Asymmetric Supercapacitors Based on $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ Porous Pattern Core-Shell Structure Cathode Materials

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ABSTRACT

In recent years, supercapacitors have been developed rapidly as a rechargeable energy storage device. And the performance of supercapacitors is depending on electrode materials, the preparation method and performance of electrode materials have become the primary goal of scientific development. This study synthesizes $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ cathode material with porous pattern core-shell structure by hydrothermal method and electrodeposition. The result samples are characterized by X-ray diffraction transmission/scanning electron microscope, and X-ray photoelectron spectroscopy. Electrochemical evaluation reveals that electrochemical performance is significantly enhanced by PPy depositing. The specific capacitance of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is 977 F g^{-1} at 1 A g^{-1} , the capacitance retention rate of 105%. Furthermore, the electrochemical performance of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}//\text{AC}$ asymmetric supercapacitor assemblies with AC as the negative electrode material is significantly better than that of $\text{MnO}_2//\text{AC}$ and $\text{Co}_3\text{O}_4//\text{AC}$. The capacity of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}//\text{AC}$ is 102.78 F g^{-1} . The capacity retention rate is still 120% for 5000 charge-discharge cycles.

Keywords : Asymmetric Supercapacitor, Manganese Dioxide, Cathode Materials, Core-Shell Structure, Electrochemical Performance

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1. Introduction

At present, the main energy source is petroleum fuel, which is widely used to meet the needs of all social strata. However, limited resources are not enough to support the progress of the industry in the future. At this time, finding alternative energy has become the top priority in today's society. Under such urgent conditions, the development of economical energy storage system and equipment is a general trend of the current social development [1]. In order to solve these problems, researchers have begun to develop energy devices, such as batteries, fuel cells, electrochemical supercapacitor [2,3]. The supercapacitor is mainly composed of high-performance electrode material, electrolytes, porous membranes, fluid collection and outer packaging materials. The supercapacitor is divided into three categories by

energy storage mechanism and the difference in active materials [4], electrochemical capacitor [5], electric double layer supercapacitor [6], and hybrid supercapacitor [7]. The supercapacitor has many excellent electrochemical performances, as excellent charge and discharge efficiency, high efficiency capacitance retention rate, and stable cycle performance, etc. These advantages play a vital role in the practical application of supercapacitor.

The electrode material of electric double layer supercapacitor is high surface area carbon-based active materials. During operation, the electrode material not produces faraday reaction, the explosion hazard of supercapacitor is avoided at cycle charge and discharge period [8]. The energy storage mechanism of electric double layer supercapacitor is electrostatic interaction between the ions on the contact area of the active electrode material and the electrolyte [9]. The process only takes a few seconds, the performance depends on the activity and kinetic characteristics of the electrochemical electrode. Therefore, electrode material must have high specific surface area, large porosity and uniform pore distribution.

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bution [10]. The electrode material of is electrochemical capacitor is transition metal oxides with pseudo capacitance and conducting polymer [11]. The energy storage mechanism of electrochemical capacitor is the rapid reversible faraday REDOX reaction occurs to or near the surface of the electrode material [12]. Compared with the electric double layer supercapacitor, the electrochemical capacitor has high capacitance and energy density, however, the power density, cycle performance, and rate capability are poor [13]. Hybrid ultracapacitor has the characteristics of electric double layer supercapacitor and electrochemical capacitor, and the energy density and power density are between the two capacitors [14].

The electrochemical performance of the supercapacitor strongly relies upon the type, properties and the surface structure of the electrode material, which should have a high surface area, great electrical conductivity and high chemical stability [15]. At present, the electrode materials of the supercapacitors are mainly electrode materials three categories: carbon materials (graphene [16], activated carbon [17], and Carbon nanotubes [18]), conducting polymer (Poly benzene [19], polypyrrole [20], and polyaniline [21]), and transition metal oxide (RuO_2 [22], IrO_2 [23], MnO_2 [24,25], NiO [26], and Co_2O_3 [27,28]). Among many transition metal oxides, Co_2O_3 , NiO , and V_2O_5 have relatively narrow potential windows and low energy density [22-29]. The MnO_2 as pseudocapacitive electrode material is extensively researched due to higher theoretical ratio of capacitance, low cost and abundant resources, etc [24,25]. However, manganese dioxide still has many drawbacks: (1) The actual specific capacitance is lower than the theoretical specific capacitance; (2) The poor conductivity seriously affects the ion transfer rate for charging and discharging; (3) Poor cycling stability, surface passivation or dissolution in the long cycling process affects the capacitance of the material. Therefore, the drawbacks could be solved by preparation of porous and high conductivity materials. The porous and laminated materials could shorten the diffusion path of ions and provide a large number of reactive sites [30]. The core-shell structure with MnO_2 as outer layer degraded at long cycle process. At the reaction with electrolyte, the surface of electrode forms the insulating layer due to the Mn^{4+} moves towards the electrolyte, ions and protons are exited and embedded. The insulating layer is referred to as solid electrolyte

interphase (SEI) [31]. The condition causes irreversible loss of material capacitance. The researchers propose to apply the polymer to a surface coating or substrate, the polypyrrole (PPy) is considered one of the most attractive polymers [32,33]. The PPy can not only reduce the resistance in the electrochemical reaction of charge transfer, but also prevent the passivation between the active substance and electrolyte [34]. More importantly, the electrode material is protected by PPy coating. This condition contributes to prevent SEI membrane ruptures during electrochemical process, to ensure the coulomb efficiency and long-term stability of the cycle [35]. The combination of the PPy layer and the oxide is an effective method to improve the electrochemical performance, such as SnO_2/PPy [36], $\text{Fe}_2\text{O}_3@\text{PPy}$ [37], and $\text{MnO}_2@\text{PPy}$ [38].

To improve the electrochemical performance of MnO_2 , we synthesize $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ composite electrode by using the Co_3O_4 nanowire and PPy as the core and shell, respectively. Through testing, we found that the “core-shell-shell” structure makes use of synergistic effect [39-42] to obviously promote the process of charge transfer, obtain higher capacitance, and improve the material’s multiplier ability and cycling stability. In addition, the application of electrodeposition to protect the PPy coating is conducive to stabilizing the SEI membrane and protecting the structural collapse of manganese dioxide during the long cycle.

2. Experimental

2.1 Co_3O_4 precursor synthesis

The Co_3O_4 precursor (the molar ratio of CoO and $\text{CH}_4\text{N}_2\text{O}$ is 1:5) is synthesized by hydrothermal method. Firstly, the CoO and $\text{CH}_4\text{N}_2\text{O}$ are dissolved in deionized water in quantities of 30 mL. Continuous agitation of the solution at room temperature is conducted until the solution becomes pink. Then, the pre-treated nickel foam is placed vertically into the PTFE reactor with hydro-thermal treatment at 160°C for 6 h in vacuum drying oven. When the reaction completed, the reactor is laid aside for 12 hours. The pre-treated nickel is washed several times in deionized water and dried at 80°C for 3 h on hot plate. Finally, the precursor is calcined at 350°C for 3 h in box-type furnace then the precursor is obtained.

2.2 $\text{Co}_3\text{O}_4@\text{MnO}_2$ synthesis

First, the KMnO_4 is dissolved in deionized water in

quantities of 30 mL at the appropriate molar ratio, the solution is heated at 90°C for 15 min in water bath kettle, and continuous agitation of the solution at room temperature is conducted until the solution becomes purple. Then, the Co_3O_4 precursor is placed vertically into reactor and the solution is poured into reactor. Hydro-thermal treatment at 160°C for 6 h is carried out with reactor in vacuum drying oven. Finally, the $\text{Co}_3\text{O}_4@\text{MnO}_2$ composite electrode is obtained after the pre-treated nickel is washed several times in deionized water and dried at 80°C for 3 h on hot plate.

2.3 $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ synthesis

The PPy thin film is grown on $\text{Co}_3\text{O}_4@\text{MnO}_2$ composite electrode surface by electrodeposition method. The electrodeposition process is carried out in three-electrode electrochemical station with $\text{Co}_3\text{O}_4@\text{MnO}_2$ composite electrode as the working electrode, platinum plate as the opposite electrode, and Ag/AgCl as the reference electrode. Electrolyte for the PPy electrodeposition is synthesized by dissolving the appropriate molar ratio of PPy and KOH in deionized water in quantities of 20 mL. The $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ composite electrode is synthesized at a voltage of 1.0 V for 600 s. Finally, the final sample is obtained after the $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ composite electrode is washed several times in deionized water and anhydrous ethanol dried at 60°C for 2 h on hot plate.

2.4 Synthesis of asymmetric supercapacitor

2.4.1 Synthesis of negative electrode material

The nickel foam is washed by wash several times in deionized water and anhydrous ethanol, then the nickel is dried at 60°C for 12 h in vacuum drying oven. The negative electrode of asymmetric supercapacitor is prepared by mixing 90 wt% activated carbon and 10 wt% PTFE, followed by adding anhydrous ethanol until the slurry formed. The slurry is coated on nickel (1 cm²), the nickel is dried in hot plate at 60°C for 3 h and pressed under pressure of 15 MPa. Finally, the negative electrode materials of asymmetric supercapacitor is obtained.

2.4.2 Assembly of asymmetric supercapacitor

The PVA-KOH gel electrolyte is prepared by adding PVA (4 g) into solution of 2 M KOH (40 mL) in beaker and stirred with magnet stirrer at 90°C for 3 h to dissolve the PVA. The positive and negative electrode materials and diaphragm are immersed in PVA/

KOH gel electrolyte for 10 min, the positive and negative electrode materials are separated with the diaphragm, and the asymmetric supercapacitor is assembled sequentially with aluminum foil as the outer packing.

2.5 Materials characterization

The crystal structures of pure MnO_2 (Tianjin Zhiyuan Chemical Reagent Co. LTD), $\text{Co}_3\text{O}_4@\text{MnO}_2$, and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ are characterized by XRD with a $\text{CuK}\alpha$ ($\lambda=0.15418$ nm) radiation source (D/max-2500, Japan). The surface morphologies of the samples are identified by FE-SEM (Sigma-500, Germany), and the structure and diffraction method are further identified and discussed by TEM (JEM-2100F, Japan). The surface composition of materials are marked and identified by XPS (250Xi, USA).

2.6 Electrochemical characterization

The electrochemical measurements for three kinds of samples are performed by electrochemical station (Ivium, Netherlands) in the three-electrode mode in 2 mol·L⁻¹ KOH aqueous solutions as electrolytes at room temperature. The electrochemical performance is carried out by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements.

The electrochemical performance of asymmetric supercapacitors is tested by double-electrode system of electrochemical workstation (CHI 660E), and by cyclic voltammetry, galvanostatic charge-discharge, and long-cycle tests are performed, respectively. The battery cycle stability is tested by Xinwei battery test system BTS8.

3. Results and Discussion

3.1 Morphology and structure analysis

The particle morphology structure of pure MnO_2 , $\text{Co}_3\text{O}_4@\text{MnO}_2$, and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ are displayed in Fig. 1. The pure MnO_2 displayed nanosheet structure with the staggered lap is in a multi-channel state (Fig. 1(a)). The morphology of $\text{Co}_3\text{O}_4@\text{MnO}_2$ forms rod structure is influenced by substrate shape, and resulting in the formation of porous pattern core-shell structure with radiation-outward growth at the center (Fig. 1(b)). The $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is obtained after the PPy is deposited on the surface of $\text{Co}_3\text{O}_4@\text{MnO}_2$ (Fig. 1(c)). Compared with the

Fig. 1. Comparison of the morphology of pure MnO₂, Co₃O₄@MnO₂, and Co₃O₄@MnO₂@PPy: (a, b, and c) sample pure MnO₂, sample Co₃O₄@MnO₂, and sample Co₃O₄@MnO₂@PPy; (d, e, and f) and (g, h, and i) show the SEM, structure, and selection diffraction patterns of Co₃O₄@MnO₂ and Co₃O₄@MnO₂@PPy.

Co₃O₄@MnO₂, the Co₃O₄@MnO₂@PPy has a larger rod diameter, and it can be proved from the side that the PPy layer is successfully deposited on the surface of Co₃O₄@MnO₂. The particle size and morphology of Co₃O₄@MnO₂ are displayed in Fig. 1(d, e). The interplanar distance of 0.25 nm correspond to (321) of α -MnO₂, and the interplanar spacing of 0.3 nm correspond to (422) of Co₃O₄. The obvious core-shell boundary is observed in the porous pattern structure of Co₃O₄@MnO₂, the low conductivity of MnO₂ is improved with highly conductive material Co₃O₄ as the “core” and MnO₂ as the “core-shell”. The selection diffraction pattern of Co₃O₄@MnO₂ in Fig. 1(f), the polycrystalline structure of Co₃O₄@MnO₂ is observed by two obvious distinct diffraction rings with corresponding (411) of α -MnO₂ and (420) of Co₃O₄. The high resolution TEM diagram of Co₃O₄@MnO₂@PPy is displayed in Fig. 1(g). The interplanar spacing of 0.18 nm correspond to (220) of Co₃O₄, the interplanar spacing of

0.26 nm and 0.103 nm correspond to (510) and (220) of Co₃O₄. The TEM diagram of Co₃O₄@MnO₂@PPy in Fig. 1(i). The successful deposition of PPy is improved by the nanorods are 261 nanometers in diameter (including the outermost shell), which is 1.7 times the diameter of the Co₃O₄@MnO₂ nanorods. The selection diffraction test of Co₃O₄@MnO₂@PPy is displayed in Fig. 1(i). Three main diffraction rings are corresponded to (320) and (220) of α -MnO₂, and (311) of Co₃O₄, respectively. The polycrystalline structures of Co₃O₄@MnO₂ and Co₃O₄@MnO₂@PPy are improved by selection diffraction. The PPy thin film grows on the surface of the porous pattern structure Co₃O₄@MnO₂ composite electrode, the condition greatly facilitates the diffusion of electrolyte ions in electrode materials, improves the utilization rate of active sites, resulting in the material has excellent electrochemical performance.

The crystalline structures of Co₃O₄@MnO₂, and

Fig. 2. XRD patterns of prepared $\text{Co}_3\text{O}_4@\text{MnO}_2$ and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$: (a) $2\theta=10\text{--}80^\circ$; (b) $2\theta=10\text{--}43^\circ$; (c) $2\theta=60\text{--}70^\circ$.

$\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ cathode materials characterization are displayed by XRD in Fig. 2. The crystalline structures of $\text{Co}_3\text{O}_4@\text{MnO}_2$, $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$, and three distinct peaks are Ni basal peak in Fig. 2(a). The enlarge figure of $\text{Co}_3\text{O}_4@\text{MnO}_2$, and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ at $10^\circ\text{--}43.8^\circ$ and $60^\circ\text{--}70^\circ$ in Fig. 2(b, c). As presented in Fig. 2(b, c), the coexistence phenomenon of $\alpha\text{-MnO}_2$ (JCPDS 44-0141, denote as ◆) and Co_3O_4 (JCPDS 42-1467, denote as ☆). It can be seen that the diffraction peak of all $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is basically the same as the diffraction peak of the $\text{Co}_3\text{O}_4@\text{MnO}_2$, which proves that there is the N in-situ polymerizes on the $\text{Co}_3\text{O}_4@\text{MnO}_2$, and the structure is amorphous. Additionally, the crystallinity of Co_3O_4 is improved by PPy, the content of Co_3O_4 is much higher than MnO_2 , and the electrochemical performance of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is improved due to PPy with high conductivity has excellent electrical conductivity.

3.2 Chemical valence analysis

The chemical composition of $\text{Co}_3\text{O}_4@\text{MnO}_2$ and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ are tested and researched by X-ray photoelectron spectroscopy (XPS) in Fig. 3, MnO_2 sample is not discussed. The C, O, Ni, Mn, Co, and N elements are observed in $\text{Co}_3\text{O}_4@\text{MnO}_2$ cathode material, among them, the Ni element is provided by foamed nickel. Moreover, the N element derived from highly conductive PPy, and compared with the $\text{Co}_3\text{O}_4@\text{MnO}_2$, the intensity of each element of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ declined. The high-resolution measurement area of two samples in Mn 2p are

displayed in Fig. 3(b), three peaks at 641.9, 643.0, and 653.9 eV. Furthermore, the Mn 2p XPS resulted for corresponding to Mn 2p_{1/2} and Mn 2p_{3/2}, respectively, with the spin energy separation of approximately 12.0 eV. Demonstrating that Mn element is predominant in the whole material^[42]. The three weaker Co 2p_{1/2} peaks at $\text{Co}_3\text{O}_4@\text{MnO}_2$, because the Co peak is weakened for MnO_2 on the surface of Co_3O_4 , Co peak in $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is messy, demonstrating that the PPy grows on the surface of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ (Fig. 3(c)). The three peaks on behalf of Mn-O-Mn, Mn-O-H, and H-O-H, respectively, at 529.6, 531.7, and 532.5 eV are measured in O 1s spectra in Fig. 3(d). Compared with the binary core-shell structure $\text{Co}_3\text{O}_4@\text{MnO}_2$, the content of Mn-O-Mn in ternary core-shell structure $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is significantly decreased, which is mainly attributed to the existence of oxygen vacancy. In addition, as shown in Fig. 3(e) the C 1s spectra can be deconvoluted into five individual peaks, and the three main peaks at 284.3, 292.2, and 295.2 eV are consistent with $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$. Only one peak at 397.8 eV from N bonds in PPy is existed in N 1s spectra in Fig. 3(f). Therefore, these results also confirm that a lot of PPy is deposited on the surface of $\text{Co}_3\text{O}_4@\text{MnO}_2$ to form a hybrid hierarchical network composes of a lot of cross-sectional nanometers. Such a hybrid architecture, combines with highly conductive active materials, is more conducive to the electrochemical performance improvement brought by three-dimensional synergistic effect.

Fig. 3. (a) XPS spectra for $\text{Co}_3\text{O}_4@\text{MnO}_2$ and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ sample; (b, c, d, and e) XPS spectra for Mn 2p, Co 2p, O 1s, and C 1s for the $\text{Co}_3\text{O}_4@\text{MnO}_2$ and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ sample; (f) XPS spectra for N 1s for the $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ sample.

3.3 Electrochemical properties

The electrochemical performance of pure MnO_2 , $\text{Co}_3\text{O}_4@\text{MnO}_2$, and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is displayed in Fig. 4. Three positive electrode materials exhibit two distinct plateaus, the pseudo capacitance and excellent reversibility of three materials is

proved in Fig. 4(a), and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ has the largest electrical capacity of three materials. The capacitance contribution of three positive electrode materials, and the excellent electrochemical performance of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ is proved by pseudo capacitance contribution percent of 68% (Fig. 4(b)).

Fig. 4. Electrochemical test of pure MnO_2 , $\text{Co}_3\text{O}_4@\text{MnO}_2$, $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$: (a) Cyclic voltammetry of three samples; (b) Capacitive contribution of three samples; (c) Charging and discharging curves of three samples; (d) Cycle test of three samples after 400 cycles; (e) Nyquist diagram of three samples; (f) Warburg coefficient of three samples.

The specific capacities of MnO_2 , $\text{Co}_3\text{O}_4@\text{MnO}_2$, and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ are obtained from Fig. 4(c), which are 220, 449, and 977 F g^{-1} at 1 A g^{-1} , respectively. As presented in Fig. 4 (d), the cycle process of MnO_2 presents downtrend, the cycle retention rate is up to 82% after 400 cycles. The cycle process of $\text{Co}_3\text{O}_4@\text{MnO}_2$ keeps smooth, the cycle retention rate

is up to 99% after 400 cycles. The cycle process of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ presents unstable rising state in 135 cycles, the cycle retention rate is up to 105% after 400 cycles, the increase of the capacity retention rate confirms that the effective ion insertion/exfoliation occurred in the lattice. Compared with pure MnO_2 , the materials with layered porous pattern

core-shell structure can storage high electrochemical energy, and reduced the migration path of electrolyte ions. To explore the electrochemical performance of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$, the internal resistance of the material is analyzed by ac impedance in Fig. 4(e, f). Compared with the $\text{Co}_3\text{O}_4@\text{MnO}_2$, the $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ has smaller charge transfer resistance and Warburg coefficient. It is proved that the preparation of $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ with core-shell structure by electrodeposition method can improve electrochemical performance as a positive electrode material of supercapacitor.

3.4 Electrochemical characterization of the asymmetric supercapacitors

To explore the electrochemical performance of pure MnO_2 , $\text{Co}_3\text{O}_4@\text{MnO}_2$, $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$, and AC electrode for practical applications, the prepared materials are used as positive electrode materials for asymmetric supercapacitors, respectively, and activated carbon (AC) is used as negative electrode materials. The CV measurements are performed in the two-electrode mode (Fig. 5). The CV of pure MnO_2 , $\text{Co}_3\text{O}_4@\text{MnO}_2$, and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$, at

Fig. 5. Cyclic voltammetry (CV) tests and capacitance contribution of electrode materials and asymmetric supercapacitors $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}//\text{AC}$ at different scanning rates: (a) Cyclic voltammetry of four samples; (b) Cyclic voltammetry of three capacitors; (c, d, and e) Cyclic voltammetry of pure $\text{MnO}_2//\text{AC}$, $\text{Co}_3\text{O}_4@\text{MnO}_2//\text{AC}$, and $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}//\text{AC}$ at 10-100 mV s^{-1} scan rate, respectively; (f) Diffusion capacitance of three samples at different scanning speeds.

Fig. 6. (a) GCD test of MnO₂//AC, Co₃O₄@MnO₂//AC, Co₃O₄@MnO₂@PPy//AC; (b) GCD test of Co₃O₄@MnO₂@PPy//AC at Different current densities.

10 mV s⁻¹ in Fig. 5(a). The CV curves displayed good capacitive behavior with symmetrical rectangular shapes. This indicates that Co₃O₄@MnO₂@PPy has excellent reversibility and capacitance. The AC is activated carbon material, which is a typical double-layer material, the CV curve presented fusiformis. This finding indicates that the capacitive contribution of AC is less than anode material, and the positive electrode material determines the performance of the supercapacitor. The CV of MnO₂//AC, Co₃O₄@MnO₂//AC, and Co₃O₄@MnO₂@PPy//AC at 10 mV s⁻¹ in Fig. 5(b). The CV curves of MnO₂//AC, Co₃O₄@MnO₂//AC occur obvious distortion high at a high cell voltage window of 0-1.8 V. The CV curve of Co₃O₄@MnO₂@PPy//AC has the biggest area and minimum distortion. It explains that ternary core-shell structure has better electrochemical performance. The CV curve shape of the three electrodes remain relatively unchanged at 10 to 100 mV s⁻¹, it can explain the electrodes has excellent stability (Fig. 5(c, d, e)). The diffusion capacitance of the three electrodes at different scanning speeds in Fig. 5(f). The capacitive contribution of MnO₂//AC, Co₃O₄@MnO₂//AC, and Co₃O₄@MnO₂@PPy//AC increase from 26% to 75%, 30% to 52%, and 47% to 80% at 10, 20, 30, 50, and 100 mV s⁻¹, respectively. The capacitive contribution of the three electrodes increase with the increase of scanning speed, and the ternary core-shell structure always maintained the best capacitive performance. According to the above CV test, compared with the MnO₂//AC and Co₃O₄@MnO₂//AC, Co₃O₄@MnO₂@PPy//AC have better capacitance performance. To prove the point, the three electrodes are charged and discharged with

Fig. 7. The capacity retention of MnO₂//AC, Co₃O₄@MnO₂//AC, Co₃O₄@MnO₂@PPy//AC after 5000 cycles at the current density of 15 mA cm⁻².

constant current (Fig. 6). The GCD curve of the three electrodes at 1 A g⁻¹ between 0 and 1.8 V in Fig. 6(a). The charging-discharge curves of the three electrodes are almost symmetrical, indicating their excellent electrochemical reversibility and coulomb efficiency. The specific capacitance of the three asymmetric supercapacitors is 35.56, 45.56, and 102.78 F g⁻¹. The capacitance of Co₃O₄@MnO₂@PPy//AC has 2.9-fold with MnO₂//AC. The specific capacitance of Co₃O₄@MnO₂@PPy//AC is 102.78, 102.22, 97.78, 83.33, and 84.44 F g⁻¹ at 1, 2, 4, 6, and 8 A g⁻¹, it shows excellent rate capability (Fig. 6(b)). The capacitance retention rate of MnO₂//AC, Co₃O₄@MnO₂//AC, and Co₃O₄@MnO₂@PPy//AC at 15 mA cm⁻² for 5000 cycles in Fig. 7. As presented in Fig. 7, MnO₂//AC and

Fig. 8. (a) Power density and energy density calculation of MnO₂//AC, Co₃O₄@MnO₂//AC and Co₃O₄@MnO₂@PPy//AC; (b) Power density and energy density calculation of MnO₂//AC, Co₃O₄@MnO₂//AC and Co₃O₄@MnO₂@PPy//AC at different current densities.

Table 1. Contents of samples in XPS (%)

Samples	Mn-O-Mn	Mn-O-H	H-O-H
Co ₃ O ₄ @MnO ₂	72.9	13.3	13.8
Co ₃ O ₄ @MnO ₂ @PPy	69.9	14.3	15.8

Co₃O₄@MnO₂//AC have a rising trend and the capacitance retention rate drops to 78% and 87% after 5000 cycles, respectively. The Co₃O₄@MnO₂@PPy//AC achieves an excellent cycling capability, the capacitance retention rate is up to 120% after 5000 cycles. This condition is due to add highly conductive PPy increases the active site of the material and improves the free embedding/de-embedding state of ions, the capacitance ratio of the material is improved by synergistic effect of ternary core-shell structure, and the electrical conductivity of materials is improved by fast electron conduction channel of porous flowery structure. As presented in Fig. 8(a), the energy density of MnO₂//AC, Co₃O₄@MnO₂//AC, and Co₃O₄@MnO₂@PPy//AC are 58, 73, and 166 Wh kg⁻¹, respectively, and power density are 3.6, 3.2, 3.3 KW kg⁻¹. Compared with the MnO₂//AC, the energy density of Co₃O₄@MnO₂//AC increases by only 15 Wh kg⁻¹, the energy density of Co₃O₄@MnO₂@PPy//AC increases by 108 Wh kg⁻¹, and the power density of Co₃O₄@MnO₂@PPy//AC is significantly improved. As presented in Fig. 8(b), at different current densities, although the energy density of Co₃O₄@MnO₂@PPy//AC is reduced, the power density increased from 3.3 to 25.7 kW kg⁻¹. Compared with the asymmetric MnO₂ based supercapacitors reported by others, the Co₃O₄@MnO₂@PPy//AC supercapacitors has obvious advantages, such as

MnO₂/PPy//AC (38.6 Wh kg⁻¹) [43], Co₃O₄@MnO₂//MEGO (17.7 Wh kg⁻¹) [44], and MnO₂/C//AC (30.2 Wh kg⁻¹) [45].

4. Conclusions

This study synthesizes supercapacitor anode material Co₃O₄@MnO₂@PPy by hydrothermal and electrodeposition. The structure, morphology, chemical constitution, and electrochemical properties are analyzed and discussed by XRD, FE-SEM, TEM, XPS, electrochemical workstation, and Land battery tester. Compared with the Co₃O₄@MnO₂, the Co₃O₄@MnO₂@PPy has smaller charge transfer resistance and warburg coefficient. The specific capacitance of Co₃O₄@MnO₂@PPy is 977 F g⁻¹ at 1 A g⁻¹, the capacitance retention rate of 105% after 400 cycles. The capacitive contribution of Co₃O₄@MnO₂@PPy is 68%. As the supercapacitor, the specific capacitance of Co₃O₄@MnO₂@PPy//AC is 102.78, 102.22, 97.78, 83.33, and 84.44 F g⁻¹ at 1, 2, 4, 6, and 8 A g⁻¹. The capacitive contribution of Co₃O₄@MnO₂@PPy//AC increase from 47% to 80% at 10, 20, 30, 50, and 100 mV s⁻¹. The capacitance retention rate of Co₃O₄@MnO₂@PPy//AC is 120% after 5000 cycles at 15 mA cm⁻². The special structure of the porous pattern Co₃O₄@MnO₂@PPy anode material is conducive to a

sufficient reaction with the electrolyte. The PPy nanosheet hybrid hierarchical network on the surface of $\text{Co}_3\text{O}_4@\text{MnO}_2$, the hybrid architecture is combined with a highly conductive reactive material, this is more conducive to the electrochemical performance. The positive electrode material $\text{Co}_3\text{O}_4@\text{MnO}_2@\text{PPy}$ has the characteristics of high capacity and stable circulation, and has certain practical value.

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