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Highly transparent 3D NiO-Ni/Ag-nanowires/FTO microsupercapacitor electrodes for fully transparent electronic device purpose

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ABSTRACT

In this work, the 3D NiO-Ni/ANWs/FTO electrode for micro-supercapacitor application is fabricated by facile electrochemical deposition and post annealing process. At the optimal under annealing conditions, the composite electrodes demonstrate an excellent specific capacity up to 344 mAh g^{-1} at 2.5 A g^{-1} based on GCD result in 2 mol L^{-1} KOH as electrolyte. In particular, our original welding treatment by rapidly annealing process of the 3D ANWs network dramatically increases the lifetime and stability, ~100% capacitance retention after 20000 cycles. Meanwhile, the NiO-Ni/ANWs composite own high average transmittance in visible and near infra-red regions as high as 82%, which is suitable for fully transparent electronic device application. For on-chip purpose the FTO substrate has perfect compatibility can also be easily replaced by any shape or form p/n-Si, metal, semiconductor, and any other conductive substrates.

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1. Introduction

In recent years, energy storage and renewable energy conversion devices have achieved rapid progress. Among them, supercapacitors (SCs) own characteristics of high power density, high energy density, short charging time, long service life and good cycle performance [1–4]. However, recent advances in SCs have been required to develop micro-supercapacitors (m-SCs) to reduce the device volume and facilitate easy integration into micro devices or cater on-chip requirements [5–8]. Relative to SCs, m-SCs have unique features, the compact size, minimization of the use of electrode materials and inconvenience for maintenance and replacement [9,10]. This will require more reliable performance and stability. Meanwhile, the small size feature makes it become less important to choose a low-cost electrode materials comparing with the SCs for driving power source purpose. So, there are more

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options to design better composite electrodes and structures to achieve the best performance of m-SCs. Nowadays, m-SCs have been designing with various electrode materials, such as, carbonaceous materials [11–13], metal oxides [14,15] and conducting polymers [16,17]. Among them, transition metal oxides have shown promising potential, because they possess several oxidation states for efficient redox charge transfer and can also exhibit various special morphologies, micro/nanostructures and porosity, which can provide higher energy density compared with carbon materials and more stable performance compared with conducting polymers.

NiO with rich reserve has high theoretical capacitance value (up to 2573 F/g) [18,19], good chemical stability, facile preparation, and good electrochemical performance [20]. Therefore, NiO is one of the most promising electrode materials for m-SC applications. Considerable efforts have been devoted to synthesizing NiO with various designed morphologies and structures to achieve improved capacitance values. For instance, Yuan and his coworkers reported a practical and efficient strategy for synthesizing hierarchical porous NiO nano/micro spherical structure for SCs with high capacitance (710 F g⁻¹ at 1 A g⁻¹) and stability (98% maintained after 2000 cycles) [21]; A layered structure was prepared by the combination of single layer graphene and nickel oxide nanosheets [22];





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Mesoporous NiO nanoarrays with large surface area have already been reported by Senthilkumar's team [23]. However, the capacitances of most of them are less than 1500 F g⁻¹ usually accompanied with poor rate capability and stability. Compared with the theoretical value of NiO, there is still a large gap. To solve these problems and improve capacity performance, one of the importance strategies is to combine NiO with materials possessing excellent conductivity and larger specific area, such as carbon nanotubes [24] and graphene [25], Au [26], Ag [27], or oxides like Co₃O₄ [28] and Fe₂O₃ [29]. Among them, Ag and its nanostructure should be ideal current collector material due to its high conductivity, relative low cost and high surface area. Wu et al. [27] prepared highly porous NiO/Ag composite films with specific capacities 330 F g⁻¹ at 2 A g⁻¹, it is much higher than that of the pure NiO film. Ag/NiO composite nanosheets and empty microspheres were fabricated by Lu'group [30], showing that Ag/NiO composites has exhibited electrocatalytic activity.

Recently, transparent electronic devices such as fully transparent displays and multi-stacked renewable energy systems such as the integrated device of transparent solar cell layer and transparent supercapacitor layer require energy storage materials own excellent visible light transparency and stability. Nevertheless, works on this aspect is barely reported. So, many attempts need to be tried to achieve more reliable devices with excellent transparency property.

Herein, we report three-dimensional (3D) NiO-Ni/Ag-nanowires (ANWs)/FTO electrode for micro-supercapacitor application, which is transparent to visible light. We use 3D ANWs network to achieve high conductivity and large surface area of the electrode materials. The specific capacity is as high as 344 mAh g^{-1} . The welding process by high temperature annealing dramatically enhances the stability of the electrode material, and the electrode obtain nearly 100% capacity retention over 20000 cycles. Considering the requirements of on-chip application, we chose FTO as the current collector material for its mature technique and the excellent compatibility with silicon chip. If necessary, it can be also changed into any shape or form p/n-Si, metal, semiconductor, and any other conductive substrates. The average transmittance of the NiO-Ni/ ANWs electrode material in visible light and near infra-red regions is as high as 82%, so it has a great prospect in the application of transparent electronic devices.

2. Experimental section

2.1. Material preparation

The fabrication procedure of the NiO-Ni/ANWs/FTO electrodes is presented in Fig. 1. First, silver nanowires (ANWs) with high aspect ratio were synthesized by hydrothermal method [31]. Then they were spined on the FTO conductive glass for 50 times to ensure that the ANWs network was sufficiently dense. And then, the ANWs/ FTO composite was rapidly annealed for 30 min at 300 °C under Ar atmosphere to weld ANWs to form junctions. The heating rate is 28 °C/s from room temperature to 300 °C. The welding process can effectively reduce the resistance of the ANWs and get solid structure to improve its cycle life. Next, Ni layer was deposited on the surface of the ANWs/FTO composite in a bath composed of 0.1 mol L⁻¹ NiSO₄ and 0.1 mol L⁻¹ Na₂SO₄ by chronopotentiometry electrochemical deposition at room temperature. The bath pH was set to 2.65 by dilute sulfuric acid. The deposition time and deposition current were 30 s and 10 mA respectively. Graphite electrode, saturated calomel, and ANWs/FTO sub-stratas were used as the counter electrode, reference electrode, and working electrode, respectively. Finally, the Ni/ANWs/FTO composite was annealed in a furnace tube at 300, 400 and 500 °C temperature for 1 h, 2 h, or 3 h, respectively, in air atmosphere to oxidize the Ni layer. Then high transparency NiO-Ni/ANWs/FTO electrode materials were fabricated.

2.2. Characterization

The study on the morphology and crystal structure of electrode materials is mainly based on the following instruments: field emission scanning electron microscopy (SEM, Quanta 250, FEI), transmission electron microscopy (TEM, Tecnai G2 F20, FEI), high resolution Raman spectrometry (LabRAM HR Evolution, HORIBA JOBIN YVON S. A. S), and X-ray diffraction (XRD, D8-Advance, Bruker). The transmittance spectra were measured using a UV–vis–NIR spectrophotometer (UV-3600, Shimadzu) equipped with an integratingsphere. The sheet resistances were measured by a four-point probe method with a source/meter (Keithley 2162A) and probe station (ECOPIA, ESP300).

2.3. Electrochemical measurements

Electrochemical measurements of cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (Zahner/Zennium E 6.0) using a threeelectrode system with 2 mol L^{-1} KOH aqueous solution at room temperature. NiO-Ni/ANWs/FTO electrode material was used as working electrode. The graphite electrode, saturated calomel (SCE) were used as the counter electrode and reference electrode respectively. The potential of saturated calomel reference electrode (SCE) is 0.245 V vs. SHE. CV tests were measured between 0 and 0.5 V (vs. SCE) at various scan rates. GCD measurements were performed in the potential range between 0 and 0.5 V (vs. SCE) at current density of 2.5, 3.8, and 6.4 A g⁻¹. The EIS data was collected over the frequency range from 100 kHz to 0.1 Hz at amplitude of 5 m V referring to the open circuit potential. Cycle stability test of the NiO-Ni/ANWs/FTO electrode was measured at 2 mA for 20000 cycles.

Specific capacity (C_{SP}) is the capacitance per unit mass for one electrode. In CV measurement, the C_{SP} (F g⁻¹) is calculated by the equation:

$$C_{SP} = \frac{\int IdV}{2m\Delta V v_0} \tag{1}$$

where *I* is the current, is the voltage, ΔV is the voltage window, v_0 is the scan rate, and *m* is the loading mass of NiO.



Fig. 1. Schematic map of the cross-section of NiO-Ni/ANWs/FTO electrode materials.

In GCD measurements, the C_{SP} (F g⁻¹) is calculated using the following equation:

$$C_{SP} = \frac{I \times \Delta t}{m \times \Delta V} \tag{2}$$

where I (A) is the constant discharge current, t (s) is the discharge time, V (V) is the voltage drop upon discharging (excluding the *IR* drop), and m (g) is the mass of the active materials NiO.

To exhibit pure faradaic behavior, The corresponding capacity will be expressed in coulombs, C, or mAh.The reference formula is as follows:

$$Q = C \times \Delta U \tag{3}$$

Where is the charge stored (mAh, or C), *C* is the amount of charge stored when a 1 V window is used, ΔU is the width of the voltage window (V) [32–34].

3. Results and discussion

3.1. Structural and morphological characterizations

Fig. 2a presents the XRD pattern of the as-prepared and annealed Ni/ANWs/FTO electrodes at 300, 400 and 500 °C. For all curves, peaks at 38.06, 44.34, and 65.71° are the characteristic peaks of metallic Ag (JCPDS no.04-0783). Peaks locate at 26.5, 33.7, 37.5, 51.5, 61.7, and 65.8° are the characteristic peaks of cassiterite SnO₂ (JCPDFS 77-0452). Peaks located at 44.5 and 51.8° are attributed to Ni layer (JCPDS no.04-0850). For the annealed electrodes, there is no peaks of AgO, which proves that the high temperature annealing treatment does not oxidize the ANWs yet. However, after annealing, the characteristic peaks of NiO appear, located at 37.324, 43.34, and 62.89°, respectively (JCPDS no.44-1159). Crystallite size could be estimated according to the Scherrer's equation:

$$D = K\lambda / B\cos\theta \tag{4}$$

where *D* is the crystal size at the direction normal to the diffraction plane; K is the Scherrer constant; λ is the wavelength of x-ray; *B* is the full width at half maximum and θ is the diffraction angle [35]. For the diffraction peak located at 43.35°, the B value decreases from 0.364 to 0.203 and the D values are determined to be 24.62, 31.46, 44.17 nm respectively with the increase of temperature. It demonstrates that the crystallization of NiO crystal is better with

higher annealing temperature. The structural assignment is further corroborated by Raman spectroscopic analysis (Fig. 2b). It can be seen that there are two peaks at 555, 1090 cm⁻¹ for NiO-Ni/ANWs/ FTO electrodes (red line) and there is no peak for the as-prepared Ni/ANWs/FTO (black line) electrodes. Compared with the original Raman spectra of NiO [36,37], we can assign the peak at 550 cm⁻¹ to the first-order longitudinal optical (LO) phonon modes of NiO which shifts down in frequency about 15 cm⁻¹. The peak at 1090 cm⁻¹ can be assigned as combination of 2 LO modes. Above all, XRD and Raman analysis indicate that the electrode material is NiO-Ni/ANWs/FTO composite.

Fig. 3a clearly shows a perfect 3D ANWs network, which offers a larger surface area than barely NiO-Ni/FTO (Fig. S1a of the Supplementary information). The average diameter of the ANWs is 100 nm and length of 50 µm (more details in Fig. S1b, Supplementary Information). After a rapid annealing treatment, the ANWs are welded together at the overlapping sections, as the dotted line circles shown in Fig. 3b. These welding points can reinforce the 3D ANWs network structure and improve the conductivity of the hole structure to facilitate electron transfer. Fig. 3c is the ANWs network covered with a Ni layer via electrochemical deposition at room temperature. Obviously, the diameter of the ANWs are increased by 50-100 nm, and the morphology of the substrate changes, which means that Ni layer is deposited on the surface of both ANWs and substrate. This Ni layer can further strengthen the connections between two ANWs and ANW with substrate. Fig. 3d-f present SEM images of NiO-Ni/ANWs/FTO electrodes annealed at 300, 400, and 500 °C for 2 h respectively. Compared with Fig. 3c. the morphology of ANWs after annealing treatment at 300 °C is nearly unchanged. This may be due to the temperature is not high enough to oxidize the nickel layer. The low relative intensity of NiO peaks in XRD result also confirms this point. When the annealing temperature is up to 400 °C, the nickel layer is oxidized to form a nanosheet NiO layer with larger surface area. Meanwhile, many new nodes are formed by the NiO layer, marked by the white dashed circle in Fig. 3e. The node further enhances the firmness of the network structure. However, when the annealing temperature is set to 500 °C, the NiO layer is composed of grainy NiO and all NiO/ANWs combined together. The gaps between ANWs are filled up. This structure has losed the advantage of larger surface for the 3D ANWs network. Overall, 400 °C is the optimal temperature. Fig. 3g is the SEM image of NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 1 h. Although the node is formed between NiO-Ni/ANWs, the NiO nanosheet is not



Fig. 2. (a) XRD pattern of as-prepared and annealed Ni/ANWs/FTO electrodes with different annealing temperature of 300, 400 and 500 °C for 2 h. (b) Raman spectra of Ni/ANWs/ FTO electrodes (black line) and NiO-Ni/ANWs/FTO electrodes (red line) at 400 °C for 2 h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. SEM images of (a, b) ANWs/FTO before and after rapid annealing at 300 °C for 30 min. (c) Ni/ANWs/FTO electrode. (d, e, f) NiO-Ni/ANWs/FTO electrodes annealed at 300, 400, and 500 °C for 2 h respectively. (g) NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 1 h (h) NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 3 h.

big enough to offer abundant surface to contact with the electrolyte. When the annealing time increases to 3 h, the NiO nanosheets and ANWs are melted and broken, as shown in Fig. 3h. Given the above, we obtained the optimal 3D NiO-Ni/ANWs nanostructure with larger surface area at 400 $^\circ$ C for 2 h.

As can be seen from the SEM images, the NiO-Ni/ANWs/FTO electrode owns perfect 3D structure, which could offer larger enough surface area of the electrode materials NiO. We chose FTO as the current collector for its mature technique, planar structure, and excellent compatibility with silicon chip. If necessary, it can be also changed into any shape or form p/n-Si, metal, semiconductor, and any other conductive substrates to cater to requirements of the m-SCs application.

Fig. 4a and b are the low magnification TEM images of the NiO nanosheets obtained by oxidation process at 400 °C for 2 h. We can further confirm that the NiO nanostructures are spindly willow-leaf-like nanosheets with a lot of little holes on surface. The element mapping in Fig. 4c reveals that Ni has a uniform distribution in NiO-Ni/ANWs/FTO electrodes, which may be due to Ni deposited on the surface of both ANWs and substrate. In contrast, O and Ag mapping have more clear patterns similar to the SEM image. And Fig. S2 (in the Supplementary information) shows the energy dispersive X-ray spectrometry (EDX) spectrum which exhibits peaks of O, Ni, Ag, and Sn of the NiO-Ni/ANWs/FTO composites. Overall, the ANWs are evenly distributed on the FTO, and the NiO layer is successfully obtained on the surface of ANWs via high



Fig. 4. (a, b) TEM images of NiO-Ni/ANWs/FTO electrode with different magnification. (c) SEM image of NiO-Ni/ANWs/FTO electrode and corresponding elemental mapping.

Fig. 5 illustrates the transmission spectra of NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 2 h, ANWs/FTO, and FTO, respectively. The range of the measurement wavelength is 300-1100 nm. With the increase of the wavelength, the transmittance of the three materials first increased and then decreased. The red line is almost parallel to the green line, which means that 3D ANWs network laver has no obvious characteristic absorption peaks or characteristic absorption rage. The decrease of transmittance after ANWs layer coated on FTO is just caused by the light blocking effect. However, when the NiO-Ni layer added, the transmittance (the blue line) not only has an obvious decline, but also changes the shape. Namely, besides the light blocking effect, NiO-Ni layer absorb some wavelength of light, especially for 400-600 nm. Overall, the NiO-Ni/ANWs/FTO electrode has superior optical transparency, exceeding 65% at 670 nm. As presented in inset (b) of Fig. 5, the NiO-Ni/ANWs films exhibit an average optical transparency of ~82% in the visible and near infra-red regions, which eliminates the effects of the FTO substrate. Compared with the previously reported optical transmittance of NiO films (transmittance no more than 60% in the visible range) [38,39], the transparent nickel selenide electrode (transmittance ~70% in the visible range) [40], and the transparent conductive polymer/ANWs electrode for organic solar cells (transmittance ~92% at wavelengths of 450-700 nm) [41], the NiO-Ni/ANWs film shows an excellent transmittance in the visible region, which mean an good prospect in all transparent electronic devices, such as all transparent monitor and smart phone. The inset (a) of Fig. 5 shows an optical photo of FTO electrode with two half parts coated by NiO-Ni/ANWs and ANWs, respectively. We can intuitively see that both parts have excellent transparency. The yellow dashed line is the boundary between the two parts. Such high transmittance of the NiO-Ni/ANWs composition is suitable for fabricating electronic components for fully transparent display application and other transparent electronic devices.

3.2. Electrochemical properties

To confirm the optimum annealing conditions, a series of electrochemical tests were carried out for NiO-Ni/ANWs/FTO electrodes annealed at 300, 400 or 500 °C for 1, 2 or 3 h, respectively. Fig. 6a and d are CV curves with potential window rang of 0-0.5 V and scan rate of 5 mV s⁻¹. By calculating the geometric area of CV



Fig. 5. Optical transmittance spectra of NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 2 h, ANWs/FTO, and FTO respectively. (Insert: (a) photo for the NiO-Ni/ANWs/FTO electrode, (b) the optical transmittance spectra of NiO-Ni/ANWs film.).

curves, the specific capacity values are 18.1 mAh g^{-1} , 801.8 mAh g^{-1} , and 33.4 mAh g⁻¹ for the NiO-Ni/ANWs/FTO electrodes annealed at 300, 400, and 500 °C for 2 h, respectively in Fig. 6a. And the specific capacity values are 80.4 mAh g^{-1} , 801.8 mAh g^{-1} , and 126.3 mAh g⁻¹ for the NiO-Ni/ANWs/FTO electrodes annealed at 400 °C for 1, 2, and 3 h, respectively in Fig. 6d. Noticeably, the electrodes annealed at 400 °C for 2 h has the best CV performance with biggest curve area and obvious redox peaks centered at ~0.25 and ~0.45 V. Fig. S3 (in the Supplementary information) shows the CV curves of NiO-Ni/ ANWs/FTO annealed at 400 °C for 2 h with different scan rates ranging from 5 to 200 mV s^{-1} . All of the redox peaks are nearly symmetrical at lower scan rates, implying excellent reversible redox reaction at the surface of NiO-Ni/ANWs/FTO electrode. Galvanostatic discharge curves of the corresponding NiO-Ni/ANWs/ FTO electrodes at current density of 2.5 A g⁻¹ are shown in Fig. 6b and e. All the curves have obvious pseudo capacitance platforms indicating that redox reaction occurred during the charge storage process, which is consistent with reported results [3,42,43], and the potential of the discharge platforms dovetails beautifully with the reductive peak of CV curves in Fig. 6a. Based on the galvanostatic discharge results, Based on the galvanostatic discharge results, the specific capacity values are 47.8 mAh g^{-1} , 344.0 mAh g^{-1} , and 51.9 mAh g^{-1} for the NiO-Ni/ANWs/FTO electrodes annealed at 300, 400, and 500 °C for 2 h, respectively in Fig. 6b. And the specific capacity values are 186.1 mAh g^{-1} , 344.0 mAh g^{-1} , and 104.2 mAh g⁻¹ for the NiO-Ni/ANWs/FTO electrodes annealed at 400 °C for 1, 2, and 3 h, respectively in Fig. 6e. That is to say the NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 2 h owns the maximum specific capacity. EIS results explore the kinetics of electrode material. The inset (Fig. 6c) presents equivalent circuit diagram of impedance spectra of the electrodes, which involves R1, double layer capacitance (CPE), charge transfer resistance (R2) at NiO-electrolyte interface, Warburg element (W) which is related to R2 between the surface of the film and the electrolyte, and pseudocapacitance (C) [44]. Fig. 6c and f shows the Nyquist plots of the corresponding NiO-Ni/ANWs/FTO electrodes in Fig. 6a and d. The consistency of the fitting curve and the original curve shows the accuracy of the equivalent circuit. Table 1 clearly shows the parameters R1, CPE, R2, W and C by fitting results. It can be found that R1 increases from 7.88 Ω to 9.07 Ω , and then to 18.2 Ω when the annealing temperature increase from 300 to 500 °C. This may be caused by the increasingly thick NiO layer which owns larger resistivity than Ni. However, R1 is smallest when annealing time is 2 h, even smaller than that of 1 h, which could attribute to the special morphology of willow-leaf-like nanosheet of NiO with large surface area. It is clear from the Fig. 3c-h that the surface area of the NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 2 h is the maximum, and the large surface area increases the active nanoparticles, thus reducing the electrode resistance. The highest R2 value is obtained for the electrodes at the highest annealing temperature and the longest annealing time. This could attribute to the barrier effect induced by the microscopic structure of nanocomposite: the exfoliated oxidation of nickel hinder the entrance of hydroxyl ions, increasing the charge transfer resistance. The Warburg impedance is lowest when annealing temperature and time are 400 °C and 2 h, which benefits from that the lamellar microstructure facilitate the diffusion process, as shown in Fig. 3e. The NiO-Ni/ANWs/FTO electrode obtained with suitable annealing temperature and time exhibits enhanced electrode/electrolyte interface areas, providing high electrochemically active regions and short diffusion lengths. At the same time, NiO-Ni/ANWs/FTO electrode with high porosities in contact with liquid electrolytes facilitates better charge transfers and lower resistance. Above all, 400 °C and 2 h are the optimal annealing conditions.

To investigate the effect of the 3D ANWs network layer,



Fig. 6. Electrochemical performance of NiO-Ni/ANWs/FTO electrodes at annealing temperatures of 300, 400 and 500 °C for 1, 2, and 3 h, respectively. (a, d) CV curves with scan rate of 5 mV s⁻¹ (b, e) GCD curves at 2.5 A g⁻¹ (c, f) Nyquist plots.

electrochemical performances of NiO-Ni/FTO and NiO-Ni/ANWs/ FTO electrodes annealed at 400 °C for 2 h were carried out. Fig. 7a shows the CV curves of the two electrodes. Apparently, the area of the CV curve of NiO-Ni/ANWs/FTO is significantly larger than that of NiO-Ni/FTO. And the specific capacity value of the NiO-Ni/ANWs/FTO electrode and NiO/FTO electrode are 801.8 mAh g⁻¹ and 2.5 mAh g⁻¹ respectively, indicating that the 3D ANWs network layer greatly enhances the specific capacity of the electrode

Table 1

EIS fitting parameters of NiO-Ni/ANWs/FTO electrode under different conditions. T and t are annealing temperature and annealing time, respectively.

Electrode	T/°C	t/h	$R1/\Omega$	CPE/F	$R2/\Omega$	$W/\Omega s^{-1/2}$	C/F
NiO-Ni/FTO	400	2	23.23	1.22	6.85	0.047	0.000939
NiO-Ni/ANWs/FTO	300	2	7.88	0.51	0.60	0.034	0.000831
NiO-Ni/ANWs/FTO	400	2	9.07	4.80	1.34	0.019	0.000615
NiO-Ni/ANWs/FTO	500	2	18.20	3.57	5.40	0.028	0.000674
NiO-Ni/ANWs/FTO	400	1	14.90	1.97	3.02	0.096	0.000757
NiO-Ni/ANWs/FTO	400	3	15.91	0.64	6.48	0.350	0.000553

materials. And Table 1 shows their parameter values of R1, CPE, R2, W and C from fitting plots (Fig. 7c and d). Based on Table 1, R1 and R2 of NiO-Ni/ANWs/FTO electrode are both much lower than that of NiO-Ni/FTO electrodes, which indicates that the ANWs can significantly reduce the electrode resistance and ion transport resistance by increasing the surface area of the electrode materials. The large CPE impedance of NiO-Ni/ANWs/FTO electrode shows that the charge transfer efficiency of interfacial is higher than that of NiO-Ni/FTO electrode, which suggests that the surface area of the former is higher than that of the latter, and it can be found clearly in Fig. 3e and Fig. S1. Meanwhile, after the addition of ANWs, the W value is decreased, which indicates that the charge transfer rate between the film surface and the electrolyte is accelerated. GCD results of NiO-Ni/FTO and NiO-Ni/ANWs/FTO electrodes with potential window of 0-0.5 V at various current are presented in Fig. 7e and f. The charging and discharging time of the NiO-Ni/ ANWs/FTO electrode is apparently much longer than that of NiO-Ni/FTO electrode, and the curves of NiO-Ni/ANWs/FTO have obvious pseudo capacitance platform indicating that the active material occurred a redox reaction, which is also consistent with



Fig. 7. (a) CV curves of NiO-Ni/FTO and NiO-Ni/ANWs/FTO electrodes at 5 mV s⁻¹ (b) EIS curves of NiO-Ni/FTO and NiO-Ni/ANWs/FTO electrodes. (c,d) Nyquist plot of NiO-Ni/ANWs/ FTO electrode and NiO-Ni/FTO electrode respectively, inset is equivalent circuit diagram of impedance spectra of electrode. (e, f) GCD results of NiO-Ni/FTO and NiO-NiO/ANWs/FTO electrodes at different current densities.

locations of the CV redox peaks.

The rate capability of the NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 2 h was investigated by varying the current density, shown in Fig. 8a. With the increase of the current density from 2.5 to 12.8 A g⁻¹, the capacitance value decrease by only 18.3%. And the specific capacity value reaches 344.0 mAh g⁻¹ (2476.8 F g⁻¹) and 280.9 mAh g⁻¹ (2022.4 F g⁻¹), when the current density is 2.5 and 12.8 A g⁻¹. The stability of NiO-Ni/ANWs/FTO electrode with and without the welding treatment of ANWs network via rapidly annealing is examined by cycling GCD testing at a current density of 25 A g⁻¹ (red and blue lines in Fig. 8b). For the blue line, the capacity value decreases sharply by ~44.83% during the first 1000 cycles. And with the increase of cycling times, capacity value gradually reduce to 31.03% at the 7000 cycles. This is due to the spin coated ANWs are connected by van der Waals forces [45,46], the ANWs network is easy to fall off in the electrolyte. However, for the red line, no obvious decrease is observed for capacity value in the 20000 cycles and the retention of capacity value is ~100%, which strongly confirms the effect of the welding treatment in the constructing of solid 3D nanostructures.

Comparing the present work with reported results based on NiO electrode materials (see the Table. S1 in the Supplementary Information), the specific capacity value, cycle number, and capacitance retention of NiO material are improved by the addition of the 3D ANWs network and the welding treatment by rapidly annealing. The excellent capacitance retention and long lifetime properties are extremely suitable for maintenance-free on-chip supercapacitor application.

4. Conclusion

We successfully fabricated the NiO-Ni/ANWs/FTO electrodes by facile electrochemical deposition and post annealing process. By comparing the electrochemical performance of NiO-Ni/ANWs/FTO



Fig. 8. (a) Dependency between specific capacity and current density of NiO-Ni/ANWs/FTO electrode annealed at 400 °C for 2 h (b) Cycling performance of electrodes at a constant current density of 35 A g⁻¹. Red line is annealed at 400 °C for 2 h and blue line is NiO-Ni/ANWs/FTO electrode without rapidly annealing treatment of ANWs network before deposition of Ni layer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrodes, the optimal under annealing conditions 400 °C and 2 h are confirmed. The composite electrodes demonstrate an excellent specific capacity value up to 344.0 mAh g^{-1} at 2.5 A g^{-1} based on GCD result and 801.8 mAh g⁻¹ at scan rate of 5 mV s⁻¹ based on CV data in 2 mol L^{-1} KOH as electrolyte, the potential window is 0-0.5 V. By our original welding treatment of the 3D ANWs network, the composite electrodes keep ~100% capacitance retention after 20000 cycles. The excellent capacitance retention and long lifetime properties are extremely suitable for maintenancefree on-chip supercapacitor application. Meanwhile, the NiO-Ni/ ANWs composite own high average transmittance in visible and near infra-red regions as high as 82%, which is suitable for future fully transparent electronic device application. The planar structure and FTO substrate is easily to transplant onto chips for its mature technique and the excellent compatibility with silicon chip of FTO. If necessary, it can be also replaced by any shape or form p/n-Si, metal, semiconductor, and any other conductive substrates.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2017.11.011.

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