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. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it 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.
Optimizing the Charge Transfer Process by Design of Co$_3$O$_4$@PPy@MnO$_2$ Ternary Core-Shell Composite

Bin Wang,$^a$ Xinyi He,$^a$ Hongpeng Li,$^a$ Qi Liu,$^a$ Jun Wang,$^a$,* Lei Yu,$^a$ Huijun Yan,$^a$ Zhanshuang Li$^a$ and Peng Wang$^b$

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this paper, the incorporation of high conductive material (Polypyrrole) into binary metal oxide core-shell structured composite is adopted to optimize the charge transfer process to further improve electrochemical performance. Due to enhanced electron transfer ability, charge transfer resistances of the ternary core-shell structured composites are all reduced and the electrochemical performances are also improved. For example, the Co$_3$O$_4$@PPy@MnO$_2$ ternary core-shell heterostructured composite exhibits high specific capacitance and excellent rate capability (53% of capacity retention rate at 40 A/g compared with 782 F/g at 0.5 A/g). The composite shows good cycling stability with 97.6% capacity retention over 2000 cycles at 5 A/g. These results demonstrate the potential of core-shell composites to further improve high performance in supercapacitor electrodes.

1. Introduction

The rapid increase of demand for renewable energy has driven the development of electrochemical energy storage (EES) devices. Electrochemical capacitors (ECs), also known as supercapacitors, are considered one of the key technology systems which have a wide range of application due to their high power density, long cycling lifestyle and environmental-friendliness [1,2]. With respect to the core of ECs, the electrode materials can be divided into three groups: (i) carbon materials [3,4] (ii) conducting polymers [5,6] and (iii) metal oxides [7-10]. Apart from high specific surface area, the design of nanoarchitectures for EC electrodes is an effective way to improve electrochemical performance. This is because the nanoarchitecture gives a broader real reaction area and enhances the efficient charge and mass exchange [11,12]. Three-dimensional (3D) nanostructured materials, such as 3D carbon materials [13-15] and the advanced core-shell heterostructure materials [16-19], have attracted most of the researchers’ attention in recent years because of their superior performance [20,21].

Core-shell nanostructured material, is a hybrid material, comprising various types of materials in arbitrary combination, such as metal oxide/metal oxide [22-24], metal oxide/metal hydroxide [25-27], metal oxide/conductive polymer [28,29], and carbon materials/metal oxide [30-33]. The testing results show that the synergistic effect caused by the structure has an advantageous effect on electrochemical performance. The charge transfer resistance ($R_{ct}$) of the hybrid core/shell materials is relatively high, especially for MnO$_2$ based core/shell materials, as shown in Table S1. The highest $R_{ct}$ is 155 $\Omega$ (Aligned Carbon Nanofiber Arrays@MnO$_2$) and even the more improved values are between 3-5 $\Omega$. Other metal oxide based core materials also show a higher $R_{ct}$. Electrochemical performance is closely linked with the charge transfer resistance, so a reduction in $R_{ct}$ results is a significant improvement in electrochemical performance. Optimizing the core material becomes a feasible option. Lee and his group choose ITO nanowires as core; their contrastive electrochemical results demonstrate that higher conductivity core material improves the charge transfer process [10,34,35]. Moreover, a porous core material also accomplishes this effect [36]. Therefore, the purpose of this article is to find an effective way to further reduce the charge transfer resistance.

The unique hierarchical core-shell and heterostructured configuration, along with the synergistic effects of the combined materials, clearly promote charge transfer process [8,9,16,30,32,37]. This indicates that the structure has the potential to be further investigated. In the present work, our main approach is to incorporate higher conductive material into the binary core-shell structure to solve the problem of high charge transfer resistances.
transfer resistance. Through the layer-by-layer process, the ternary core-shell nanostructure is fabricated. As proof, Co3O4@PPy@MnO2 ternary core-shell composite is described in detail. Compared with the binary core-shell composite, the electrochemical analysis results show that the charge transfer process of Co3O4@PPy@MnO2 ternary core-shell composite is improved: the value of $R_d$ declines significantly (0.94 Ω, compared with Co3O4@PPy: 12.87 Ω and Co3O4@MnO2: 60.9 Ω). And it’s easy to understand that the electrochemical performance of Co3O4@PPy@MnO2 is better than either Co3O4@PPy or Co3O4@MnO2: the specific capacitance is 2–3 times higher than the binary core-shell composite (782 F/g, 265 F/g and 306 F/g respectively). In addition, we analyze the electrochemical behavior of other ternary core-shell composites: Co3O4@PPy@NiOOH, Co3O4@PANI@MnO2 and Co3O4@PANI(polyaniline)@NiOOH. Compared with binary core-shell structured composites, the $R_d$ of ternary core-shell structured composites all decline significantly, showing that the charge transfer process is optimized. These results indicate that incorporation of high conductive material is an effective way to improve the electrochemical performance of binary core-shell structured composites.

2. Results and Discussion

The ternary core-shell Co3O4@PPy@MnO2 was synthesized by a layer-by-layer process: First, Co3O4 nanowires were grown onto the Cu foil vertically by a hydrothermal method, followed by calcination. Secondly, a PPy layer was coated onto Co3O4 nanowires via monomer polymerization. Finally, MnO2 nanoparticles were onto Co3O4@PPy through the reaction of MnO2 solution and Co3O4@PPy nanowire (Figure 1A). Figure 1A shows the SEM image of Co3O4@PPy@MnO2 ternary core-shell composite. As proof, Co3O4@PPy@MnO2 ternary core-shell composite was soaked in MnO2 solution completely. In addition, we reduced the concentration of KMnO4 solution and the reaction time (details seen in methods in ESI). Finally, we repeated the operation to increase the quality of MnO2. The contrastive scanning electron microscopy (SEM) images of the prepared binary core-shell composites and the ternary core-shell composite are shown in Figure 1. After the coating process, all core-shell composites remain as nanowire-structures (seen in Figure S1 A-D in ESI), while the density of the composites changes: the interspace among ternary core-shell composite is the smallest (Figure S1 D in ESI); the binary core-shell composites are larger (Figure S1 B,C in ESI); and the pure Co3O4 nanowires are larger (Figure S1 B,C in ESI).

Figure 2 shows the transmission electron microscopy (TEM) images of the prepared core-shell nanostructured composites. Compared with the single Co3O4 nanowires (Figure 2A), all of the core-shell composites reflect a typical hierarchical structure (seen in Figure 2B for Co3O4@PPy and Figure S2 A in ESI for Co3O4@MnO2). As shown in Figure 2B, the PPy layer is covered onto the Co3O4 nanowires, the embossment is also appeared, which is consist with Figure 1B. Figure 2C-D gives the structure...
of CoO₄@PPy@MnO₂ ternary core-shell composite with one repeat number of growing MnO₂. PPy is coated onto CoO₄ nanowires and a small amount of MnO₂ is coated onto the PPy layer. This is more obvious on the embossment part in Figure 2D. When the repeat number is increased, the incorporated PPy layer is covered with MnO₂ nanosheets (Figure 2E), and this is consist with the SEM image in Figure 1D. Because the incorporated PPy layer also reacts with KMnO₄, the outer layer is composed of MnO₂ nanosheets (compared with the CoO₄@MnO₂). In addition, the repeat number also plays a role. Moreover, the diverging nanosheet structure supplies a broader contact area with the electrolyte. This is one of the reasons why the electrochemical performance of CoO₄@PPy@MnO₂ is better than CoO₄@MnO₂.

The X-ray diffraction (XRD) pattern of CoO₄@PPy@MnO₂ composite shows the characteristic peaks of CoO₂ (at 2θ=38.1°) and MnO₂ (at 2θ=12.5°, 25.6° and 36.2°) (Figure 3A) \[15,38\]. The Fourier transform infrared spectroscopy (FTIR) image in Figure 3B shows the existence of the PPy layer. The bands at 1579 and 1440 cm⁻¹ are attributed to the antisymmetric and symmetric vibrations of the pyrrole ring. Bands at 1156 and 850 cm⁻¹ correspond to δCH. All of these confirm the presence of PPy. In addition, the characteristic peaks appear at about 633, 530 cm⁻¹ belong to Co-O in CoO₄ and the peak at 425 cm⁻¹ is indicative of vibrations Mn-O in MnO₂, indicating the existence of CoO₄ and MnO₂. These results are consistent with the literatures. [29,39,40]. A comparison with the energy-dispersive X-ray spectroscopy (EDS) mapping analysis achieves the same result as FTIR (Figure S3 and S4 in ESI). The X-ray photoelectron spectroscopy (XPS) patterns is used to further analyze the CoO₄@PPy@MnO₂ composite. As shown in N 1s XPS pattern in Figure 3D, the two pronounced peak centers at 399.4 eV (-NH-) and 397.6 eV (-N-) testify the existence of PPy layer. \[41-43\] In addition, the Co 2p (Figure 3C) and the Mn 2p (Figure 3E) XPS patterns confirm the cobalt existing in the form of CoO₄ and the manganese existing in the form of MnO₂. \[15,42\] The above analysis certify the successful preparation of CoO₄@PPy@MnO₂ composite.

The electrochemical performance of the core-shell composites is tested in 1 M KOH aqueous solution with the three-electrode system. Figure 4A and 4B give a comparison of the cyclic voltammetry (CV) curves and galvanostatic charge/discharge (CD) curves of the pure CoO₄, binary core-shell composites (CoO₄@PPy and CoO₄@MnO₂), and the ternary core-shell composite (CoO₄@PPy@MnO₂). The repeat number of growing MnO₂ onto CoO₄ nanowires and CoO₄@PPy nanowires is four. All CV curves reflect pseudocapacitive behavior: the asymmetrical shape and the redox peaks. The CV curves exhibit one anodic peak (0.5V) and two cathodic peaks (0.428V and 0.366V), which correspond to Co²⁺/Co³⁺ (Eq.1) and Co³⁺/Co⁴⁺ (Eq.2) \[44\].

\[
\begin{align*}
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad \text{(1)} \\
\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- & \leftrightarrow 3\text{CoOOH} + e^- \quad \text{(2)} \\
\end{align*}
\]

Compared with pure CoO₄, the CV curves of the binary core-shell composites are expanded, indicating much better electrochemical performance due to the hierarchical heterostructure. Among the core-shell composites, the current response of the CoO₄@PPy@MnO₂ composite is the highest, indicating the best electrochemical performance. In addition, the CV curve of the CoO₄@PPy@MnO₂ composite is roughly rectangular in shape (Figure 4C) when excluding the effect of CoO₄, this is due to the pseudocapacitance mechanisms of MnO₂ (Eqs.3 and 4) in KOH solution \[45\].

\[
\begin{align*}
\text{(MnO}_2)_\text{surface} + K^+ & \leftrightarrow (\text{MnO}_2)^{2-}K^+ \quad \text{(3)} \\
\text{(MnO}_2)_\text{bulk} + K^+ + e^- & \leftrightarrow (\text{MnOOK})_\text{bulk} \quad \text{(4)}
\end{align*}
\]

Reaction (3) is related to the real contact area of MnO₂ with the electrolyte solution, and a more convenient ion diffusion pathway also has a reactive role (associated with the structure). In this work, the unique hierarchical core-shell heterostructure not only has a high specific surface area but also facilitates electrolyte penetration, while the key to reaction (4) is whether electrons can transfer inside the composite effectively.
The CD curve of the pure Co$_3$O$_4$ is 352 F/g at 0.5 A/g, and the rate capabilities of Co$_3$O$_4$@PPy and Co$_3$O$_4$@PPy@MnO$_2$ are 58% (306 F/g at 0.5 A/g and 174 F/g at 40 A/g) and 38% (265 F/g at 0.5 A/g and 100 F/g at 40 A/g). A comparison of the data indicates that the intermediary PPy layer improves the rate capability of ternary core-shell structured composite. The area capacitance is another crucial factor for the supercapacitor electrode. The average loading masses of the four composites are 0.2 mg/cm$^2$ (pure Co$_3$O$_4$), 0.35 mg/cm$^2$ (Co$_3$O$_4$@PPy), 0.5 mg/cm$^2$ (Co$_3$O$_4$@PPy@MnO$_2$), and 0.7 mg/cm$^2$ (Co$_3$O$_4$@PPy@MnO$_2$). The specific areas capacitances of Co$_3$O$_4$@PPy@MnO$_2$ composite at 0.5, 1, 2, 5, 10 A/g are 0.55, 0.49, 0.45, 0.42 and 0.38 F/cm$^2$; even at 40 A/g, the value is 0.29 F/cm$^2$ (Figure S6 in ESI). The value is 3–6 times higher than binary core-shell structured composites (0.093 and 0.153 F/cm$^2$ at 0.5 A/g for Co$_3$O$_4$@MnO$_2$ and Co$_3$O$_4$@PPy, respectively). Furthermore, this value is much higher than MnO$_2$ coated core-shell composites, such as hydrogenated single-crystal ZnO/amorphous ZnO-doped MnO$_2$ core-shell nanocables (138.7 mF/cm$^2$ at 1 mA/cm$^2$) [46], WO$_3$@Au@MnO$_2$ core-shell nanowires onto carbon fabric (105 mF/cm$^2$ at 0.6 mA/cm$^2$) [23], NiO@MnO$_2$ nanoflakes (0.4 F/cm$^2$ at 5 mA/cm$^2$) [16], hydrogenated TiO$_2$@MnO$_2$ nanowires (70 mF/cm$^2$ at 2 mA/cm$^2$) [47], and so on [48-50]. Figure 4F gives the cycling performance of Co$_3$O$_4$@PPy@MnO$_2$ composite at the current density of 5 A/g. At first the composite is active and the performance is fluctuating and becomes stable at about 250$^{th}$ cycling. Finally the specific capacitance remains 97.6% after 2000$^{th}$ cycling, showing a fairly good stability.

Remarkably, the electrochemical performance of Co$_3$O$_4$@PPy@MnO$_2$ ternary core-shell composite is better than Co$_3$O$_4$@MnO$_2$ and Co$_3$O$_4$@PPy. As we mentioned above, the incorporated higher conductivity PPy layer optimizes the charge transfer process, so the reduction of charge transfer resistance will provide the most intuitive performance. A further study of electrochemical impedance spectroscopy (EIS) is shown in Figure 5. The EIS patterns in Figure 5B reflect a hybrid control process: 1) charge transfer controlled at high frequency, showing
the semicircle in EIS. The shape in our test deviates from the standard semicircle, due to the heterogeneity of the electrode/solution interface (such as the electrode surface roughness, different electrochemical activity and uneven electric field) and can be expressed as the constant phase angle part \((Z_C P)\). The charge transfer resistance \(R_{ct}\) and the equivalent series resistance \(R_e\) (including the active material, the current collector and the electrolyte) can be obtained by the diameter of the semicircle and the intercept of the X axis. 2) The diffusion, controlled at low frequency, shows a straight line with the slope close to infinity. This is caused by the adsorption of ions onto the electrode surface (reactions 1-4 need the participation of ions from the solution). The equivalent circuit diagram is shown in Figure 5A: \(Z_w\) is the Warburg resistance (composed of the diffusion resistance and the diffusion capacitance) and \(C_t\) is the capacitance limit. The \(R_e\) of Co\(_3\)O\(_4\)@PPy@MnO\(_2\) is 0.94 \(\Omega\), the value is much smaller than Co\(_3\)O\(_4\)@MnO\(_2\) (60.9 \(\Omega\)) and Co\(_3\)O\(_4\)@PPy (12.87 \(\Omega\)), indicating a successful outcome. When we increase the repeat number of growing MnO\(_2\) onto Co\(_3\)O\(_4\)@PPy, the \(R_{ct}\) value is enlarged (Figure 5C and the data are shown in Table S7 in ESI). The largest value (11.55 \(\Omega\)) is smaller than the Co\(_3\)O\(_4\)@MnO\(_2\) layer, showing the effectiveness of the PPy layer.

![Figure 5](image)

The above analysis shows that because of the high conductivity of PPy as the sandwich layer, the electrochemical performance of Co\(_3\)O\(_4\)@PPy@MnO\(_2\) ternary core-shell structured composite is superior to the binary core-shell structured composites. The reasons are as follows: 1) Inheriting the core-shell structure’s active role in decreasing \(R_{ct}\). The unique 3D hierarchical core-shell heterostructure has larger specific area and is beneficial to ionic diffusion of the electrolyte. 2) Taking advantage of the high conductivity of PPy to further reduce \(R_{ct}\). Poor conductivity is a common failing of the metal oxide compared with the carbon material. The sandwiched PPy layer serves as a transition (the electrochemical performance of itself cannot be ignored), and the charge transfer will become more effective. So the pseudocapacitor behaviors of MnO\(_2\) and Co\(_3\)O\(_4\) are optimized. As a result, the \(R_{ct}\) of the whole course is reduced.

3) Providing a larger real reaction area. Compared with pure Co\(_3\)O\(_4\) nanowires, the surface area of the nanowires after coating the PPy layer is enlarged (because the diameter of the nanowires is increased). In addition, different structures of MnO\(_2\) on different nanowires also play a role on the electrochemical performance (Figures 1 and 2). Compared with nanoparticles (Figure S2 A in ESI), the MnO\(_2\) nanosheet structure on Co\(_3\)O\(_4\)@PPy provides more favorable reaction conditions.

![Figure 6](image)

Figure 6. (A) The schematics for the optimization function by the intervened high conductive layer. Compared EIS (B), CD (C) and CV (D) curves for Co\(_3\)O\(_4\)@PANI@NiOOH (curve a), Co\(_3\)O\(_4\)@PANI (curve b), Co\(_3\)O\(_4\)@NiOOH (curve c).

To further verify the effect of the interpolation layer on decrease of \(R_{ct}\), Co\(_3\)O\(_4\)@PANI@NiOOH ternary core-shell structured composite is tested (the SEM and TEM images are shown in Figure S1-2 in ESI). The \(R_{ct}\) of Co\(_3\)O\(_4\)@PANI@NiOOH is 0.6 \(\Omega\), which is much smaller than Co\(_3\)O\(_4\)@PANI (13.1 \(\Omega\)) and Co\(_3\)O\(_4\)@NiOOH (20.6 \(\Omega\), Figure 6B and Table S10 in ESI). The electrochemical performance of the ternary core-shell composite is the best: the highest current response (Figure 6C) and a longest discharge time (Figure 6D). The specific capacitance of Co\(_3\)O\(_4\)@PANI@NiOOH (673 F/g) is 2.5 times larger than Co\(_3\)O\(_4\)@PANI@NiOOH (256 F/g) Co\(_3\)O\(_4\)@PANI (253 F/g). Furthermore, the \(R_{ct}\) of Co\(_3\)O\(_4\)@PPy@NiOOH and Co\(_3\)O\(_4\)@PPy@MnO\(_2\) are both reduced compared with the corresponding binary core-shell composites (Figure S8 and S9 in ESI). The four groups of data demonstrate that our method (by incorporating high conductive material) reduces \(R_{ct}\).

**Conclusions**

In summary, high conductive PPy or PANI layer is incorporated into the binary core-shell composite to reduce charge transfer resistance and improve electrochemical performance. The charge transfer process of the four ternary core-shell structured composites (Co\(_3\)O\(_4\)@PPy@MnO\(_2\), Co\(_3\)O\(_4\)@PANI@NiOOH, Co\(_3\)O\(_4\)@PPy@NiOOH, Co\(_3\)O\(_4\)@PANI@MnO\(_2\)) are greatly improved, with the performances better than binary core-shell composites. These positive results indicate that our design has potential in the construction of the next generation of
supercapacitors with high performance.

**Acknowledgments**

This work was supported by National Natural Science Foundation of China (21353003), Special Innovation Talents of Harbin Science and Technology (2013RFQXJ145), Fundamental Research Funds of the Central University (HEUCFZ), Natural Science Foundation of Heilongjiang Province (B201316), Program of International S&T Cooperation special project (2013DFA50480), the fund for Transformation of Scientific and Technological Achievements of Harbin (2013DB4BG011).

**Electronic Supplementary Information (ESI)**

Electronic Supplementary Information is available from the Internet or from the author.

**Notes and references**


