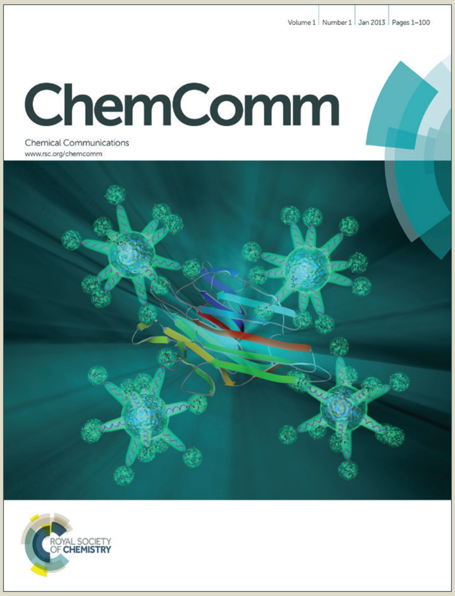

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Polypyrrole Encapsulation on Flower-like Porous NiO for Advanced High-performance Supercapacitors

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Polypyrrole (PPy) encapsulated 3D flower-like NiO was prepared to investigate the role of PPy coating for high-performance electrodes. The NiO@PPy showed a better electrochemical performance than pure NiO, and a "trade-off effect" between electrical conductivity and ion diffusion resistance was observed with different PPy coating thickness.

Supercapacitor is known as a new type of energy storage devices with high power density, long life span and wide potential applications in portable electronic devices.[1-4] Pseudoactive materials, such as RuO_2,[5] NiO,[6-8] Co_3O_4[9,10] and MnO_2,[11-13] are often utilized for their high theoretical capacitance. However, they still suffer from low electrical conductivity and poor stability caused by the large volume change during the charge/discharge processes. To improve the electrical conductivity and mechanical property of metal oxide, compositing with highly conductive materials such as graphene,[14] carbon nanotubes,[15,16] or conductive polymers[17,18] is an effective method. Particularly, conductive polymer composite with metal oxide can effectively improve their electrochemical performance. For example, Jaidev *et al.*[19] reported a hybrid based on polyaniline and MnO_2 nanotube for supercapacitor, which showed specific capacitance of 626 F g^{-1} and corresponding energy density of 17.8 Wh kg^{-1}. Xia *et al.*[20] synthesized oxide MnO_2/polymer/Co_3O_4 hierarchical structure, which exhibits a remarkable cycling stability and delivers a capacitance of 353 F g^{-1}, with capacitance retention of 90.2% after 20,000 cycles. The tightly contact between metal oxide and conductive polymer is very important for constructing a conductive pathways and mechanical stress transfer network. However, previous study for conductive polymer/metal oxide hybrids are mainly based on one or two-dimensional materials so far (nanowire,[11] nanotube[21] or nanosheet[22]), three dimensional metal oxide with plenty of porous structure is seldom reported. To date, porous metal oxides grown on the conductive struts are widely reported.[23-25] However, the metal oxide films are usually several micrometers thick, and the electron diffusion rate to the outer edge of the film inside the metal oxide is still limited. Hence, further polymer coating on the outer surface of the metal oxide/conductive struts can built a sandwich structure with electrical conductive layer on both sides of the metal oxide, this may further improve the electrical performance and stability of the electrodes. Therefore, understanding the growth mechanism of *in situ* encapsulation of conductive polymer into the pores of interconnected porous nanostructure, as well as the influence of the thickness of the coated layer is important for further applications.

Herein, porous 3D flower-like NiO nanoparticle is used as a model to investigate the PPy *in situ* encapsulation and the influence of the coating thickness to the electrochemical performance. The NiO has plenty of pores inside its sphere structure, which can simulate the porous structure of porous metal oxide coated on conductive struts. The PPy coating layer can not only build the electrical conductive pathways to the active materials (NiO), also, the tightly encapsulation of PPy can buffer the mechanical stress during the volume change, making the composite a promising candidate for high performance supercapacitor material. Moreover, the PPy thickness can also influence the electrochemical performance, which is believed to be a "trade-off effect" between electrical conductivity and ion diffusion resistance. Also, this trend is believed to be suitable for conductive polymer coated on other porous metal oxide structure.

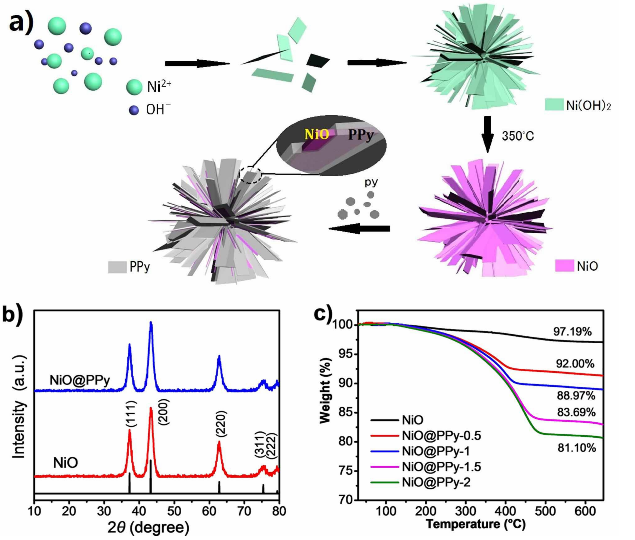

Figure 1. a) Schematic of the synthesis of flower-like $Ni(OH)_2$, NiO and NiO@PPy composite, b) the XRD patterns of the NiO@PPy and NiO; c) The TGA curves of the NiO@PPy-n (n=0.5, 1, 1.5, 2) and NiO composites.

Figure 1a illustrates the synthesis process of the NiO@PPy composites, after *in situ* polymerization, the FT-IR spectra of the NiO@PPy shows two peaks at 1120, and 1010 cm^{-1}, corresponding to the C-N bond from the PPy coating (Figure S1, see ESI). The structure of the NiO@PPy composite was also studied by X-ray diffraction (XRD). Figure 1b shows the XRD patterns of NiO and NiO@PPy, all diffraction peaks of NiO@PPy composites are identical to pure NiO (JCPDS: 47-1049), indicates the NiO crystalline structure is not affected during the polymerization process. Meanwhile, no obvious peak is observed for PPy layer in XRD pattern, owning to the non-crystalline nature of PPy shell. The mass ratio of the NiO@PPy composite was determined by the thermogravimetric analysis (TGA). Figure 1c presents the TGA curves of NiO and NiO@PPy, which is calculated to be 5.19 wt%, 8.22 wt%, 13.50 wt%, 16.09 wt% of PPy for NiO@PPy-0.5, NiO@PPy-1, NiO@PPy-1.5 and NiO@PPy-2, respectively. The XPS spectra show similar result, the N 1s peak increases with the higher pyrrole concentration (Figure S2, see ESI). As the structure of the NiO precursor is identical, the higher PPy weight percentage means the thicker layer covered on the NiO nanoflowers, this may further exhibits different electrochemical performance with different PPy thickness.

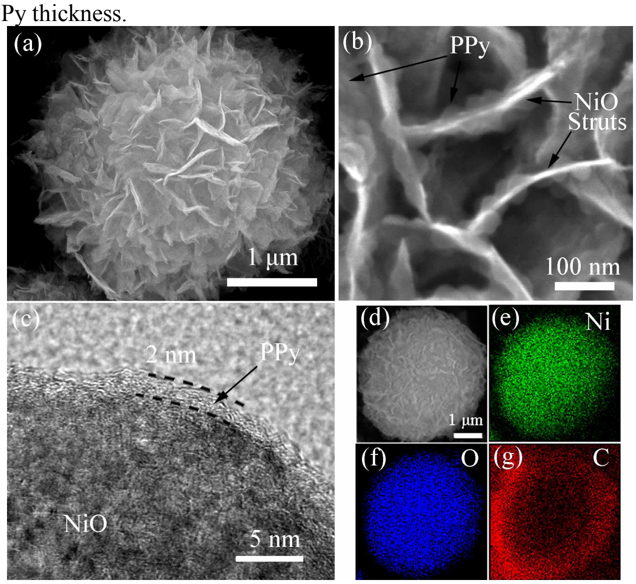

Figure 2. SEM images of the a) b) NiO@PPy nanoparticles under different magnification, c) high resolution TEM image of NiO@PPy-1, d~g) SEM image and corresponding EDS elemental mapping images of e) nickel, f) oxygen, and g) carbon.

Scanning electron microscopy (SEM) images show a nanoflower porous structure of NiO@PPy (Figure 2a), the particles have a size range of 2~3 μm, which is composed of petals with thickness of about 30 nm. This structure is simialr with the $Ni(OH)_2$ and NiO nanoparticles (Figure S3, see ESI). No collapse of the 3D-nanoflower structure is observed after calcination and *in situ* polymerization, indicating the strong mechanical strength of the 3D structure of NiO. Furthermore, the edge of petals become clearer after calcination process, indicating the better crystalline degree of NiO comparing with the $Ni(OH)_2$. Meanwhile, after encapsulation process, the edge of the nanoflakes become obscure, this further certify the non-crystalline structure of the PPy layer on the surface of composite. The high magnification image of the NiO@PPy composite shows the PPy is coated on the NiO surface (Figure 2b), and the TEM image shows a 2 nm thick PPy layer is uniformly and tightly coated on the NiO crystalline (Figure 2c). The structure of composite was also studied by EDS mapping (Figure 2d-g). The elemental of carbon shows a uniform and gradient dispersion throughout the NiO, indicating a continuous PPy coating, even inside the porous structure. The sparser of the C in the particle core is due to the porous structure of the NiO will getting "narrower" inside the core than on the edge. This suggests that the PPy coating layer not only on the edge of the spherical flower, but also "grown" into the 3D porous structure to cover the whole nanopetals.

This 3D NiO@PPy flower structure may function well as a supercapacitor electrode material because: (i) the PPy coating layer can not only build the electrical conductive pathways to the active materials, but also, the intimate encapsulation of PPy can buffer the mechanical stress by large volume change during charge/discharge process; (ii) the porous NiO nanoflower structure effectively increases the specific surface area of the electrode materials, which can facilitate the migration of electrolyte ions to the active material, especially at large current density. Meanwhile, comparing with other conductive materials (e.g. graphene or carbon nanotube), the contact type between the NiO nanoflower and the graphene or carbon nanotube is "point contact", as the conductive metrics can only contact the outer surface of the spherical flower; on the contrary, the *in situ* polymerization method can ensure the PPy layer extend into the nanoflower structure, coating the internal conductive network including the whole nanopetals surface, making the PPy and NiO to form a kind of "film contact".

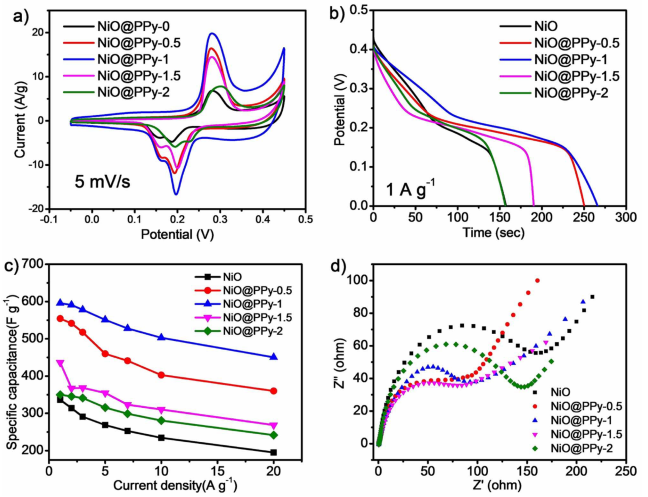

Figure 3. a) the CV curves (at 5 mV s^{-1}), b)charge–discharge curves (at 1 A g^{-1}), c) the specific capacitance and d) Nyquist plots of the hybrid electrodes (NiO@PPy-n) and the pristine electrode (NiO).

The electrochemical properties of the NiO@PPy composite were evaluated using a three-electrode system in 6 M KOH aqueous solution with Ag/AgCl as a reference electrode. To investigate the performance of NiO@PPy with different PPy thickness, a series of composite materials with different thickness of PPy layer were tested. As illustrated in the CV curves (Figure 3a), all of the composite exist a pair of peaks appear in 0.28 and 0.19 V, which are mainly from the reversible redox reaction of NiO as follows: $NiO + OH^- \leftrightarrow NiOOH + e^-$ The charge-discharge curves show similar results (Figure 3b), the discharge plateau located at 0.18-0.20 V range, identical with the CV discharge peak. Both the CV and the charge-discharge curves show typical pseudoactive properties of NiO, demonstrate the electrochemical performance is based on the NiO core, and the PPy coating may only contributing little part of capacitance, because the low weight percentage of the PPy in the composite and the poor electroactive property of PPy in KOH electrolyte.

Furthermore, the electrochemical properties of the composite material are highly influenced by the PPy layer. As shown in figure 3c, the specific capacitance of the electrodes calculated based on the discharge curves is obviously increased after the PPy coating. This results from the better electrical conductivity of the hybrid due to the conductive PPy coating, and a better electrical conductivity will obtained with the ever increasing thickness of the PPy coating. However, the PPy layer will block the ions transfer path to the active material (NiO), which may dramatically increase the ion diffusion resistance with the increasing of the PPy thickness. Hence, there might be a trade-off in terms of the electrical conductivity and the ion diffusion resistance to reach the best electrochemical performance of the NiO@PPy composite. Based on this reason, the specific capacitance of these composites show a first increase and then decrease trend with the increase of the PPy thickness, and the NiO@PPy-1 (595 F g^{-1}) shows a highest performance comparing with other composites.

AC electrical impedance spectroscopy (EIS) was carried out to explore the reason for the capacitance increasement in a frequency range from 100 kHz to 0.01 Hz. Figure 3d shows the Nyquist plots of NiO and NiO@PPy-n (n=0.5, 1, 1.5, 2) nanoflower electrode at open circuit potential. All the Nyquist plots show typical electrochemical capacitor behavior with a semicircle in the high frequency region, which indicate the charge (ions and electrons) transfer resistance between the electrolyte and electrode interface. The NiO@PPy-1 composite shows smaller semicircle, while NiO shows the largest semicircles in all the composites. This result is in line with the former deduction, that the NiO@PPy-1 shows a trade-off relation between electrical conductivity and ion transfer rate, which further explained the trend of the electrochemical performance change of the NiO and NiO@PPy-n composites.

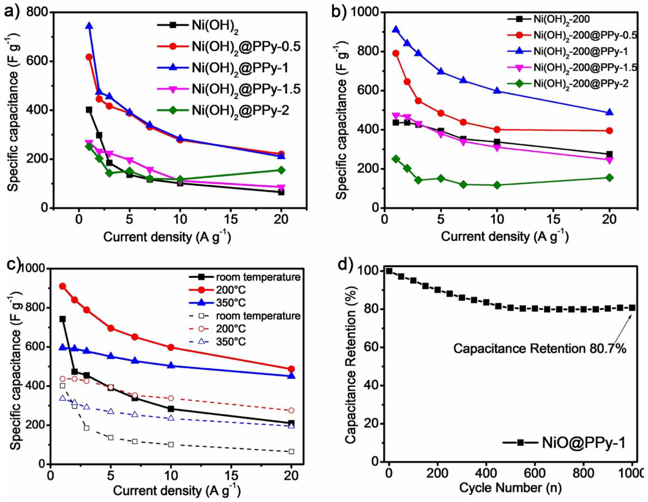

Figure 4. a), b) The special capacitance of Ni(OH)$_2$ and Ni(OH)$_2$-200 with different PPy thickness, respectively, c) comparison of the specific capacitance before (hollow) and after (solid) PPy encapsulation, d) the long-term cycling test of NiO@PPy-1at 20 A g^{-1}.

To investigate the general trend of the influence of electrochemical performance by the PPy layer, control experiments are performed by using the Ni(OH)$_2$ and 200 ºC calcined Ni(OH)$_2$ (note as Ni(OH)$_2$-200) as precursor. Both of them are coated by PPy with the same molar ratio (0.5, 1.0, 1.5, 2.0) of pyrrole monomer versus precursor (Ni(OH)$_2$ and Ni(OH)$_2$-200), respectively. The electrochemical performance of the two precursors as well as their PPy coating hybrids are shown in figure 4a and 4b, both Ni(OH)$_2$ and Ni(OH)$_2$-200 based composite show similar trend as the NiO@PPy. The Ni(OH)$_2$@PPy-1 and Ni(OH)$_2$-200@PPy-1 show a highest specific capacitance (742 and 910 F g^{-1}), respectively, indicate the best PPy layer thickness for the composite. Moreover, within these three kinds composite, the Ni(OH)$_2$-200@PPy-1 show the highest specific capacitance of specific capacitance (Figure 4c), this can be explained by the influence of the different calcination temperature of nickel based materials.[7] However, the NiO@PPy-1 electrode has the best high-rate performance, as the specific capacitance only decrease 23.4% when the current density increase from 1 to 20 A g^{-1} (71.7 and 46.5% for Ni(OH)$_2$ and Ni(OH)$_2$-200, respectively), indicating its promising application as a high-rate supercapacitor electrode. Furthermore, the good electrochemical properties of the hybrid electrode were further confirmed by the long-term cycling test (Figure 4d). During 1000 cycles testing, the specific capacitance value declined in the first 500 cycles, and then stabilized at 80.7% of the initial value at 20 A g^{-1}. The capacitance loss may due to volume change of active materials during cycling will cause the decrease of electrical conductivity between the NiO and PPy. The relatively high cyclic stability may mainly attribute to the PPy coating, which can encapsulate the electrode materials and avoid the collapse of the three-dimensional electrode structure during cycling.

In conclusion, a 3D flower-like porous structure NiO@PPy composite has been prepared via a simple hydrothermal treatment and an *in situ* polymerization process. The thickness of PPy coating can be adjusted by modifying the concentration of pyrrole monomer. The electrochemical performances of the NiO@PPy with different thickness of PPy are vary, and a "trade-off effort" between electron conductivity and ion transfer resistance is observed (the NiO@PPy-1 exhibits a specific capacitance of 595 F g^{-1} at 1 A g^{-1}, and 80.7% capacitance retention after 1000 cycles). Furthermore, this simple, low-cost, and environmentally friendly conductive polymer coating method can be readily applied to other traditional porous electroactive materials to improve their electrochemical performance.

Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details, FT-IR spectra, XPS spectras, SEM images and optical image. See DOI: 10.1039/ b000000x/

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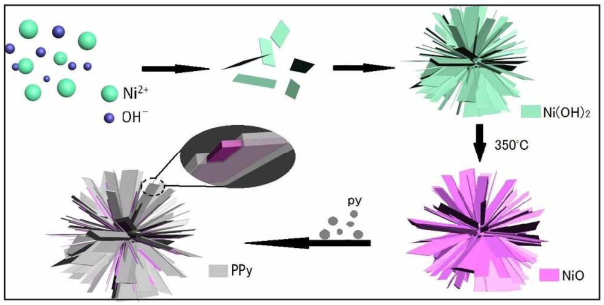

A 3D flower-like porous NiO@Polypyrrole composite is prepared to investigate the role of PPy coating for high-performance supercapacitors.