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- MnO₂ nanosheets were grown on the surface of porous NiO microtube.
- The NiO@MnO₂ nanocomposite exhibits excellent cycle performance.
- The nanocomposite exhibits specific capacitance of 266.7 F g⁻¹ at 0.5 A g⁻¹

Synthesis of NiO@MnO₂ core/shell nanocomposites for supercapacitor application

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Abstract: In this work, NiO@MnO₂ core/shell nanocomposites were fabricated by a two-step method. The morphology and structure of the nanocomposites were characterized by scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction analysis and thermal gravity analysis. In addition, the supercapacitive performances were examined by cyclic voltammogram (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS). The electrochemical results indicate that the composite exhibits a specific capacitance of 266.7 F g⁻¹ at 0.5 A g⁻¹ and excellent cycling stability (81.7% retention after 2000 cycles at 1 A g⁻¹). Therefore, this work offers meaningful reference for supercapacitor applications in the future.

Keywords: NiO tube; MnO₂ nanosheets; supercapacitor; nanocomposites

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1. Introduction

As a kind of energy storage device, supercapacitors (SCs) have its unique properties, such as high power density, fast charge–discharge rate and stable cycling performance[1]; SCs have been received great attention with the development of electric car industry in recent years. Generally, there are two type of storage energy mechanism for supercapacitors: one is ion adsorption (electrical double-layer capacitors, EDLCs), the other is fast surface redox reactions (pseudocapacitors). Potentially, pseudocapacitors can provide much higher capacitance values than EDLCs through Faradic reaction[2]. Up to now, transition metal oxides with variable valence have been widely used in pseudocapacitors, such as NiO[3], MnO₂[4], Co₃O₄ [5], and NiCo₂O₄[6].

Nickel oxide (NiO) is widely investigated as one of the most promising pseudocapacitive materials which owns unusually high theoretical specific capacitance (2573 F g⁻¹)[7] and excellent electrochemical reaction reactivity. The morphology of NiO and its controlled synthesis have large impact on its electrochemical performance because morphology is closely related to the specific surface area, a variety of porous nanostructures with large surface areas have been synthesized via surfactant-template, sol-gel, anodization and hard template methods[8]. MnO₂, an important pseudocapacitive material, has many intriguing characteristics including high theoretical specific capacitance (1370 F g⁻¹), natural abundance, low cost, environmental friendly and rich redox activity[9]. Unfortunately, the practical applications of MnO₂ are limited due to its weak rate capability and cycling stability, which can be attributed to its poor electrical conductivity[10, 11].

Meanwhile, binary metal oxide composites such as Co₃O₄@NiCo₂O₄[12], NiCo₂O₄@NiO[13], Co₃O₄@NiMoO₄[14] and NiCo₂O₄@NiCo₂O₄[15] also have received much attention as supercapacitor electrode materials. Pseudocapacitive material core-pseudocapacitive material shell

presents another intriguing core-shell design because both core and shell materials have redox reactions during charge and discharge processes, which results in high specific capacitances [16]. These materials have multiple oxidation states and structures that enable multiple redox reactions and have been reported to exhibit a higher performance than single component oxides, and binary metal oxide with core/shell structure have short ion transport pathways, superior electron collection efficiency and multifunctionalities of components. Thus, it is highly promising to design core/shell structure, in which each component's properties could be optimized [17].

In this present work, a novel binary metal oxide NiO@MnO₂ core/shell nanocomposites were fabricated by a two-step method. NiO microtubes are obtained by calcination treatment of Ni(dmgl)₂ (dimethylglyoxime = dmgl) nanorod, then MnO₂ nanosheets were grown on the surface of NiO microtubes by hydrothermal method. NiO microtubes are the "core", MnO₂ nanosheets are the "shell". To the best of our knowledge, such a unique NiO@MnO₂ core/shell nanostructure has been never reported before. By virtue of the synergetic contribution from individual constituents and the sophisticated configuration, the resulting nanocomposites exhibited high specific capacitance with high cycling stability when applied as supercapacitor electrode materials.

2. Experimental

2.1 Synthesis of NiO porous microtubes

All reagents were of analytical grade and used as received without further purification. Firstly, 19.2 g polyethylene glycol and 1.16 g dimethylglyoxime (dmgl) were dissolved in 200 mL of absolute ethanol, and then 200 mL of 0.01 M nickel chloride solution were poured into above-mentioned solution under vigorous stirring, and keep this red mixture at 0 °C for 12 h. The precursor was collected by filtration and washed with large amount of water and absolute ethanol

and dried in a vacuum oven at 60 °C over night. Then the red product was calcined at 500 °C for 3 h in a muffle furnace to obtain NiO microtubes.

2.2 Synthesis of NiO@MnO₂

The prepared 60 mg NiO microtubes were dispersed in 20 mL deionized water by vigorous stirring, then 60 ml of 0.02 M KMnO₄ solution was mixed with this dispersion. After stirring for 1h, the mixture solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave, the autoclave was heated at 120 °C for 12 h and then cooled to room temperature naturally. The as-obtained black precipitate was collected by filtration and washed with deionized water for several times. The resulting final product was dried at 60 °C for 12 h.

2.3 Structural characterization

The structure of the fabricated samples was examined by X-ray diffraction analysis (XRD) (Rigaku, model D/max-2500 system at 40 kV and 100 mA of Cu K α). The X-ray photoelectron spectroscopy (XPS) spectra were tested by an ESCALab 250 electron spectrometer (Thermo Scientific Corporation). Thermo gravimetric analysis (TGA, Q500) was conducted with a heating rate of 10 °C min⁻¹. The surface morphology of the composites was investigated by scanning electron microscope (SEM, VEGA 3, The Czech Republic, TESCAN) and a model field emission transmission electron microscope (FETEM, USA, Tecnai F30 G2 FEI CO.).

2.4 Electrochemical measurements

The working electrode materials were prepared by mixing the obtained sample, acetylene black and polytetrafluoroethylene (PTFE) in a mass ratio of 80:10:10. The hybrid was mixed with ethanol for homogeneity and then coated on nickel foam substrates (1cm×1cm) as the working electrode and dried at 60 °C for 8 h; the as-formed electrodes loaded with the hybrid were then

pressed at 10 MPa for 60s and then further dried at 80 °C overnight before using. The typical mass loading of the sample in each electrode is about 8 mg. Electrochemical measurements were performed on an Autolab Electrochemical Workstation (PGSTAT302N) by the three-electrode system, Platinum electrode and the standard calomel electrode (SCE) were used as the counter and reference electrodes respectively. 2 M KOH solution was served as the electrolyte at room temperature. Cyclic voltammogram (CV) was recorded between 0 and 0.45 V at scan rates ranging from 1 to 20 mV/s. Galvanostatic charge/discharge testing was conducted at different current densities from 0.5 to 15 Ag⁻¹ between 0 and 0.4 V. The electrochemical impedance spectroscopy (EIS) measurements were performed in a frequency range from 10⁻² Hz to 100 kHz with potential amplitude of 5 mV.

3. Results and discussion

NiO@MnO₂ core/shell nanocomposites are fabricated by a two-step method, as shown in Fig.1(a), the NiO microtubes were fabricated by the calcination of Ni(dmg)₂ microtubes, and then MnO₂ nanosheets were grown on the surface of NiO microtubes by hydrothermal method. Fig.1(b) shows the SEM image of Ni(dmg)₂ nanorods, indicating Ni(dmg)₂ has a one-dimensional morphology, the length and diameter of the straight nanorod is about 30~50 μm and 0.5~1 μm respectively. After the calcination of nanorod precursors, the NiO microtubes are formed. Fig.1 (c) and Fig.1 (d) disclose the morphology of NiO microtubes, and the image (right-inset in Fig 1(c)) demonstrates that the NiO sample has tube-like nanostructures, and porous structure of NiO microtube can be clear seen in the Fig.1 (d). As shown in Fig.1 (e) and Fig.1 (f), a layer of MnO₂ nanosheets were grown on the surface of NiO tube after hydrothermal reaction in KMnO₄ solution for 6 h. The tube-like nanostructures of NiO is still well retained even after the MnO₂ nanosheets

decorated on the surface. A representative HRTEM image (Fig.1 (g)) shows that the measured interplanar distance is 0.475 nm, this d-space consistent with the (111) plane of the cubic MnO_2 . The SAED patterns (inset in Fig.1 (g)) with well-defined rings also demonstrate the crystalline feature of NiO@MnO_2 . EDS (Fig.1 (h)) demonstrates that Ni, Mn, O elements were contained, indicating the formation of NiO@MnO_2 , which is consistent with the XPS data.

The crystal structure and purity are determined by XRD technique. Fig.2 (a) shows the XRD patterns of NiO and NiO@MnO_2 samples. For the NiO sample, the prominent diffraction peaks appeared at 2θ of 37.3° , 43.3° , 62.9° , 75.4° , 79.4° , and all strong diffraction peaks can be indexed to the standard data of the crystal structure of NiO (JCPDS No.78-0643), no irrelevant peaks are detectable, indicating the high purity of NiO. It can be seen that the diffraction peaks of the NiO@MnO_2 core-shell nanocomposites are almost in accord with the standard XRD pattern of NiO (JCPDS No.78-0643), and the first two peaks at 12.3° and 18.7° can be attributed to the MnO_2 (JCPDS No.18-0802), indicating the formation of NiO@MnO_2 nanocomposites or the products are the mixture of NiO and MnO_2 .

Thermogravimetric (TG) measurements were carried out to determine the anneal process of Ni(dmg)_2 . Fig.2 (b) shows the TG curves of Ni(dmg)_2 , it can be seen that the weight loss is about 74% at about 300°C , which is attributed to the transformation from Ni(dmg)_2 to NiO. Obviously, H_2O , CO_2 , CO , N_2 , NO_x are released during the thermal decomposition[18]. After 380°C , the TG traces are stable with no further weight loss.

Elemental composition and chemical states are further investigated by XPS in Fig.3. The survey spectrum (Fig.3 (a)) demonstrates that the products were composed of Ni, Mn, O elements, the high-resolution spectrum of O 1s, Ni 2p, Mn 2p are exhibited in the Fig (b-d). The O 1s spectrum

is shown in Fig.3 (b), three main peaks at 529.9, 531.3 and 532.1 eV are attributable to metal–oxygen bonds (M-O-M), metal-hydroxide (M-OH), and water (H-O-H) on the surface, respectively[19]. The Ni 2p spectrum, as shown in Fig.3 (c), consists of one spin-orbit doublets characteristic of Ni²⁺ and two shakeup satellites, the two peaks at binding energy of 854.6 eV and 872.1 eV are assigned to Ni²⁺[20], while the satellite peaks at 879.0 eV and 860.8 eV are two shake-up type peaks of the nickel at the high binding energy sides of the Ni 2p_{1/2} and Ni 2p_{3/2} edge [21]. The Mn 2p spectrum exhibits multiple splitting with two main peaks centered at 642.4 eV and 654.0 eV, which can be attributed to Mn 2p_{3/2} and Mn 2p_{1/2} of Mn⁴⁺ in MnO₂, respectively, and the spin-energy separation is 11.6 eV [22, 23]. Moreover, Mn³⁺ and Mn⁵⁺ species are also detected in the spectrum. However, the intensities of this two peaks are much weaker than those for Mn⁴⁺, demonstrating that element Mn in NiO@MnO₂ is presented in the dominant chemical state of Mn⁴⁺ [24].

A detailed measurement of the electrochemical performance of NiO@MnO₂ nanocomposites are shown in Fig.4. CV curves of NiO@MnO₂ are shown in the Fig.4 (a) at different scan rates in a fixed potential range of -0.1~0.45 V (vs.SCE) in 2 M aqueous KOH electrolyte. A pair of well-defined redox peaks is obviously observed in all CV curves, suggesting the typical pseudocapacitive feature of active materials, which is obviously different from the electric double-layer capacitance characterized by nearly rectangular CV curves, the redox couples correspond to the reversible reactions of and Ni²⁺/Ni³⁺ transitions. The shape of the CV curves barely changes, indicating that the electrode have a good rate capability. To further investigate the electrochemical performance of the NiO@MnO₂ electrode, we perform galvanostatic charge–discharge (GCD) curves (Fig.4b) at various current densities in a fixed potential range of

0~0.4 V (vs.SCE). The shape of charge-discharge curves is basically symmetric, suggesting good reversibility redox processes. Voltage plateaus at around 0.28 V and 0.21 V can be seen in the charge and discharge process respectively. The specific capacitances of the NiO@MnO₂ are 266.7, 253.3, 218.3, 181.7, 168.3, 147.3 F g⁻¹ at current densities of 0.5, 1, 2, 4, 6, 8, 10 A g⁻¹. CV curves have been made comparison between NiO@MnO₂ and NiO at 10 mv/s in the Fig.4(c), it can be clearly seen that the CV curve of NiO@MnO₂ electrode shows the higher integrated area than NiO electrodes, furthermore, it also can be clearly seen that the GCD curves (Fig.3d) of NiO@MnO₂ electrode shows the higher discharge time than NiO electrodes, indicating the higher specific capacitance of NiO@MnO₂ nanocomposites due to the optimal core-shell structure and the introduction MnO₂.

As shown in Fig.4 (e), contrasting with the specific capacitances of NiO@MnO₂ and NiO electrode at various charge/discharge current, the capacitance of NiO@MnO₂ reduces from 266.7 F g⁻¹ (current density of 0.5 A g⁻¹) to 120 F g⁻¹ (current density of 15 A g⁻¹) with 45% of the specific capacitance remaining, in the same process, the capacitance of NiO electrode reduces from 94 F g⁻¹ (current density of 0.5 A g⁻¹) to 52 F g⁻¹ (current density of 15 A g⁻¹) with 55% of the specific capacitance remaining, and the capacitance of MnO₂ electrode reduces from 213 F g⁻¹ (current density of 0.5 A g⁻¹) to 81 F g⁻¹ (current density of 15 A g⁻¹) with 38% of the specific capacitance remaining. This result indicates that the specific capacitance of NiO and MnO₂ electrode are both much lower than NiO@MnO₂ electrode. The higher specific capacitance of NiO@MnO₂ electrode is due to ultrathin MnO₂ nanosheets were well wrapped on the surface of NiO microtubes to form a highly porous structure, the porous nanoarchitecture and MnO₂ nanosheets provides the composites with larger surface area that means a large

electrode/electrolyte contact interface and more active sites for electrochemical reactions. We further studied the cycling performance (Fig.4 (f)) of the electrodes at 1 A g^{-1} , the capacity retention (81.7%) of NiO@MnO₂ electrode shows higher than that of NiO electrode (77.4%) and MnO₂ electrode (73.5%) after 2000 charge-discharge cycles, the cycling performance of NiO@MnO₂ is very excellent because the core/shell structure is stable during repeated charge-discharge process.

To further understand the fundamental electrochemical behavior of NiO@MnO₂ composites, EIS data of NiO, MnO₂ and NiO@MnO₂ electrode are shown in Fig.5(a). The impedance spectra display similar form with a semicircle at a high-frequency region and a straight line at low-frequency region. The intersection of the plot at the x-axis represents R_s of the electrochemical system, which contains three sections: the intrinsic resistance of the substrate, the resistance of the electrolyte and the contact resistance at the interface between active materials and current collector[25], the R_s value of NiO@MnO₂ (0.186Ω) is bigger than that of NiO (0.120Ω), but which is smaller than that of MnO₂ (0.373Ω). R_{ct} stands for charge transfer resistance between the electrode and the electrolyte[26], which corresponding to the diameter of a semicircle, the R_{ct} value of NiO@MnO₂ (0.235Ω) is much bigger than that of NiO (0.065Ω), but which is also smaller than that of MnO₂ (0.373Ω). The slope of the straight line is related to the Warburg impedance (R_w) which represents the electrolyte diffusion in the active materials[27], the higher is the slope the easier is the ion diffusion/adsorption process, Warburg impedance is reduced when the slope is increased, a line with large slope at low frequency illustrates that the ion diffusion in the solution and the adsorption of ions onto the electrode surface occur swiftly, the R_w value of NiO@MnO₂ is higher than that of that of NiO, but which is smaller than that of MnO₂. These

results indicate the introduction of poor conductivity MnO₂ lead to increase the solution resistance, the charge transfer resistance and the Warburg impedance decrease. In fact, this is the reason why the rate capability of NiO@MnO₂ electrode is inferior to NiO electrode. Moreover, we also calculate the specific capacitance NiO, MnO₂, NiO@MnO₂ from EIS data according to

$$C = \frac{1}{2\pi fZ''m}$$

where f is the operating frequency (Hz), Z'' is the imaginary parts of the total device resistance (Ohm), and m is the mass of active materials in each electrode[28,29]. The result is shown in Fig.5(b), the capacitance of them is high at low frequency, and it start to decrease with the increasing frequency.

conclusion

In summary, we have successfully synthesized NiO@MnO₂ core/shell nanocomposites with distinct morphologies by a facile and scalable strategy. NiO@MnO₂ nanocomposites show a high specific capacitance of 266.7 F g⁻¹ at 0.5 A g⁻¹, excellent rate capability and remain at 81.7% of initial capacitance after 2000 cycles at 1 A g⁻¹. These results indicate that this kind of composites with excellent electrochemical properties can be a promising electrode material for supercapacitors.

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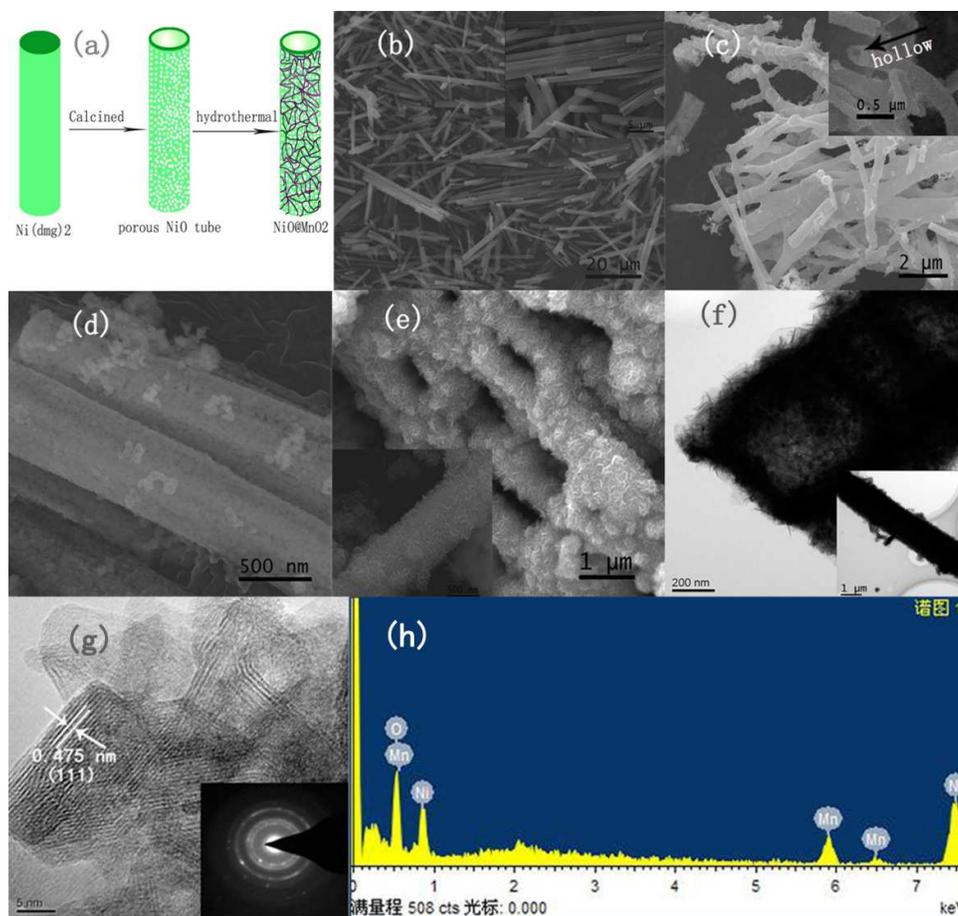


Fig.1 (a) Schematic illustration of the formation of NiO@MnO₂. (b) SEM image of Ni(dmg)₂ and (c, d) NiO microtube, (e, f) SEM and TEM image of NiO@MnO₂. (g) HRTEM image of NiO@MnO₂ and SEAD Pattern of NiO@MnO₂. (g) Corresponding EDS spectrum of NiO@MnO₂.

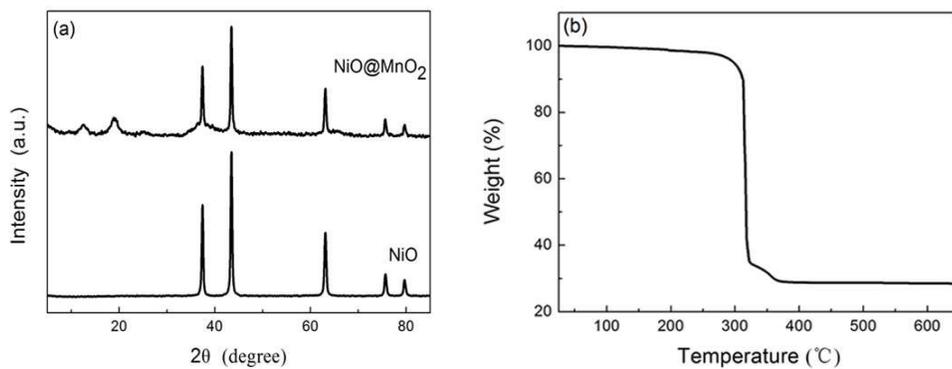


Fig.2 (a) XRD pattern of the NiO@MnO₂ nanocomposites, (b)TG Curve of Ni(dmg)₂ nanorod.

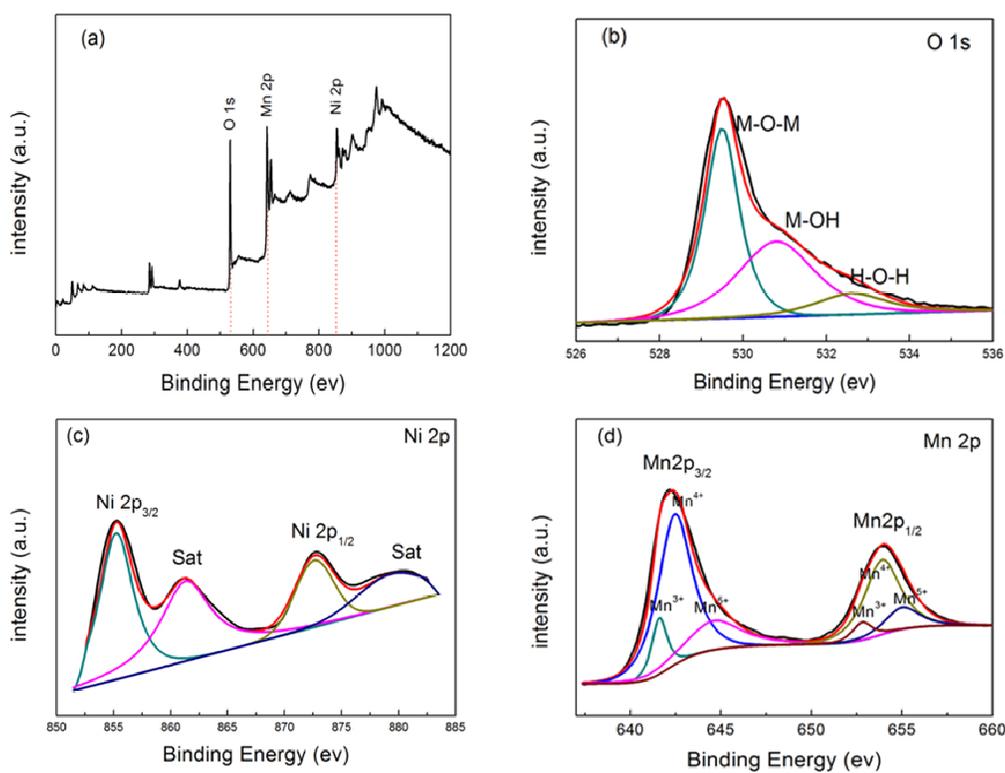


Fig.3 XPS spectra of (a) survey spectrum, (b)O 1s, (c)Ni 2p and (d) Mn 2p for NiO@MnO₂ nanocomposites.

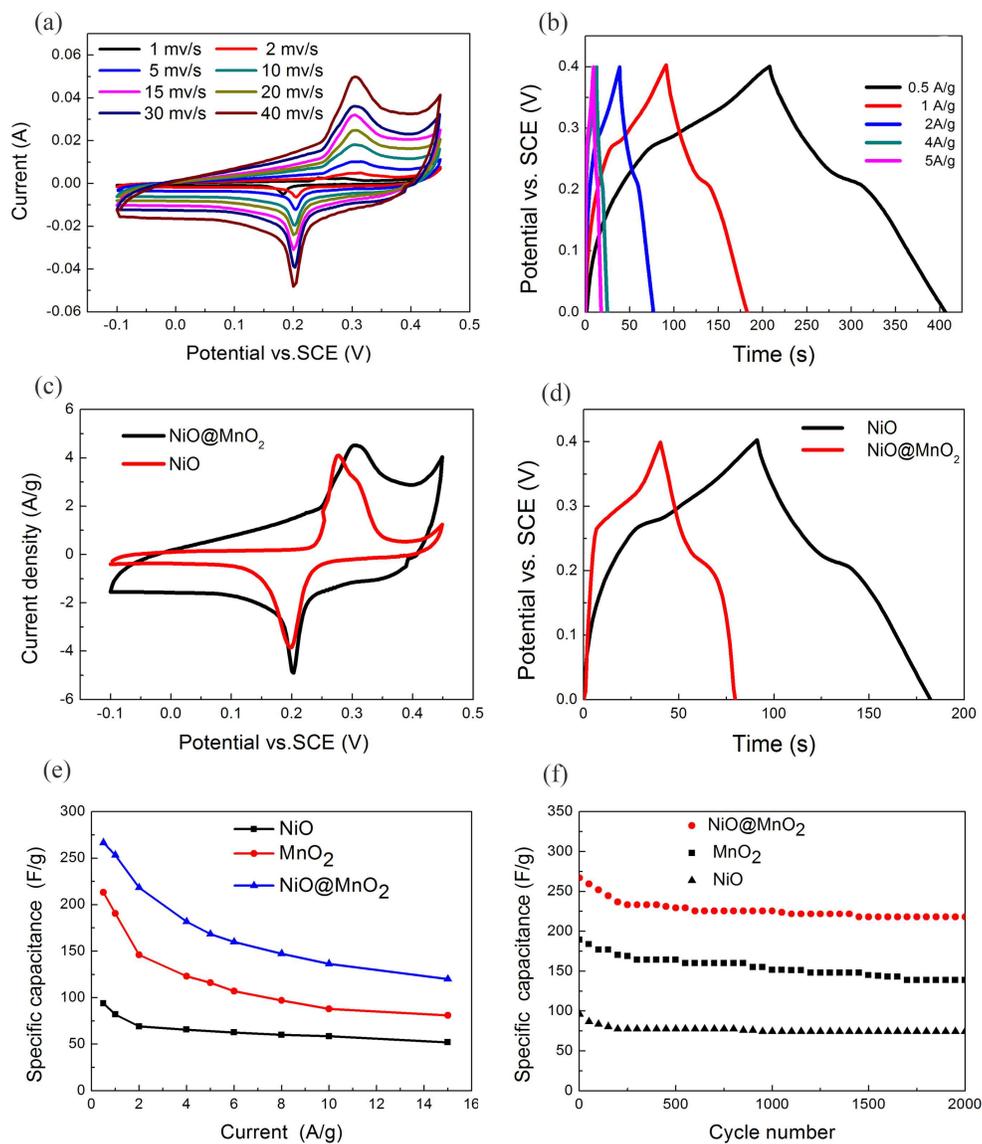


Fig.4 (a) Cyclic voltammetry curves of NiO@MnO₂ at various scan rates. (b) Galvanostatic charge/discharge curves of NiO@MnO₂ at different current densities. (c) CV curves of NiO@MnO₂ and NiO at 10mv/s. (d) Galvanostatic charge/discharge curves of NiO@MnO₂ and NiO at 1 A/g. (e) Specific capacitances of NiO@MnO₂, MnO₂ and NiO electrodes at different current densities. (f) Cycling performance of the NiO@MnO₂, MnO₂ and NiO electrodes at 1 A g⁻¹.

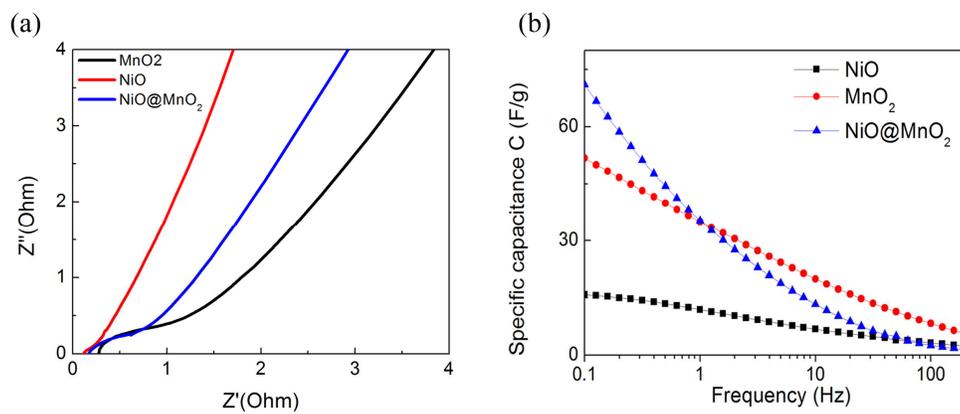
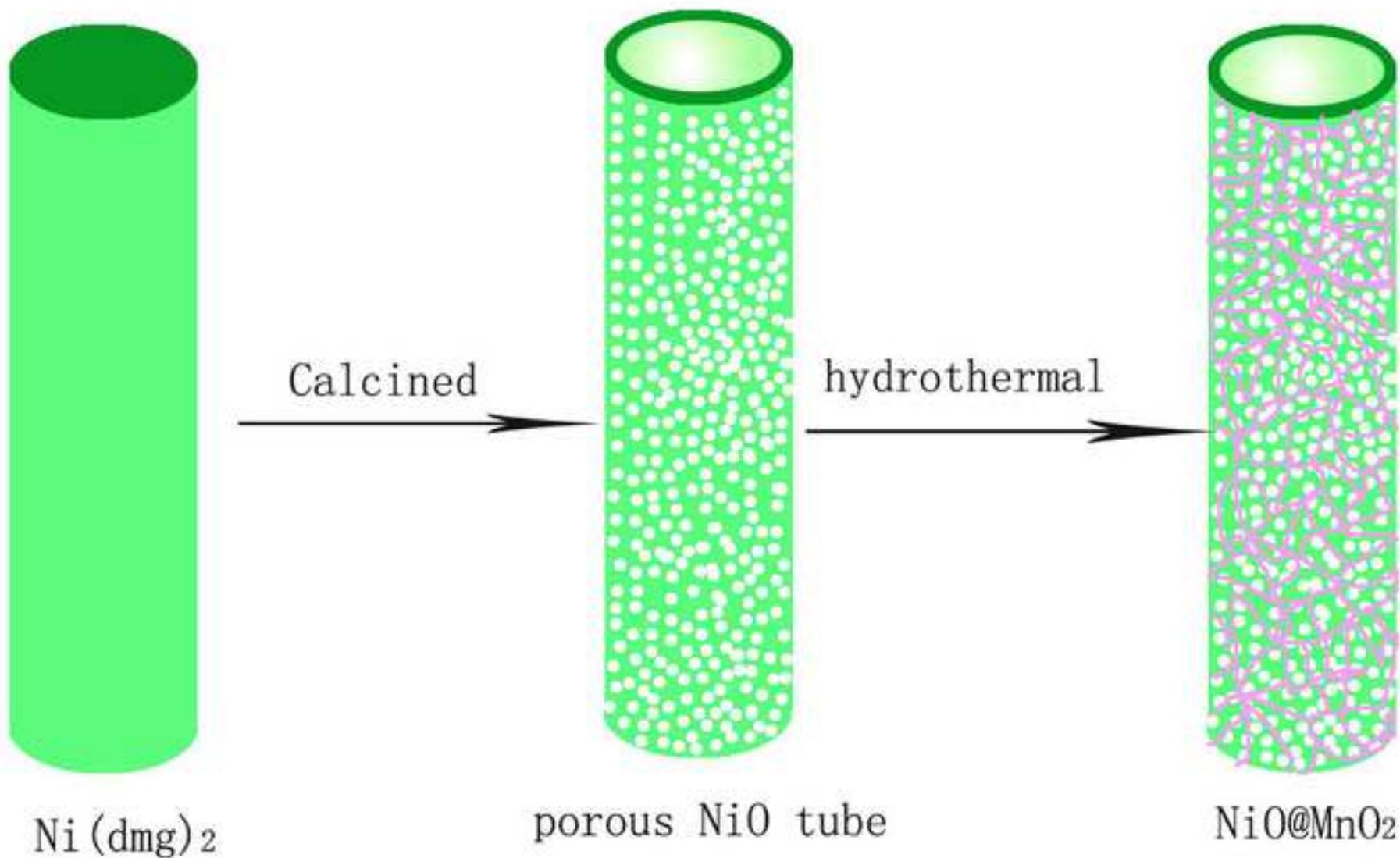


Fig.5(a) EIS data of NiO, MnO₂ and NiO@MnO₂ electrode, (b) specific capacitance plot

vs. frequency of NiO, MnO₂ and NiO@MnO₂ electrode.



supercapacitor electrode materials