This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Nanoflaky (Ni, Co, Mn) oxides have successfully grown on the surface of the β-MnO$_2$ nanorod via a simple redox reaction.
Preparation and Performance of $\beta$-MnO$_2$ nanorod @ nanoflake (Ni, Co, Mn) oxides with hierarchical mesoporous structure

Hao Wang, Qinglan Zhao, Xianyou Wang*, Youwei Zhang, Jiao Gao, Yanqing Fu, Xiukang Yang, Hongbo Shu*

(Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Hunan Province Key Laboratory of Electrochemical Energy Storage and Conversion, School of Chemistry, Xiangtan University, Hunan, Xiangtan 411105, China)

Abstract: The rational design and facile synthesis of transition metal oxides are necessary to improve their application in the supercapacitors. Herein three kinds of hierarchical mesoporous structure transition metal oxides, which are composed of a $\beta$-MnO$_2$ nanorod core and one of three different nanosheet hybrid (Ni, Co, Mn) oxide shells, are facilely synthesized via a novel in situ nucleation and growth of transition metal oxides on the surface of the $\beta$-MnO$_2$ nanorod. The crystallographic analyses demonstrated that the three kinds of hybrid oxide shells are consisted of cobalt manganese oxide (CMO), nickel manganese oxide (NMO), and nickel cobalt manganese oxide (NCMO), respectively. These transition metal oxides are evaluated as electrodes for high performance supercapacitors (SCs). The results reveal that $\beta$-MnO$_2$@CMO exhibits still a good rate capability of 35% capacity retention even at 20A g$^{-1}$, while $\beta$-MnO$_2$@NMO displays a high pseudocapacitance of 560 F g$^{-1}$ at 1 A g$^{-1}$. However, $\beta$-MnO$_2$@NCMO combined the advantages of both $\beta$-MnO$_2$@CMO and $\beta$-MnO$_2$@NMO, exhibits a high specific capacitance of 675 F g$^{-1}$ at 1 A g$^{-1}$ with

* Corresponding author: Xianyou Wang Tel: +86 731 58292060; fax: +86 731 58292061.
E-mail address: wxianyou@yahoo.com (X. Wang).

* Corresponding author: hongboshuxtu@gmail.com
excellent rate performance (about 30% capacity retention at 20A g\(^{-1}\)) and cycling
stability (83% capacity retention after 3000 cycles). The improved electrochemical
performance can be attributed to the unique hierarchical architecture and the
synergistic effect of different components.

**Key words:** Supercapacitor; Composite materials; Transition metal oxides; Core-shell
structure, Rate capability

**1. Introduction**

In recent years, advanced energy storage devices have been extensively researched
with the fast growing demand for high-power applications.\(^1\) Especially, supercapacitors (SCs) are considered to be an important renewable energy storage
device due to their faster charge/discharge process, longer lifespan, higher reliability
and lower maintenance cost.\(^2\),\(^3\) There are three major types of electrode materials
reported for SCs, including carbonaceous materials, transition metal oxides or
hydroxides, and conducting polymers.\(^4\) Among those electrode materials, the
transition metal oxide composite is a kind of promising compound to solve low
specific capacitance for carbon-based materials and poor cycling stability for
polymers.\(^5\)

Among transition metal oxides, Ni, Co, and Mn oxides, have been extensively
studied as promising candidates for SCs because of their variety of oxidation states
for charge transfer and high mass density.\(^6\),\(^7\) For example, MnO\(_2\) has a high
theoretical specific capacitance of about 1370 F g\(^{-1}\). Co\(_3\)O\(_4\) has a theoretical specific
capacitance of about 890 F g\(^{-1}\).\(^8\) However, the NiO\(_2\) and Co\(_3\)O\(_4\) suffer from poor
capacity retention and rate capacity, and the specific capacitance of MnO₂ is still limited due to the low conductivity (10⁻⁵ to 10⁻⁶ S cm⁻¹) and low diffusion coefficient of inserted cations.⁹,¹⁰ Undoubtedly, it has been reported that the rational design of transition metal oxide composite can provide a promising solution to achieve excellent supercapacitive performance due to the synergistic effects of different components, which can effectively improve the electrochemical performances of the materials.¹¹ Thus, to address these problems, one strategy is to design MnO₂-based composite oxides with highly conductive transition metal compounds. For example, NiCo₂O₄@MnO₂ core-shell nanowire arrays reported by Xu et al. present an improved capacitance (3.31 F cm⁻² at 2mA cm⁻²).¹² However, the MnO₂ is generally designed as the shell among most of the MnO₂-based composite transition metal oxides, which is still low conductivity.¹³,¹⁴,¹⁵ Even though, many scholars try to prepare MnO₂ as the core of the composites, the shell covered on the surface of the MnO₂ may be not uniform.¹⁶,¹⁷

In this work, a facile hydrothermal method has been designed to synthesize three hierarchical nanocomposites with a β-MnO₂ nanorod core and hybrid nanosheet shell. As KMnO₄ is reduced by low valence metal ions (Ni²⁺, Co²⁺) under the hydrothermal process, the resultant MnO₂ and Ni-Co hydroxides are in situ nucleation on the surface of the β-MnO₂ nanorods prepared as the template. The hybrid shell offers several advantages: one is that the β-MnO₂, with stable crystal structure in both nanosheet shells and cores can form a stable framework owing to its high surface areas and interconnected porous nanostructures which could better accommodate
structural changes;\textsuperscript{18,19} the other is that the NiO\textsubscript{2}, Co\textsubscript{3}O\textsubscript{4} or NiCo\textsubscript{2}O\textsubscript{4} embedded in the framework can improve the conductivity of the composites. Besides, the morphologies and electrochemical properties of the as-prepared three novel composites are discussed in details.

2. Experiment

2.1. Sample synthesis

All the reagents were of analytical grade and used without further purification. The template of \(\beta\)-MnO\textsubscript{2} nanorods was prepared as in Ref.\textsuperscript{20} \(\beta\)-MnO\textsubscript{2}@CMO nanocomposites are synthesized in a simple process, 0.2 g of as-prepared \(\beta\)-MnO\textsubscript{2} nanorod was dispersed in 75 mL of deionized water and ultrasonic treatment for 30 min, and then 0.2 g KMnO\textsubscript{4} and 1.2 g CoSO\textsubscript{4}.7H\textsubscript{2}O were added to form a homogeneous purple solution, followed by stirring for 1h. After that, the above solution was transferred into a Teflon-lined autoclave (100 ml), sealed and put in an electric oven at 120 \(^\circ\)C for 12 h, and then cooled down to ambient temperature naturally. Finally, the precipitation was filtered, washed with distilled water, vacuum dried and then calcined at 350 \(^\circ\)C for 2h in flowing argon at a ramping rate of 1 \(^\circ\)C.

The process of synthesis of \(\beta\)-MnO\textsubscript{2}@NMO, and \(\beta\)-MnO\textsubscript{2}@NCMO nanocomposites are the same as above route. The details are as follows: for \(\beta\)-MnO\textsubscript{2}@NMO, 1g NiSO\textsubscript{4}.6H\textsubscript{2}O, 0.2 g KMnO\textsubscript{4} and 0.2 g \(\beta\)-MnO\textsubscript{2} nanorods were mixed in 75 ml deionized water, then the mixture were maintained at 130 \(^\circ\)C for 24h; while for \(\beta\)-MnO\textsubscript{2}@NCMO, the designed amount of CoSO\textsubscript{4}.7H\textsubscript{2}O and NiSO\textsubscript{4}.6H\textsubscript{2}O were mixed with 0.2 g \(\beta\)-MnO\textsubscript{2} nanorods in 75 ml deionized water, and then maintained at 140\(^\circ\)C.
for 12h.

2.2. Physicochemical properties characterization

The crystallographic analyses of samples were carried out by X-ray diffraction (XRD) (D/max-2550 Rigaku, Japan). Morphology of samples was characterized using field-emission scanning electron microscopy (FESEM Nova NanoSEM 230). The morphology and structure of the nanocomposites were further investigated by transmission electron microscopy (TEM) (JEM-2100F, JEOL). The specific surface area and pore structure of the samples were determined by N\textsubscript{2} adsorption/desorption isotherm at 77 K (JW-BK 112) after the prepared samples were degassed at 110 °C overnight.

2.3. Electrochemical measurements

The working electrodes were prepared by the mixed slurry containing active materials (80 wt%), acetylene black (10 wt%) and polyvinylidene fluoride (PVDF 10 wt%) in N-methyl-2-pyrrolidone (NMP). The slurry was painted onto a nickel mesh with the area of 1 cm\textsuperscript{2} then dried and pressed. Electrochemical measurements were performed on an electrochemical workstation (VersaSTAT3, Princeton Applied Research, USA) by using a three-electrode mode in an aqueous KOH (6.0 M) with a nickel mesh and Hg/HgO as the counter and reference electrode.

3. Results and discussion

3.1. Morphology and Structural Analysis

The fabrication processes of the novel architectures are schematically illustrated in Figure 1(a)-(d). The β-MnO\textsubscript{2} nanorod provides a suitable template for homologous
MnO$_2$ nucleating and growing because the surface of the β-MnO$_2$ nanorod is consisted of perfect crystals. Firstly, when the β-MnO$_2$ nanorod was added to the mixed solution containing KMnO$_4$, CoSO$_4$ and NiSO$_4$ or either one of the two low valence sulfates and stirred, the mixed solution will be adsorbed on the surface of the β-MnO$_2$ nanorod. Then, along with the occurrence of the redox reaction during the hydrothermal process, the reducted product MnO$_2$ will be *in situ* nucleating on the surface of the β-MnO$_2$ nanorod, and the metal ions (Ni$^{2+}$, Co$^{2+}$) can be oxidized, and then their hydroxides will be nucleated followed by MnO$_2$. Finally, those novel architectures with hybrid nanosheet shells and a β-MnO$_2$ nanorod core are easily formed via this simple hydrothermal method. Besides, in the redox reaction process, the quantity of CoSO$_4$ and NiSO$_4$ can be controlled in any desired ratios within certain ranges, and the corresponding products will be obviously different.

**Figure 1** Schematic illustration of the formation of nanoflaky Ni, Co, Mn composite oxides *in situ* growing on the surface of the MnO$_2$ nanorod.
The morphology of the as-synthesized samples was examined with scanning electron microscopy (SEM). As shown in Figure 2(a-c), Co, Ni and Co-Ni hydroxides grow uniformly on the surface of β-MnO$_2$ templates in company with MnO$_2$. The yield of the shell is so high that the β-MnO$_2$ nanorods with a smooth surface are not observed in the nanocomposites. Obviously, among all composite oxides, the slice of the hybrid shell for β-MnO$_2$@CMO-precursor is the thickest and tightest. Besides, for β-MnO$_2$@NMO-precursor and β-MnO$_2$@NCMO-precursor, the flower texture layer with highly porous structure is uniformly deposited on the surface of the β-MnO$_2$ nanorods. It also can be seen that the diameter of the β-MnO$_2$@CMO-precursor is the least, the β-MnO$_2$@NMO-precursor has the most abundant pores, and β-MnO$_2$@NCMO-precursor shows the largest pore size and diameter. In addition, these nanoflaky shells are not changed after high temperature annealing as shown in Figure 2(d-f). The stability of those architectures can probably be attributed to the crystal structure of β-MnO$_2$, which has the most stable structure among all crystals of MnO$_2$. As a typical example, the low-magnification SEM image of β-MnO$_2$@CMO is displayed in Figure 2g, it can be seen that the nanocomposites represent uniform distribution. The β-MnO$_2$ nanorod templates are also displayed in Figure 2h, where the nanorods show a smooth surface and uniform diameter. The porous structures are characterized by BET measurements. As shown in Figure 2i, the nitrogen adsorption/desorption isotherms of all prepared samples are the combination of type II and IV according to the IUPAC classification. The β-MnO$_2$@NMO possesses the highest BET surface area of 130.9 m$^2$ g$^{-1}$ with a pore volume of 0.293 cm$^3$ g$^{-1}$. The
specific surface area and pore volume of $\beta$-MnO$_2$@NCMO are 102 m$^2$ g$^{-1}$ and 0.216 cm$^3$ g$^{-1}$, respectively. Besides, the $\beta$-MnO$_2$@CMO also possesses a high BET surface area are 88.3 m$^2$ g$^{-1}$ with a pore volume of 0.185 cm$^3$ g$^{-1}$. The BJH pore size distributions of $\beta$-MnO$_2$@CMO, $\beta$-MnO$_2$@NMO and $\beta$-MnO$_2$@NCMO are shown in Figure 2i insert. It can be found that the pore sizes of $\beta$-MnO$_2$@CMO, $\beta$-MnO$_2$@NMO and $\beta$-MnO$_2$@NCMO are concentrated at 7.0 nm, 5.5 nm and 6.0 nm, respectively. Obviously, the pore size of $\beta$-MnO$_2$@NCMO is intermediate between those of $\beta$-MnO$_2$@CMO and $\beta$-MnO$_2$@NMO.

**Figure 2** SEM images of (a) $\beta$-MnO$_2$@CMO-precursor; (b)
β-MnO$_2$@NMO-precursor; (c) β-MnO$_2$@NCMO-precursor; (d) β-MnO$_2$@CMO; (e) β-MnO$_2$@NMO; (f) β-MnO$_2$@NCMO; (g) Low-magnification SEM image of β-MnO$_2$@CMO; (h) β-MnO$_2$ templates. (i) Nitrogen adsorption-desorption isotherms and pore-size distribution curves (inset) of the nanocomposites nanostructures.

The hierarchical hybrid structure is further illustrated from the TEM images from Figure 3. The low-magnification TEM images show that the surface of β-MnO$_2$ nanorods is uniformly covered with Ni, Co, Mn composite oxide nanosheets and formed a core-shell structure. In addition, the thickness of the different nanosheets and layers can be contrasted in the TEM images (Figure 3b, e, h). It can be found that the layers of the β-MnO$_2$@CMO, β-MnO$_2$@NMO and β-MnO$_2$@NCMO are about 75 nm, 95 nm and 97 nm thick, respectively. Besides, the slice of the β-MnO$_2$@NMO is thinner than that of two others. The HR-TEM is used to investigate the lattice of surface layer hybrid metal oxide. The lattice spacing of 0.467 nm and 0.31 nm were observed in Figure 3c, which are in a good agreement with the theoretical interplanar spacing of Co$_3$O$_4$ (111) and β-MnO$_2$ (110) planes. As shown in Figure 3(f, i), the interplanar spacing of 0.31 nm corresponds well to the (110) plane of β-MnO$_2$, the 0.48 nm and 0.47 nm can correspond to the (003) plane of NiO$_2$ and (111) plane of NiCo$_2$O$_4$, respectively. Therefore, it can be concluded that the shells of those nanocomposites are consisted of β-MnO$_2$ and Ni/Co composite oxides.
Figure 3 Low-magnification and high-magnification TEM images of (a-c) \(\beta\)-MnO\(_2\)@CMO; (d-f) \(\beta\)-MnO\(_2\)@NMO; (g-i) \(\beta\)-MnO\(_2\)@NiCMO.

The crystallographic structures of the as-prepared \(\beta\)-MnO\(_2\) nanorod, \(\beta\)-MnO\(_2\)@NCMO-precursor and crystalline \(\beta\)-MnO\(_2\)@NCMO nanocomposite obtained by annealing the precursors at 350 °C for 2h were verified by XRD, as shown in Figure 4a. The diffraction peaks of the MnO\(_2\) nanorod represent all of the characteristic peaks of pure pyrolusite-type MnO\(_2\) (JCPDS 24-0735) phase without any impurities. And the three broad diffraction peaks are located at around 29°, 37° and 57° in the XRD pattern of MnO\(_2\), which correspond to the diffraction bands (110), (101) and (211) of \(\beta\)-MnO\(_2\), respectively. Besides, the diffraction peaks of \(\beta\)-MnO\(_2\)@NCMO-precursor can be well indexed of (Co, Ni)O(OH) (JCPDS 29-0491) apart from the dominant peak of \(\beta\)-MnO\(_2\). There is no contaminant detected, indicating that the precursor is composed of \(\beta\)-MnO\(_2\) and Ni-Co hydroxide. The
patterns of β-MnO$_2$@NCO reveal that the nickel cobalt oxide (NiCo$_2$O$_4$) (JCPDS 20-0781) can be found after the precursor was calcined at 350°C for 2h. Furthermore, Figure 4b shows that all the diffraction peaks are assigned to pure cobalt oxide (Co$_3$O$_4$) (JCPDS 43-1003) and nickel oxide (NiO$_2$) (JCPDS 85-1977) without any impurity apart from β-MnO$_2$.

![XRD patterns](image)

**Figure 4** XRD patterns of (a) β-MnO$_2$, β-MnO$_2$@NCMO-precursor and crystalline β-MnO$_2$@NCMO nanocomposites; (b) β-MnO$_2$, β-MnO$_2$@CMO and β-MnO$_2$@NMO nanocomposites.

### 3.2. Electrochemical Analysis

The supercapacitive performances of as-prepared products were evaluated by electrochemical technology. Figure 5a shows the cyclic voltammograms (CVs) of β-MnO$_2$ nanorod and nanocomposite electrodes at a scan rate of 5 mV s$^{-1}$. Clearly, a pair of well-defined redox peaks within 0.1-0.5 V (vs. Hg/HgO) is visible in the CV curve of the pure β-MnO$_2$, which corresponds to redox couple of MnO$_2$/MnO$_{2-}$, where M represents H$^+$ or K$^+$ ions.$^{10}$ Moreover, it can be seen that the three hybrid nanocomposites have not only the redox peaks of MnO$_2$ but also a pair of redox peaks...
within the -0.45-0.1 V (vs. Hg/HgO), which correspond to the reversible reaction of
Co$^{3+}$/Co$^{4+}$ or Ni$^{2+}$/Ni$^{3+}$ transitions associated with anions OH$^-$. It is obvious that
the integrated area of $\beta$-MnO$_2$@NCMO in the current-potential curve is more than
that of any others, and the increase of the CV integrated area will lead to a much more
pseudocapacitance. Thus, the $\beta$-MnO$_2$@NCMO gives a highest capacity. This may
be ascribed to the synergistic effects of different components. Besides, it can be
known from these CV curves that both the hybrid nanosheet shells and the $\beta$-MnO$_2$
core can contribute to the pseudocapacitance of nanocomposite.

Galvanostatic charge-discharge measurements were conducted between -0.45 to
0.5 V (vs. Hg/HgO) at different current densities ranging from 1 to 20 A g$^{-1}$ to further
evaluate the properties of the nanocomposites. As shown in Figure 5(b-d), it can be
observed that there are two voltage plateaus at around -0.35 and 0.25. The specific
capacitance is calculated by the formula, $C = (I\Delta t)/(m\Delta V)$, where $I$ is the discharge
current, $\Delta t$ is the discharge time, $\Delta V$ is the voltage range and $m$ is the mass of the
active material. The specific capacitance of $\beta$-MnO$_2$@CMO is as high as 437, 395,
250, 200 and 149 F g$^{-1}$; for $\beta$-MnO$_2$@NMO is about 560, 510, 220, 132 and 70 F g$^{-1}$,
and for $\beta$-MnO$_2$@NCMO is about 675, 593, 357, 254 and 190 F g$^{-1}$ at the current
density of 1, 2, 5, 10, 20 A g$^{-1}$, respectively. The specific capacitances of the three
nanocomposite electrodes derived from the discharging curves at different current
densities were compared, as shown in Figure 5e. The $\beta$-MnO$_2$@CMO electrode
delivered a specific capacitance of 437 F g$^{-1}$ at the current density of 1 A g$^{-1}$, which is
lower than those of $\beta$-MnO$_2$@NMO and $\beta$-MnO$_2$@NCMO electrode. However, at the
high current density of 20 A g\(^{-1}\), the \(\beta\)-MnO\(_2@CMO\) electrode still delivered a high specific capacitance of 149 F g\(^{-1}\), indicating much better rate capability compared to the \(\beta\)-MnO\(_2@NMO\) electrode which has a high specific capacitance of 560 F g\(^{-1}\) but decay fast to merely 70 F g\(^{-1}\) when the current density increased from 1 A g\(^{-1}\) to 20 A g\(^{-1}\). It also can be seen clearly that the \(\beta\)-MnO\(_2@NCMO\) electrode exhibits best pseudocapacitance and rate capability among three nanocomposites.

The cycling stability of the nanocomposites and \(\beta\)-MnO\(_2\) nanorod electrodes are evaluated by the repeated charging-discharging measurement at constant current density of 5 A g\(^{-1}\), as shown in Figure 5f. A significant specific capacitance loss can be seen for \(\beta\)-MnO\(_2\) nanorod electrode that only 51% of the initial capacitance is retained after 3000 cycles. While for \(\beta\)-MnO\(_2@NMO\) and \(\beta\)-MnO\(_2@NCMO\) electrodes, the specific capacitances are about 220 and 360 F g\(^{-1}\) in the 1\(^{st}\) cycle, and remained 173 and 305 F g\(^{-1}\) after 3000 cycles, the corresponding capacitance loss is 21% and 17%, respectively. In addition, the cycling stability of \(\beta\)-MnO\(_2@CMO\) is slightly better than that of the other two electrodes, which the capacitance loss is about 14% after 3000 cycles. It can be known that the nanocomposite electrodes show a much better cycling stability than pure \(\beta\)-MnO\(_2\).

The results reveal that \(\beta\)-MnO\(_2@CMO\) exhibits a good rate capability, while \(\beta\)-MnO\(_2@NMO\) displays a high pseudocapacitance. These differences in performances can be mainly attributed to the morphological characteristics of the mesoporous and the nanosheets architectures, as well as the composition of constituents. Evidently, the mesoporous and nanosheets within those architectures can
provide more active sites and path for efficient electrolyte ions transportation.\textsuperscript{24}

Therefore, the fact that $\beta$-MnO$_2$@NMO displays a much higher pseudocapacitance can be dependent on its much higher BET surface area than $\beta$-MnO$_2$@CMO. Besides, compared with the other two nanocomposites electrodes, $\beta$-MnO$_2$@CMO exhibits the best rate capability. It may be attributed to its largest BJH pore sizes which can facilitate the diffusion of ions and improve charge accumulation. Moreover, $\beta$-MnO$_2$@NCMO combines the advantages of both $\beta$-MnO$_2$@CMO and $\beta$-MnO$_2$@NMO, exhibiting a high specific capacitance and cycling stability. Those good performances can be attributed to not only full utilization of individual constituents, but also a strong synergistic effect of different components. However, since the pure transition metal oxide composites still suffer from low conductivity, some efforts remain to be done to further improve the cycling performance and depress the capacity decay of $\beta$-MnO$_2$@NCMO, such as combination with high conductivity graphene, carbon or conducting polymer.
Figure 5 (a) CV curves of as-synthesized samples at a scan rate of 5 mV s\(^{-1}\); Constant-current charge-discharge profiles of (b) \(\beta\)-MnO\(_2\)@CMO, (c) \(\beta\)-MnO\(_2\)@NMO, and (d) \(\beta\)-MnO\(_2\)@NCMO; (e) Specific capacitance of these electrodes at various rates and (f) Cycling stability of as-synthesized samples at a constant current density of 5 A g\(^{-1}\).

Figure 6a shows the CV curves of \(\beta\)-MnO\(_2\)@NMO at various scan rates of 5-40 mV s\(^{-1}\). It can be found that with the increase of the scan rate, the shapes of CV curves...
show slight distortion and the areas surrounded by the CV curves are not significantly influenced, implying good rate capability of the $\beta$-MnO$_2$@NCMO electrode. Electrochemical impedance spectroscopy (EIS) was further employed to detect the properties of ion diffusion and electron transfer in the three kinds of nanocomposite electrodes in the frequency range of 100 kHz to 10 mHz with an AC voltage of 5 mV. The Nyquist plots are shown in Figure 6b and the inset shows the expanded plots at high frequency region. The impedance spectra of three electrodes are almost similar in form with a semicircle at the high frequency and an inclined line following at the low frequency, which corresponds to the interfacial charge-transfer impedance and the diffusive impedance of OH$^-$ ion within the electrode. The slopes of the semicircle at high frequency of the three electrodes are also almost the same, indicating nearly equal value of charge-transfer impedance. The diffusive impedance of OH$^-$ ion within the $\beta$-MnO$_2$@CMO and $\beta$-MnO$_2$@NCMO are much lower than that of $\beta$-MnO$_2$@NMO.

**Figure 6** (a) The CV curves of the $\beta$-MnO$_2$@NCMO at different scan rates; (b) Nyquist plots for the three nanocomposite electrodes, the inset is the expanded plots at high frequency region.
4. Conclusion

Accompanying with the formation of MnO₂, the nanoflaky Co₃O₄, NiO₂ and NiCo₂O₄ have successfully grown on the surface of the β-MnO₂ nanorod via a simple redox reaction between KMnO₄ and Co²⁺/Ni²⁺ during a hydrothermal process. The electrochemical properties of these three hybrid nanostructured composites are evaluated as electrode materials for SCs and all of them show good electrochemical performance. Especially, the β-MnO₂@NCMO, which has a good rate capability (about 30% capacity retention at 20A g⁻¹) and excellent pseudocapacitance (about 675 F g⁻¹ at 1 A g⁻¹), shows superior to both β-MnO₂@CMO and β-MnO₂@NMO which exhibit good rate capability (35% capacity retention at 20A g⁻¹) and high specific capacitance (560 F g⁻¹ at 1 A g⁻¹), respectively. In addition, due to the synergistic effect of different metal oxides, the nanocomposites show good cycle stability, which is evidently much better than that of pure β-MnO₂ (only 51% capacity retention after 3000 cycles). Therefore, the hierarchical transition metal oxide composites will be a kind of promising electrode materials for the application of high performance SCs and other energy storage fields, e.g., electrocatalysis and Li-ion batteries.

Acknowledgements

This work is funded by the National Natural Science Foundation of China under project No. 51272221, Scientific and Technical Achievement Transformation Fund of Hunan Province under project No. 2012CK1006, Key Project of Strategic New Industry of Hunan Province under project No. 2013GK4018, and Science and Technology plan Foundation of Hunan Province under project no. 2013FJ4062.
Reference


