretical capacities.

In this work, regarding the lattice structural similarity between Co(OH)$_2$/CoOOH and Ni(OH)$_2$/NiOOH redox couples and the serious effect of film thickness of supercapacitive materials on charge storage, a very thin layer of NiO nanoworms (NiONWs) were grown on
anodized Ni foil (a-NF) by using a facile and scalable hydrothermal method. To the best of our knowledge, this is the first report on the growth of wormlike NiO nanostructure under the mild conditions for SC applications. Moreover, 3D network-like Co$_3$O$_4$ nanosheets were electrodeposited on a-NF/NiONWs by using a simple sequential-electrodeposition method. Finally, a solid state asymmetric supercapacitor was fabricated by assembling a-NF/NiONWs/Co$_3$O$_4$ as a negative electrode and NF/graphene as the positive electrode. Remarkably, the fabricated asymmetric supercapacitor (ASC) shows preeminent cycling stability with a slight decay after 2000 charge/discharge cycles in the potential window of 0 to 1.4 V with a high specific capacitance.

2. Experimental and methods

**Fabrication of a-NF/NiONWs/Co$_3$O$_4$ electrode**

For the fabrication of a-NF/NiONWs/Co$_3$O$_4$ electrode, at first, Ni foil (NF) was anodized under the applied anodic potential. For the preparation of anodized Ni foil (a-NF), Ni foil (2.0×0.5 cm$^2$) was polished with a fine emery paper (1200 SiC paper) and then was cleaned by consecutive sonication in deionized (DI) water, ethanol, and acetone for 10 min. Anodization of NF was performed in a 100-ml solution containing 94.5 ml glycerol (C$_3$H$_8$O$_3$), 5.0 ml DI water and 0.50 g KOH. Pre-cleaned NF was anodized in a two-electrode electrochemical cell with NF (2.0×0.5 cm$^2$) as anode and Pt foil (1.0×1.0 cm$^2$) as cathode by applying +60 V for 45 min. Finally, anodized nickel foil (a-NF) was rinsed with DI water, sonicated for 10 min to remove residual electrolyte and dried in ambient air.

NiO nanoworms (NiONWs) were grown on a-NF in a supersaturated alkaline solution of Ni$^{2+}$. The solution was prepared by the addition of appropriate amounts of 0.20 M nickel acetate solution into 20.0 mL of 1.0 M NaOH solution at 65 °C until a slight Ni(OH)$_2$ precipitate appeared in solution. Then, prepared a-NF was vertically immersed in a stirred saturated alkaline Ni$^{2+}$ solution at 65 °C for 120 min. Finally, the fabricated a-NF/NiONWs electrode was washed with DI water and dried in air.

Network-like Co$_3$O$_4$ nanosheets were directly electrodeposited on a-NF/NiONWs by cycling the potential using cyclic voltammetric technique. The deposition was performed in a three-electrode electrochemical system including Ag/AgCl, Pt foil and a-NF/NiONWs as reference, counter and working electrodes, respectively. The electrodes were immersed in an electrochemical deposition bath including 15.0 ml of 0.1 M Co(NO$_3$)$_2$·6H$_2$O and 5.0 ml of 2.0 M NaNO$_3$. The pH of the solution was adjusted to 7.40 by adding an appropriate amount
of 0.1 M NaOH to the solution. The potential was cycled 8 times between -1.2 V to +1.0 V at the scan rate of 50 mV s^{-1} (Scheme 1).

A solid-state asymmetric supercapacitor (ASC) device based on a-NF/NiONWs/Co_{3}O_{4} as positive electrode and graphene-deposited NF (RGO/NF) as negative electrode was fabricated. For the fabrication of negative electrode, reduced graphene oxide (RGO) was deep-coated on NF by sequential immersing of the substrate into an aqueous GO solution (1.0 mg L^{-1}) and drying in the oven at 60 °C for 30 min (5 times) and annealed at 300 °C for 3 h. Then, ASC device was simply assembled by using saturated filter paper with 1.0 M KOH as a separator.

Scheme 1

3. Results and discussion

Morphology, surface analysis, and characterizations

The anodic polarization of NF was performed at a two-electrode system by immersing NF as anode and a Pt foil as cathode in an organic-aqueous solution under the applied potential of +60 V. The preliminary experiments based on FE-SEM image analysis showed that the anodization at the applied potentials lower than +60 V did not proceed as well. So, the anodic polarization was carried out at a constant voltage of +60 V at different anodization times of 5, 30, 45 and 60 min in a solution containing 94.5 %v glycerol, 5.0 %v DI water and 0.50 %w KOH. The surface morphology of the resulted anodized Ni foil (a-NF) samples was investigated by FE-SEM (Fig. 1).

Fig. 1

Fig. 2 shows CVs of the anodized Ni foil at a constant voltage of +60 V at different anodization times of 5, 30, 45 and 60 min. Two distinct oxidation and reduction peaks are attributed to the electrochemical oxidation-reduction of Ni(OH)_{2}/NiOOH species. Based on these findings and CVs of the resulted a-NF samples, a-NF sample which was prepared under the applied voltage of +60 V at 45 min with higher transported charge (the integrated area of CV curves) was selected as optimized sample for further experiments.
During the anodization process, Ni species at the electrode surface is oxidized to Ni$^{2+}$ ions. On one hand, Ni(OH)$_2$ and NiOOH species can be formed at the electrode surface because of the basic nature of the solution. On the other hand, the resulted Ni$^{2+}$ from the anodic oxidation of Ni at the electrode surface can be expelled into the electrolyte because of the applied electric field.

Wormlike NiO nanostructures were grown on a-NF by immersing a-NF into the saturated alkaline solution of Ni$^{2+}$ without adding any additional reagent at different times of 1, 2 and 3 h. The FE-SEM images of a-NF/NiONWs samples are shown in Fig. 3. As it is clear, NiO nanoworms (NiONWs) with few tens of nanometers in diameter have been grown on a-NF substrate under the mentioned experimental conditions. The growth mechanism can be explained as follows. In a saturated alkaline solution of Ni$^{2+}$, the concentration of dissolved Ni$^{2+}$ species are at sub-nanomolar (~nM) level even at the elevated temperatures. Also, Ni(OH)$_3^-$ species would not be formed in such a solution and there would not be any equilibria including Ni(OH)$_3^-$ or Ni(OH)$_4^{2-}$ species. So, it seems that three distinct equilibria proceed in a saturated alkaline solution of Ni$^{2+}$ and a-NF//solution interface:

\[
\text{Ni}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Ni(OH)}_2^{0} \text{(aq)} \quad (6)
\]

\[
\text{Ni(OH)}_2^{0} \text{(aq)} \rightleftharpoons \text{Ni(OH)}_2 \text{(ads)} \quad (7)
\]

\[
\text{Ni(OH)}_2 \text{(ads)} \rightleftharpoons \text{NiO (ads)} + \text{H}_2\text{O} \quad (8)
\]

where, Ni(OH)$_2^{0}$ (aq) and Ni(OH)$_2$ (ads) are dissolved and adsorbed nickel hydroxide, respectively, and NiO (ads) is the adsorbed NiO at the electrode surface. So, for the growth of hydrated Ni(OH)$_2$ at the electrode surface, among the well-known solubility equilibrium (Eq. 6), the adsorption/desorption equilibrium (Eq. 7) should also be considered. In a saturated alkaline solution of Ni$^{2+}$ at the elevated temperatures (here, 65°C), hydrated Ni(OH)$_2$ can be in equilibrium with adsorbed NiO (i.e. dehydrated Ni(OH)$_2$) species or deposited NiO at a-NF surface during anodization (Eq. 8).
Fig. 3 shows that the preferred morphology is wormlike at the first 1 h of the hydrothermal reaction. The average thickness of NiONWs thin film is about 50 nm and the average thickness of the anodized film is about 0.4 μm. Energy dispersive x-ray spectroscopy (EDS) of a-NF/NiONWs confirms the presence of Ni and O elements at the surface of sample (Fig. S2a).

After the growth of NiONWs on a-NF, followed by the activation of electrode surface by cycling the potential between 0 to +0.5 V (50 cycles) in 1.0 M KOH solution, Co$_3$O$_4$ nanosheets were directly electrodeposited on a-NF/NiONWs by cycling the potential (8 cycles) between -1.2 V to +1.0 V at the scan rate of 50 mV s$^{-1}$ by using cyclic voltammetry. The surface morphology of the resulted a-NF/NiONWs/Co$_3$O$_4$ electrode was shown in Fig. 4a-c. As it is clear, porous Co$_3$O$_4$ nanosheets are deposited on NiONWs forming uniform network-like structure. Such 3D interconnected nanostructures offer a large specific surface area and therefore, provide efficient contact between the electrode surface and the electrolyte, leading to fast faradic reactions.

The average thickness of Co$_3$O$_4$ nanosheets and the interspaces between them are about 30 nm and 200 nm, respectively. This architecture offers a facilitated ion transport during fast charge/discharge processes and provides appropriate V-type channels for ion diffusion through the porous layer with greatly reduced diffusion length over which ions can transport. Energy dispersive x-ray spectroscopy (EDS) of a-NF/NiONWs/Co$_3$O$_4$ confirms the presence of Ni and Co elements at the surface of sample (Fig. S2b). XRD patterns of the as-deposited Co$_3$O$_4$ (a-NF/NiONWs/Co$_3$O$_4$) and annealed samples were examined (Fig. 5).
the annealed sample, among three characteristics diffraction peaks of Ni substrate, the peaks at 20 values of 19.03°, 31.29°, 36.99°, 39.12°, 44.60°, 55.65°, 59.45 and 65.37° are attributed to (111), (220), (311), (222), (400), (422), (511) and (440) crystal planes, respectively, and the pattern is indexed to the cubic Co₃O₄ (JCPDS 073-1701). The average crystal size of Co₃O₄ was calculated by Scherrer equation and obtained to be 15.2 nm.

**Fig. 5**

FTIR-ATR spectra of as-prepared and annealed a-NF/NiONWs/Co₃O₄ samples are shown in Fig. S4. The characteristic peaks of 630 cm⁻¹, 667 cm⁻¹, and 776 cm⁻¹ are attributed to M-O-M vibrations of Co₃O₄. The peaks at 3359 cm⁻¹ and 1641 cm⁻¹ are attributed to the stretching and bending modes of hydroxyl group of adsorbed H₂O, respectively, and are vanished after annealing. The appeared peaks at around 1400 cm⁻¹, 1230 cm⁻¹ and 1057 cm⁻¹ are seems to be attributed to the carbonate group originating from the CO₂ during ATR analysis.

**Electrochemical properties of a-NF/NiONWs/Co₃O₄ electrode**

CVs and galvanostatic charge-discharge curves were obtained in a three-electrode cell to evaluate the electrochemical properties of a-NF/NiONWs/Co₃O₄ and a-NF/Co₃O₄ electrodes. **Fig. 6a** shows the CVs of a-NF/NiONWs/Co₃O₄ at different scan rates within the potential window of 0 V to +0.5 V. The oxidation-reduction peaks of Co₃O₄/CoOOH species are observed in voltammograms, indicating the pseudocapacitive behavior of the fabricated electrode. The electrochemical oxidation-reduction reactions of Co₃O₄ are shown in the following equations:

\[
\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- \rightleftharpoons 3 \text{CoOOH} + \text{e}^- \quad (6)
\]

\[
\text{CoOOH} + \text{OH}^- \rightleftharpoons \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (7)
\]

A couple of anodic peaks exhibited at +0.12 V and +0.37 V at the scan rate of 0.02 V s⁻¹ are attributed to the oxidation processes of cobalt species (equations 6 and 7), and a couple of cathodic peaks at about +0.10 V and +0.25 V are due to their corresponding reduction processes.

Notably, the charge transport of annealed a-NF/NiONWs/Co₃O₄ electrode was examined by using cyclic voltammetry (Fig. 6c). Compared to as-prepared electrode, the annealed samples showed one order of magnitude lower current densities and did not show well-defined oxidation-reduction peaks corresponding to the oxidation process of cobalt species.
Finally, as discussed above, before the electrodeposition of $\text{Co}_3\text{O}_4$, a-NF/NiONWs electrode was electrochemically activated in alkaline solution by consecutive cycling the potential between 0 to $+0.5 \text{ V}$ (50 cycles) in 1.0 M KOH solution.

**Fig. 6**

Galvanostatic charge-discharge (GCD) curves of a-NF/$\text{Co}_3\text{O}_4$ and a-NF/NiONWs/$\text{Co}_3\text{O}_4$ electrodes in the potential range of 0 to $+0.50 \text{ V}$ at a constant current density of 6.0 mA cm$^{-2}$ are shown in **Fig. 7a**. Two visible and separated plateaus in the charge-discharge process of a-NF/NiONWs/$\text{Co}_3\text{O}_4$ electrode resulting from the redox reactions of $\text{Co}_3\text{O}_4$ species indicate the pseudocapacitive behavior, which is consistent with the peaks observed in their corresponding CVs (**Fig. 6**). Also, the GCD plots exhibit asymmetric charge-discharge profiles for both a-NF/NiONWs/$\text{Co}_3\text{O}_4$ and a-NF/$\text{Co}_3\text{O}_4$ electrodes. **Fig. 7b** shows the charge-discharge curves of a-NF/NiONWs/$\text{Co}_3\text{O}_4$ electrode at various current densities of 4, 6, 8 and 12 mA cm$^{-2}$. The GCD curve is highly symmetric at low current densities, revealing the excellent electrochemical reversibility of supercapacitive active materials at the electrode surface. According to Eq. (2), the discharge capacitance of a-NF/NiONWs/$\text{Co}_3\text{O}_4$ at 8 mA cm$^{-2}$ is 1164 mF cm$^{-2}$, which is about 10 times higher than that of a-NF/$\text{Co}_3\text{O}_4$ electrode (110 mF cm$^{-2}$), demonstrating the advantage of NiONWs thin film layer in improving the pseudocapacitance performance of electrode.

The areal discharge capacitances ($C_D$), which are more important in practical applications, were calculated to be 859.2, 1164, 1195.2 and 1320 mF cm$^{-2}$ at the current densities of 12, 8, 6 and 4 mA cm$^{-2}$, respectively. The coulombic efficiency ($\eta$), energy density ($E$) and power density ($P$) of the fabricated electrode was calculated and obtained to be 94.28%, 69.4 Wh kg$^{-1}$, and 1666.6 W kg$^{-1}$, respectively. The decrease in specific capacitance by increasing the current densities is attributed to the limited ion migration inside the active materials in shorter times. A maximum areal specific capacitance of 1320 mF cm$^{-2}$ was reached at 4 mA cm$^{-2}$.

**Fig. 7**

**A solid state asymmetric a-NF/NiONWs/$\text{Co}_3\text{O}_4$/RGO/NF supercapacitor studies**

Cyclic voltammetry was performed in a three electrode system to find the electrochemical potential windows of the positive and negative electrodes (**Fig. 8a**). As it is clear from CVs,
the potential windows are in the ranges of -0.8 to 0.0 V for negative electrode and 0.0 to +0.5 V for positive electrodes and the capacitances of two electrodes are almost equal. The working potential window of 0 to 1.4 V was selected, where the oxidation/reduction of water at the end of potential window was not occurred and the transport of charge density was higher. The voltammetric responses of ASC were also investigated at different scan rates in the capacitive potential range of 0.0 to 1.4 V (Fig. 8c). Furthermore, GCD curve at the current density of 3.0 mA cm$^{-2}$ was investigated to study the capacitive performance of the fabricated ASC device (Fig. 8d). A maximum areal specific capacitance of 471.4 mF cm$^{-2}$ was achieved for ASC at the current density of 3 mA cm$^{-2}$.

Fig. 8

The cycle life of the proposed ASC is a critical parameter which plays an important role in the performance of device. So, the cycle life of ASC was investigated by GCD technique at the current density of 4.0 mA cm$^{-2}$. The capacitive retention of ASC as a function of cycle numbers was shown in Fig. 9a. The proposed ASC preserves more than 75% of its initial specific capacitance after 2000 successive cycles, indicating the excellent long cycle life and electrochemical stability of fabricated ASC supercapacitor.

Electrochemical impedance spectroscopy (EIS) of assembled ASC was investigated to measure the conductivity and the charge transfer resistance of NiONWs/Co$_3$O$_4$ thin film (Fig. 9b). The fitted data and the equivalent circuit model are reported in Table 1 and Fig. 9c, respectively. The $R_s$ value, i.e. the combination of ionic and electronic resistance, intrinsic resistance of the electrode materials, and diffusive and contact resistance at electrode/current collector interface, is 0.0977 Ω cm$^{-2}$ that shows the high conductivity of fabricated supercapacitor.

Fig. 9

Table 1. Electrochemical impedance spectroscopic data of asymmetric SSC cell calculated from the fitted data.

| $R_s$ (Ω cm$^{-2}$) | $R_{ct}$ (Ω cm$^{-2}$) | $R_p$ (Ω cm$^{-2}$) | CPE$_{p}$ (S s$^{n}$ cm$^{-2}$) | n | CPE$_{dl}$ (S s$^{n}$ cm$^{-2}$) | n | W (S s$^{0.5}$ cm$^{-2}$) |
|------------------|------------------|------------------|-----------------|---|-----------------|---|-----------------|
| 0.0977           | 185              | 2.98             | 0.0047          | 0.700 | 0.0097          | 0.791 | 0.0265         |
4. Conclusions
A new facile method was proposed for the fabrication of a-NF/NiONWs/Co$_3$O$_4$ supercapacitive electrode with high capacitive performance. NiONWs were grown on an anodized Ni foil by using a facile and scalable hydrothermal method at the ambient pressure and the mild temperature conditions. To the best of our knowledge, the proposed method for the growth of the wormlike NiO nanostructures has not been reported yet. Finally, unique 3D network-like Co$_3$O$_4$ nanosheets were directly electrodeposited on a-NF/NiONWs by the cyclic voltammetry. The morphology of the thin films was characterized with FE-SEM. The fabricated Ni/NiONWs/Co$_3$O$_4$ electrode provides a high capacitance of 1320 mF cm$^{-2}$ at a current density of 4 mA cm$^{-2}$, higher than that for a-NF/Co$_3$O$_4$ electrode. Finally, an all-solid-state asymmetric a-NF/NiONWs/Co$_3$O$_4$/RGO/NF supercapacitor was assembled and it exhibited a high specific capacitance, good rate capacity, excellent energy density and long cycling life of 2000 cycles. Table 2 compares the performance of the fabricated supercapacitor electrode with recently reported cobalt oxide-based supercapacitor electrodes.

Table 2. Comparison of the performance of a-NF/NiONWs/Co$_3$O$_4$ supercapacitor electrode with recently reported cobalt oxide-based supercapacitor electrodes.

| Supercapacitor electrode composition       | Specific capacitance (F g$^{-1}$) | Current density (A g$^{-1}$) | Energy density (Wh kg$^{-1}$) | Power density (W kg$^{-1}$) | Potential window (V) | Ref. |
|-------------------------------------------|-----------------------------------|-----------------------------|------------------------------|-----------------------------|----------------------|-----|
| Co$_3$O$_4$ nanoparticle                  | 523                               | 0.5                         | -                            | -                           | 0.6                  | 56  |
| Co$_3$O$_4$/N-doped carbon particle       | 316.2                             | 1.0                         | -                            | -                           | 1.0                  | 57  |
| Co$_3$O$_4$/Polyaniline                   | 1302                              | 1.0                         | 41.5                         | 15.9                        | 1.6                  | 58  |
| Co$_3$O$_4$ Microdumbbell                 | 407.5                             | 1.0                         | -                            | -                           | 0.6                  | 59  |
| Co$_3$O$_4$/activated carbon              | 202                               | 1.0                         | 24.5                         | 225                         | 1.5                  | 60  |
| Ni/Co$_3$O$_4$@NiO                        | 1236.67                           | 1.0                         | 61.83                        | 300                         | 1.4                  | 61  |
| Ni/Co$_3$O$_4$ nanosheets                 | 610                               | 1.0                         | 136                          | 750                         | 1.7                  | 62  |
| Ni/NiO-Co$_3$O$_4$                        | 801                               | 1.0                         | -                            | -                           | 0.9                  | 63  |
| Ni/Co$_3$O$_4$@Ni(OH)$_2$                 | 1306.3                            | 1.2                         | 40                           | 3455                        | 1.7                  | 64  |
| Ni/NiO@Co$_3$O$_4$                       | 437                               | 1.0                         | -                            | -                           | 0.5                  | 65  |
| Co$_3$O$_4$/N-doped CNT                   | 406                               | 2.0                         | -                            | -                           | 1.0                  | 66  |
| Graphene@Co$_3$O$_4$                      | 670                               | 1.0                         | -                            | -                           | 0.8                  | 67  |
| a-NF/NiONWs/Co$_3$O$_4$                   | 2000                              | 6.0                         | 69.4                         | 1666.6                      | 1.4                  | This work |

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**Figure & Scheme Captions**

**Scheme 1.** Schematic representation of the fabrication of a-NF/NiONWs/Co$_3$O$_4$ electrode

**Fig. 1.** FE-SEM images of anodized Ni foil (a-NF) at the applied voltage of +60 V at various anodization times of (a) 5 min, (b) 30 min, (c) 45 min and (d) 60 min. The composition of the anodization solution was: 94.5% $v$ glycerol, 5.0% $v$ DI water and 0.50 %$w$ KOH.

**Fig. 2.** Cyclic voltammograms of the anodized Ni foil at a constant voltage of +60 V at different anodization times of 5, 30, 45 and 60 min.

**Fig. 3.** FE-SEM images of a-NF/NiONWs at the hydrothermal reaction times of 1 h (a,b) and 2 h (c). (d) Cross section FE-SEM image of a-NF/NiONWs electrode.

**Fig. 4.** FE-SEM images of network-like Co$_3$O$_4$ nanosheets electrodeposited on a-NF/NiONWs at different magnifications of (a) 200 x, (b) 10 Kx and (c) 50 Kx. (d) FE-SEM image of Co$_3$O$_4$ electrodeposited on a-NF.

**Fig. 5.** XRD pattern of the fabricated electrodes: (a) a-NF/NiONWs, (b) as-prepared a-NF/NiONWs/Co$_3$O$_4$, and (c) annealed a-NF/NiONWs/Co$_3$O$_4$ at 450 °C for 1h.

**Fig. 6.** Cyclic voltammograms of (a) a-NF/NiONWs/Co$_3$O$_4$ electrode at different scan rates of 10, 20, 50 and 100 mV s$^{-1}$ in 1.0 M KOH solution. (b) CV curves of a-NF/Co$_3$O$_4$, a-NF/Co$_3$O$_4$, and a-NF/NiONWs/Co$_3$O$_4$ electrodes at the scan rate of 20 mVs$^{-1}$. (c) CV curves of annealed and as-prepared a-NF/NiONWs/Co$_3$O$_4$ electrodes with and without activating a-NF/NiONWs electrode before the electrodeposition of Co$_3$O$_4$.

**Fig. 7.** (a) Charge-discharge curves of a-NF/Co$_3$O$_4$ and a-NF/NiONWs/Co$_3$O$_4$ electrodes at a constant current density of 6.0 mA cm$^{-2}$. (b) Charge-discharge curves of a-NF/NiONWs/Co$_3$O$_4$ electrode at various current densities of 4, 6, 8 and 12 mA cm$^{-2}$.

**Fig. 8.** Electrochemical characteristics of the fabricated asymmetric supercapacitor a-NF/NiONWs/Co$_3$O$_4$/RGO/NF: (a) Cyclic voltammograms of a-NF/NiONWs/Co$_3$O$_4$ (positive) and NF/RGO (negative) electrodes in a three-electrode cell in 1.0 M KOH at a scan rate of 0.02 V s$^{-1}$. (b) Cyclic voltammograms of ASC device at different potential windows. (c) Cyclic voltammograms of ASC device at different scan rates from 0.01 to 0.2 V s$^{-1}$. (d) Charge-discharge curve of ASC at a current density of 3.0 mA cm$^{-2}$.

**Fig. 9.** (a) Capacitance retention during 2000 successive cycle numbers. (b) Nyquist plot of ASC. (c) The fitted equivalent circuit model.
Fig. 3

Fig. 4
Fig. 7

Fig. 8
Fig. 9