Fe₂O₃-decorated millimeter-long vertically aligned carbon nanotube arrays as advanced anode materials for asymmetric supercapacitors with high energy and power densities†

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Construction of high-energy density asymmetric supercapacitors is often hindered by unsatisfactory matching between the anode and cathode. Thus, it is crucial to develop composite anodes with high specific capacitance to match that of cathodes. In this work, a novel anode material with well-dispersed Fe₂O₃ decorated on vertically aligned carbon nanotubes has been synthesized by a facile two-step method, consisting of supercritical carbon dioxide (SCCO₂) assisted impregnation and subsequent thermal annealing. Due to the advantageous nanostructure, the Fe₂O₃/VACNT composites exhibit a large specific capacitance of 248 F g⁻¹ at 8 A g⁻¹ in 2 M KOH between −1.2 and 0 V versus SCE. An asymmetric supercapacitor operating at 1.8 V is assembled using the Fe₂O₃/VACNTs as the anode and the NiO/VACNTs as the cathode in a 2 M KOH aqueous electrolyte. The NiO/VACNTs/Fe₂O₃/VACNT asymmetric supercapacitor achieves an extremely high energy density of 137.3 W h kg⁻¹ at a power density of 2.1 kW kg⁻¹, and still retains 102.2 W h kg⁻¹ at the high power density of 39.3 kW kg⁻¹. Moreover, it also shows an outstanding cycling stability with ~89.2% capacitance retention after 5000 cycles. The facile and effective synthesis method, as well as the superior electrochemical performance of the Fe₂O₃/VACNT composites, pave a way for promising applications in high-performance energy storage.

1. Introduction

Owing to the tremendously increasing energy consumption of modern societies, the development of sustainable energy storage devices has attracted great attention. Supercapacitors, including electric double-layer capacitors (EDLCs) and pseudocapacitors, bridge the storage gap between high energy batteries and high power dielectric capacitors. Furthermore, they are currently at the forefront of various emerging energy applications and considered as an important class of energy source for high power supplies, electric and hybrid vehicles, and portable electronics.1–5 However, practical applications of supercapacitors are severely restricted because their energy densities are still far lagging behind without sacrificing the power density and cycle life.6 According to the equation of energy density $E = 1/2CU^2$, the energy density of supercapacitors can be increased by increasing the specific capacitance (C) and/or broadening the operating potential window (U); the latter is more effective. Using ionic liquids which possess the advantages of higher electronic conductivity, electrochemical safety and ease of manufacture is an effective way to increase the operation voltage.7 Besides, constructing aqueous-based asymmetric supercapacitors with different negative and positive electrode materials is also a more desirable strategy. This method can couple two electrode materials possessing well-separated potential windows to maximize the output voltage of asymmetric supercapacitors.8

In order to develop high energy density electrodes, until now, transition-metal oxides/hydroxides have attracted great attention since they exhibit large specific capacitance and can offer high energy densities based on faradaic reactions. Thus they are usually employed as cathode materials for asymmetric supercapacitors with aqueous electrolytes.9–11 Besides, carbon-based materials have been widely used as anodes for asymmetric supercapacitors due to their large surface area, excellent electrical conductivity and outstanding stability.12–16 However, compared with pseudocapacitive cathodes, the specific capacitance of carbon materials is so low that it severely limits the energy density of asymmetric supercapacitors, according to the equation of $1/C = 1/C_{\text{an}} + 1/C_{\text{cat}}$ ($C_{\text{an}}$: capacitance of the anode, $C_{\text{cat}}$: capacitance of the cathode).17 Even though tremendous
research efforts have been devoted to the nanostructures and composites of cathode materials, there are only a few reports of nanostructured pseudocapacitive anode materials. Thus, it is highly desirable to explore new anode materials with high capacitance and conductivity to meet the charge balance with the cathodes to improve the energy density of asymmetric supercapacitors.

Among the few reported pseudocapacitive anodes, compared with transition metal oxides (TMOs), such as MoO$_3$, V$_2$O$_5$, and some metal nitride, Fe$_2$O$_3$ holds great promise for asymmetric supercapacitors because of its high theoretical specific capacitance, suitable potential window (−1.2 V), low cost, abundance, and non-toxicity. However, similar to most other transition metal oxides, a small surface area and poor electronic conductivity are still two obstacles that limit the specific capacitance and power capability of Fe$_2$O$_3$. To address this issue, tremendous efforts have been devoted, mainly in two directions: constructing unique nanostructures of TMOs and combining these nanostructures with conductive materials including carbon-based materials, such as 1D carbon nanotubes, 2D graphene and 3D graphene aerogels. As a typical 3D carbon-based nanostructure, the vertically aligned carbon nanotube arrays (VACNTs) are supposed to be an ideal architecture for electrode materials, owing to their large specific surface areas, high conductivity, and excellent chemical stability. CNTs in the arrays could be considered as many mutually parallel nanoscale electrodes with the same orientation, promoting plenty of well-oriented 1D conductive paths for the motions of electrons along the same direction. Then, as the support for TMOs, VACNTs with a thickness above 1000 μm is advantageous since both the mass and volume energy densities of supercapacitor cells increase with increasing weight ratio of the active materials in the cell’s weight. Moreover, the appropriate intertube spacing and the regular pore structure in VACNTs can facilitate highly efficient transport of electrolyte ions and intermediate reactants. In addition, without other conductive supports or polymer binders in the preparation of the TMOs/VACNT composite electrodes, the contact resistance and inactive material mass can be drastically reduced. However, due to the nanoscale intertube spacing, the hydrophobic nature and fragile structure of high density, millimeter-long CNT arrays, the treatment of VACNTs with TMOs by wet chemistry is an issue yet to be resolved and there have been only a few reports on this aspect to date.

In this work, millimeter-long VACNTs are employed as the support of Fe$_2$O$_3$ for synthesizing a novel anode material. For the first time, Fe$_2$O$_3$/VACNT composites with 5–10 nm Fe$_2$O$_3$ nanoparticles homogenously anchored on VACNTs were successfully prepared by a facile two-step method, consisting of a supercritical carbon dioxide (SCCO$_2$) assisted impregnation process and subsequent thermal annealing. As our previous study has shown, SCCO$_2$ is effective in synthesizing the VACNT/TMO hybrid structure with a high-aspect ratio and oriented morphology. Due to the advantageous nanostructure, the Fe$_2$O$_3$/VACNT composites exhibit a high specific capacitance of 248 F g$^{-1}$ at 8 A g$^{-1}$ in a wide potential window of 0 to −1.2 V. Moreover, they also possess excellent rate performance and high power charge and discharge capacity, making them a perfect anode candidate to match with the NiO/VACNT composite cathode (173 F g$^{-1}$ at 8 A g$^{-1}$). For NiO/VACNTs//Fe$_2$O$_3$/VACNT asymmetric supercapacitors, a maximum energy density of 137.25 W h kg$^{-1}$ is obtained at the power density of 2.14 kW kg$^{-1}$. Furthermore, the asymmetric supercapacitors also have outstanding cycling stability, retaining ~89.2% capacitance after 5000 cycles. These superior energy and power performances of the asymmetric supercapacitor stem from the nanosized feature of the active materials and the 3D aligned structure of the electrode.

2. Experimental

Synthesis of vertically aligned carbon nanotube arrays

The vertically aligned carbon nanotube arrays with high density and millimeter-long thickness were synthesized by water-assisted CVD at 840 °C with high-purity ethylene (99.99%) as the carbon source. Si (100) wafers, coated with a buffer layer of a 30 nm Al$_2$O$_3$ film and catalyst films of 1.5 nm Fe, were used as substrates. High-purity Ar (99.999%) and H$_2$ (99.999%) were employed as carrier gases at 1 atm. The total flow rate was 600 sccm. A small and controlled amount of water vapor, supplied by passing a portion of Ar carrier gas through a water bubbler, was introduced to increase the catalyst lifetime. Typically, 100 sccm ethylene and a water concentration of 100–200 ppm were introduced at 840 °C for CVD growth at ambient pressure. After 10 min, VACNTs with a height of ~1 mm consisting of nanotubes with an average diameter of ~7 nm were grown.

Fabrication of TMOs/VACNT composites

Iron(II) acetylacetonate [Fe(acac)$_3$], obtained from Aldrich Chemical and employed as received, was used as the Fe precursor in SCCO$_2$. In the typical process, first, VACNTs were placed in a high-pressure vessel of 50 ml. Second, different quantities of the precursor (e.g. 10 mg, 20 mg, and 30 mg) were added to 0.75 ml benzene solution. Then, the organic solution of different concentrations was dropped in a container in the vessel. Subsequently, the vessel was sealed and connected to the gas pipeline. The reactor was preheated to 50 °C, and then CO$_2$ was pressurized to the targeted pressure by a syringe pump. After that, the vessel was heated and kept at 100 °C for 6 h, where the precursor was dissolved into the SCCO$_2$ fluids and adsorbed into VACNTs. Then, the reactor was depressurized and cooled to room temperature slowly. The amount of adsorbed precursor was determined by weighing the VACNTs before and after SCCO$_2$ treatment. Afterwards, the precursor impregnated VACNTs was transferred to a rapid thermal annealing (RTP) furnace and annealed at 400 °C in air for 3 h to convert the precursor to iron oxide. For comparison, the Fe precursor was also annealed under the same conditions to prepare pure iron oxide.

To construct the asymmetric supercapacitor, a NiO/VACNT composite with 43.4 wt% of nickel oxide was prepared by
a similar method, using nickelocene as the precursor in SCCO₂. More details can be found in the previous report.46

Characterization

The crystal structure of the composite was analyzed by X-ray diffraction (XRD, Advance D8). Raman spectra were taken on a Raman Station 400F with an excitation length of 532 nm. Morphologies of the samples were observed with field-emission scanning electron microscopy (FE-SEM, Quanta FEG450) and transmission electron microscopy (TEM). To determine the annealing conditions for the sample and the exact loading amount of the oxide on CNTs, thermogravimetric analysis (TGA, Pyris 1 TGA, Perkin-Elmer) was carried out in air. EDS (JEOL-2010) measurements were utilized to investigate the compositions of the samples.

Electrochemical characterization

All electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS), were performed with a CHI750D electrochemical workstation (Shanghai CH Instrument Company, China) at room temperature. For conventional three-electrode tests, the pristine VACNTs or TMOs/VACNT hybrids were utilized as the working electrodes, which were detached from substrates and directly pressed on a nickel mesh. The counter electrode system is calculated by

\[ E = \frac{1}{2} \left( C \cdot V \cdot C - M \right) \]

where \( E \) is the energy density, \( I \) the discharge current, \( V \) the cell voltage \( (V) \) is the discharge time, \( M \) the total mass of Fe₂O₃/VACNT composites and \( C \) the capacitance of the electrode. To assemble a full cell, the following equation is used to balance the charge between the anode and cathode, was assembled in a button cell using a porous electrolyte-soaked separator and 2 M KOH electrolyte. The cathode, was assembled in a button cell using a porous electrolyte-soaked separator and 2 M KOH electrolyte. The average specific capacitance of the electrodes in the three-electrode system is calculated by

\[ C = I \cdot \Delta t / (\Delta V \cdot m) \]

where \( I \) (A) is the discharge current, \( \Delta t \) (s) is the discharge time, \( \Delta V \) (V) is the voltage drop upon discharging, \( m \) (g) is the mass of the active material of the electrode. To assemble a full cell, the following equation is used to balance the charge between the anode and cathode,

\[ C' \cdot \Delta V' \cdot m = C' \cdot \Delta V' \cdot m' \]

where \( C \) (F g⁻¹) is the specific capacitance of the single electrode, \( \Delta V \) (V) is the working potential range, and \( m \) is the mass of the electrode. The \( C_s \) of the asymmetric supercapacitor is calculated from GCD curves by

\[ C_s = 4I \cdot \Delta t / (\Delta V' \cdot m') \]

where \( m' \) (g) is the total mass of the active material of the positive and negative electrodes. The energy and power densities of the asymmetric supercapacitor are calculated as follows:

\[ E = C \cdot V^2 / 2 \]

\[ P = E / \Delta t \]

where \( E \) (W kg⁻¹) is the energy density, \( V \) (V) is the cell voltage excluding the IR drop, \( P \) (W kg⁻¹) is the average power density, and \( \Delta t \) (s) is the discharge time.

3. Results and discussions

Scheme 1 illustrates the composite electrode design and construction of the asymmetric supercapacitor. An effective supercritical CO₂ (SCCO₂)-assisted method was developed to prepare Fe₂O₃/VACNT composites as the anode material. Briefly, it involves the impregnation of the organometallic Fe precursor in VACNTs in the supercritical fluid, and thermal annealing of the mixture in an air flow.

To obtain a high loading amount of Fe precursor on CNTs, the impregnation time was first optimized. As shown in Table S1,† the weight gain of VACNTs after the impregnation increases with the impregnation time in SCCO₂, but it approaches saturation after 6 hours. Therefore, 6 hour impregnation in SCCO₂ was believed to be efficient for making the Fe₂O₃/VACNT composite. Besides, the precursor concentration in the SCCO₂ may also affect the loading amount of the Fe precursor in VACNTs. As demonstrated in Table S2,† with the precursor mass increasing from 10 mg to 40 mg in 0.75 ml benzene solution, the loading amount increases from 0.83 mg to 3.17 mg. Based on the TGA analysis (Fig. S2†), the weight loss of Fe(acac)₃ starts from around 200 °C and continues up to 400 °C, thus the annealing temperature was determined to be 400 °C.

The corresponding weight percentages of iron oxide in the composite, after 3 h annealing at 400 °C in air, are 5.41 wt%, 13.95 wt%, 17.10 wt% and 26.06 wt% for the precursor mass of 10 mg, 20 mg, 30 mg and 40 mg (noted as VACNTs-5.41, VACNTs-13.95, VACNTs-17.10 and VACNTs-26.06, respectively. The weight percentage of iron oxide is calculated according to the equation:

\[ \text{Wt\% (Fe}_2\text{O}_3) = (M_t - M_{\text{VACNTs}})/M_t \times 100\% \]

where \( M_t \) is the total mass of Fe₂O₃/VACNT composites after annealing and \( M_{\text{VACNTs}} \) is the mass of pristine VACNTs without SCCO₂ processing.

In the present study, the NiO/VACNT composite was prepared as the cathode material using a similar method, and the weight percentage of NiO in the nickelocene/VACNTs samples after 6 h annealing at 350 °C was 42.1%.

Fig. 1a shows the XRD patterns of the pristine VACNTs and the Fe₂O₃/VACNT composites with different wt% of Fe₂O₃. Small diffraction peaks at 32.8°, 35.6°, 54.1° and 63.0° are observed, which can be attributed to the (104), (110), (116) and (214) reflections of \( \alpha \)-Fe₂O₃ (JCPDS no. 33-0664). The weak and broad humps that appeared in the XRD patterns indicate the nanocrystalline feature and/or the low degree of crystallinity of the Fe₂O₃ particles.47 Raman analysis was further carried out to characterize the as-obtained composites. As shown in Fig. 1b, the G-band at 1579 cm⁻¹ and the D-band at 1342 cm⁻¹ originate from sp² hybridized carbon atoms and imperfections in CNTs, respectively. Four Raman peaks can be observed between 200 and 700 cm⁻¹ for the Fe₂O₃/VACNT composites, which correspond to one A₁g (214 cm⁻¹) and three E_g (279, 377, and 604 cm⁻¹) Raman modes of \( \alpha \)-Fe₂O₃.48 And the peaks below 200 cm⁻¹ are ascribed to the radial breathing modes (RBMs) of small-diameter CNTs.49 Interestingly, with increasing Fe precursor concentration in SCCO₂, the characteristic peaks of CNTs (e.g. G band and D band) weaken gradually, while those of Fe₂O₃ particles become stronger, due to the increased amounts of Fe₂O₃ decorated on CNTs. The XRD and Raman results confirm the successful synthesis of the Fe₂O₃/VACNT composite.
SEM images of the pristine VACNTs are presented in Fig. S3,† in which CNTs are densely packed and grow vertically to the substrate. The aligned channels in VACNTs are advantageous in terms of ion diffusion and the electrochemical performance of electrode materials.37 Fig. 2 shows cross-sectional SEM images of the Fe2O3/VACNT composites with different weight percentages of Fe2O3 (5.41 wt%, 13.95 wt%, 17.10 wt%, and 26.06 wt%, respectively) which have been annealed in air at 400 °C for 3 h. As clearly observed, Fe2O3 nanoparticles are uniformly distributed in the VACNT arrays for all the samples. And more nanoparticles can be observed on the CNT surface with increasing wt% of Fe2O3 in the composites. However, when 40 mg of the precursor was used, apparent delamination occurs and a layer with heavy Fe2O3 loading forms on the top surface region, which can be found from the close observation of the VACNTs-26.06 sample, shown in Fig. S4.† Possibly, too much precursor concentrates on the top layer of VACNTs at the beginning of the SCCO2 impregnation due to the high concentration of the Fe precursor, which retards further transport of the precursor in VACNTs. Besides, the CNTs seem wavier and more winding as the Fe2O3 loading amount increases, but the reason is not clear yet.

EDS mapping of a typical Fe2O3/VACNT composite (e.g. VACNT-17.10) shows that both Fe and O distribute uniformly throughout the composite, suggesting the homogeneous decoration of Fe2O3 inside VACNTs. And the corresponding EDS spectrum is shown in Fig. S5.† This success is attributed to the unique advantage of SCCO2-assisted impregnation. On account of the gas-like transport properties (zero surface tension, low viscosity and fast diffusivity) and liquid-like density of SCCO2, rapid mass transfer of the precursor inside the nano-pores of VACNTs is facilitated without damage to the aligned structure of VACNTs.41 Therefore, homogeneous absorption of Fe(acac)3 molecules on the CNT forest is achieved, and Fe(acac)3 molecules are further transformed to Fe2O3 during thermal annealing.

In addition, TEM examination was conducted to get more insights into the microstructure of the composites. Fig. 3a–c show TEM images of the Fe2O3/VACNT composites with different Fe2O3 loading amounts. As can be seen, the Fe2O3 nanoparticles are uniformly distributed on the surface of CNT walls and the typical particle sizes are about 5–10 nm. More observation clearly shows the decoration of Fe2O3 nanoparticles on the outer surface of CNTs (Fig. S6†). With the Fe2O3 loading amount increasing, more Fe2O3 nanoparticles can be observed.
on CNTs, while the particle sizes remain constant. The fine-sized particles facilitate the electrolyte to access a large surface area and are thus desirable for high capacitance and high power of the supercapacitor electrode. From the HRTEM image shown in Fig. 3d, the lattice fringes with an interplanar spacing of 0.25 nm are clearly observed, which corresponds to the (110) plane of Fe$_2$O$_3$.

The electrochemical performance of the Fe$_2$O$_3$/VACNT composite was evaluated using a three-electrode system in a 2 M KOH aqueous electrolyte. For comparison, the electrochemical behavior of pristine VACNTs and Fe$_2$O$_3$ was also investigated. Fig. 4a shows typical CV curves of the VACNTs, Fe$_2$O$_3$ and the Fe$_2$O$_3$/VACNT composites in 2 M KOH solution at 30 mV s$^{-1}$. For the pristine VACNTs, quasi-rectangular CV curves are observed, indicating good electric double-layer capacitive performance of pure CNTs. In the CV curves of Fe$_2$O$_3$ and all Fe$_2$O$_3$/VACNT composite electrodes, there is a pair of well-defined peaks at about −0.65 V for the anodic scan and about −1.15 V for the cathodic scan, which is ascribed to the reversible oxidation and reduction processes between Fe$^{3+}$ and Fe$^{2+}$, following the reaction of Fe$^{3+}$O$_3$ + 2e$^-$ + 3H$_2$O $\leftrightarrow$ Fe$^{2+}$ (OH)$_3$ + 2OH$^-$. Besides, the enclosed areas of CV curves of the Fe$_2$O$_3$/VACNT composite electrodes are much larger than those of the pristine VACNTs, demonstrating that the capacitances of the Fe$_2$O$_3$/VACNT composites are much larger than those of the VACNT electrode, and the pseudocapacitance of Fe$_2$O$_3$ nanoparticles is the main contributor to the capacitance of the composites. Compared with Fe$_2$O$_3$, the larger specific capacitance of the composite also reveals advantages of the 3D electrode architecture and highly conductive support. Furthermore, as the loading amount of Fe$_2$O$_3$ increases (from 5.41 wt% to 17.10 wt%), the enclosed areas of the CV curves gradually increase, indicating enhancement in the capacitance. With further increase in the wt% of Fe$_2$O$_3$, the capacitance goes down because the uneven distribution of Fe$_2$O$_3$ results in decreasing of utilization efficiency of the active material. GCD curves shown in Fig. 4b also demonstrate the similar dependence of the capacitance on Fe$_2$O$_3$ loading. At a current density of 12 A g$^{-1}$, the pure VACNT electrode shows a typical
triangle curve like other carbon-based electrode materials. For the Fe$_2$O$_3$/VACNT electrode, a charge and a discharge platform occur at about −0.7 and −1.0 V, corresponding to the oxidation and reduction of Fe$_2$O$_3$ nanoparticles, respectively. All Fe$_2$O$_3$/VACNT composites exhibit a much longer discharge time than the VACNT electrode, indicating the significant capacitance increase after Fe$_2$O$_3$ decoration. Besides, no obvious hydrogen evolution is found in the CV and GCD curves because of the high hydrogen evolution overpotential of the Fe$_2$O$_3$ nanoparticles grown on VACNTs, thus it is reasonable to believe that the potential of 0 to −1.2 V is a safe potential window for the composites, and such a broad potential window is beneficial for enhancing the energy density of fabricated two-electrode asymmetric supercapacitors.  

The rate capability of pristine VACNTs, Fe$_2$O$_3$ and the four composite electrodes with different Fe$_2$O$_3$ loadings has been investigated and the results are shown in Fig. 4c. Although VACNTs have the lowest specific capacitance, they show a negligible decrease in capacitance when the current density increases 3 times from 8 to 24 A g$^{-1}$, while the Fe$_2$O$_3$ only retains 48.9% of its original capacitance. Of all the composite electrodes, the sample with 5.41 wt% Fe$_2$O$_3$ exhibits the best
capacitance retention (94.5%) as the current density increases from 8 to 24 A g\(^{-1}\), but its absolute capacitance is the lowest due to the small Fe\(_2\)O\(_3\) loading amount. With increasing wt% of Fe\(_2\)O\(_3\), the specific capacitances are improved, but the rate capabilities are sacrificed. At all the current densities, the VACNTs-17.10 composite shows the highest specific capacitance. And the specific capacitance is 248, 232, 220, 211 and 204 F g\(^{-1}\) (0.95, 0.89, 0.84, 0.81 and 0.78 F cm\(^{-2}\)) at 8, 12, 16, 20 and 24 A g\(^{-1}\) (30.7, 46.1, 61.4, 76.8 and 92.2 mA cm\(^{-2}\)), respectively. Meanwhile, 82.3% of the capacitance is still maintained when the current density increases from 8 to 24 A g\(^{-1}\). With further increasing the loading amount of Fe\(_2\)O\(_3\) to 26.06 wt%, electrochemical performance of the electrode material degrades, and both the specific capacitances and rate capability drop compared with those of the VACNTs-17.10 sample. Based on the SEM observation, it is known that the delamination phenomenon takes place in this case and more Fe\(_2\)O\(_3\) concentrates on the top layer of the VACNTs, which results in the decreasing of the Fe\(_2\)O\(_3\) surface area and poorer utilization efficiency of the active material. Therefore, the loading mass of Fe\(_2\)O\(_3\) and the uniform structure of Fe\(_2\)O\(_3\) nanoparticles decorated on the VACNTs are two important parameters in determining the electrochemical performance of Fe\(_2\)O\(_3\)/VACNT composite electrodes.

To understand the difference in capacitive performance of the Fe\(_2\)O\(_3\)/VACNT composite electrodes, electrochemical impedance spectroscopy (EIS) measurements were carried out and Nyquist plots of the composite electrodes are shown in Fig. 4d. In the low frequency region, all the composite samples show ideal straight lines with almost the same slope along the imaginary axis, indicating the low resistance of the Fe\(_2\)O\(_3\)/VACNT composite electrode for ion/proton diffusion. The fast ion/proton diffusion is ascribed to the ordered pores or channels inside VACNTs, which are desirable for fast charge/discharge of supercapacitors. The semi-circular loop at higher frequencies is due to the charge transfer resistance \((R_c)\). Although the \(R_c\) of the composite electrode increases with increasing Fe\(_2\)O\(_3\) content, the charge transfer resistances of all the composite samples are lower than 0.8 \(\Omega\), which is much better than that of Fe\(_2\)O\(_3\)/FGS,\(^{24}\) indicating the rapid charge transfer process at the composite/electrolyte interface. Besides, the equivalent series resistance (ESR) around 0.2 V for the Fe\(_2\)O\(_3\)/VACNT composite electrodes, indicated by the real axis intersection in the high-frequency region, is also smaller than most of the Fe\(_2\)O\(_3\)-containing composites reported,\(^{42,45,47,48}\) highlighting the superior electrical conductivity of our electrode structure. Compared with the Fe\(_2\)O\(_3\), the Fe\(_2\)O\(_3\)/VACNT composite electrodes show smaller \(R_c\) and ESR, which lead to the better rate performance of the composite in the KOH electrolyte. Besides, the increase in charge transfer resistance with increasing Fe\(_2\)O\(_3\) content indicates that a high Fe\(_2\)O\(_3\) loading sacrifices the electrical conductivity of the composite. However, if the Fe\(_2\)O\(_3\) content is too little in the composite (such as the VACNTs-5.41 sample), enhancement in specific capacitance would not be significant compared with the pristine VACNTs. Therefore, the Fe\(_2\)O\(_3\) loading amount in the composite is a crucial factor to achieve the best electrochemical performance. In the present work, the VACNTs-17.10 composite exhibits the best electrochemical performance, which is further used as the anode for the asymmetric supercapacitor.

To build the asymmetric supercapacitors, the NiO/VACNT composite with 42.1 wt% NiO was synthesized as the cathode material by a similar two-step method. The morphology of the NiO/VACNT composite was investigated by FESEM and TEM. Fig. 5a presents the FESEM image of the NiO/VACNT composite. Clearly, NiO nanoparticles are uniformly dispersed on CNTs along the alignment direction without obvious aggregation, revealing a similar nanostructure as the Fe\(_2\)O\(_3\)/VACNT composites. The typical particle sizes of NiO are about 8–10 nm, as can be observed from the TEM image (Fig. 5b). In XRD patterns, the diffraction peaks at 37.2°, 43.4°, 62.8°, 75.5°, and 79.8° can be well assigned to the NiO phase (JCPDS no. 04-0835), confirming the formation of NiO nanoparticles on CNTs. The electrochemical behavior of the NiO/VACNT composite was studied using a three-electrode system with 2 M KOH as the electrolyte. Fig. 5d shows the CV curves of the NiO/VACNT composite electrode in a positive (0 to 0.6 V vs. SCE) potential window at different scan rates (5, 10, 20, 30, 40 and 50 mV s\(^{-1}\), respectively). Similar to the Fe\(_2\)O\(_3\)/VACNT composite electrode, the NiO/VACNT composite electrode exhibits a pair of redox peaks, which reflects the reversible redox reaction of Ni\(_{2}\)O\(_3\) + OH\(^{-}\) \(\leftrightarrow\) Ni\(_{2}\)OOH + e\(^{-}\).\(^{44}\) The GCD curves in Fig. 5d demonstrate obvious charge and discharge platforms, which are consistent with the redox peaks in CV curves. The NiO/VACNT composite exhibits high specific capacitances, which are 605.9, 595.7, 582.3, 572.5, 568.4, 565.3, 562.1 and 559.1 F g\(^{-1}\) (1.57, 1.54, 1.51, 1.48, 1.47, 1.46, 1.46 and 1.45 F cm\(^{-2}\)) at 2, 4, 6, 8, 12, 16, 20, and 24 A g\(^{-1}\) (5.2, 10.4, 15.5, 20.7, 31.1, 41.4, 51.8 and 62.2 mA cm\(^{-2}\)), respectively, which correspond to the capacitance retention of 92.3%. Therefore, in terms of the specific capacitance and the rate capacity, NiO/VACNTs could be a good choice of cathode for the Fe\(_2\)O\(_3\)/VACNT anode.

Based upon the above mentioned experimental results and discussion, an asymmetric supercapacitor with the Fe\(_2\)O\(_3)/VACNT anode and NiO/VACNT cathode is expected to have a high working voltage up to 1.8 V in 2 M KOH. As shown in Fig. 6a, they exhibit large pseudocapacitances in the exactly complementary potential windows. Thus, an asymmetric supercapacitor was fabricated by using the Fe\(_2\)O\(_3\)/VACNTs as the anode and the NiO/VACNTs as the cathode in a two-electrode button cell. As shown in Scheme 1, both the Fe\(_2\)O\(_3\)/VACNT and NiO/VACNT composites are pressed into the nickel foam and used as binderless electrodes, which are separated by an electrolyte-soaked separator.

Fig. 6b shows the CV curves of NiO/VACNTs/Fe\(_2\)O\(_3)/VACNT full cell with a cell voltage window between 0 and 1.8 V at different scan rates from 5 to 50 mV s\(^{-1}\) in 2 M KOH aqueous solution. As observed, there is a couple of sharp redox peaks near 0.9 V and 1.5 V, indicating the faradaic reaction from the electrodes with 1/2Fe\(_{3}\)O\(_4\) + 3/2H\(_2\)O + e\(^{-}\) \(\rightarrow\) Fe\(_{2}\)(OH)\(_3\) + OH\(^{-}\) at the anode and Ni\(_2\)O\(_3\) + OH\(^{-}\) \(\rightarrow\) Ni\(_{2}\)OOH + e\(^{-}\) at the cathode.\(^{48}\) Fig. 6c presents GCD curves of the asymmetric supercapacitor at different current densities. In agreement with the CV curves, the GCD curves also exhibit two platforms, corresponding to the
redox reaction on the two electrodes. Calculated from GCD curves based on the mass of the whole electrodes, as shown in Fig. 6d, the asymmetric supercapacitor delivers a large specific capacitance of 305 F g⁻¹ (13.7 F cm⁻³) at 2 A g⁻¹ (90 mA cm⁻²). When the current density further increases to 24 A g⁻¹ (1080 mA cm⁻²), the full cell still maintains a specific capacitance of 227 F g⁻¹ (10.2 F cm⁻³), showing a desirable rate performance. This could be attributed to the composite electrode design for both the anode and cathode with a large surface area and good electrical conductivity. Besides, as shown in the Ragone plots (Fig. 6e), the present Fe₂O₃/VACNTs//NiO/VACNT asymmetric supercapacitor exhibits an extremely high energy density of 137.3 W h kg⁻¹ (6.2 mW h cm⁻³) at the power density of 2.1 kW kg⁻¹ (0.1 W cm⁻³), which is much larger than that of the
asymmetric supercapacitor of Fe$_2$O$_3$/FGS//MnO$_2$/FGS (50.7 W h kg$^{-1}$),$^{42}$ GF-CNT@Fe$_2$O$_3$/GF-CoMoO$_4$ (74.7 W h kg$^{-1}$),$^{43}$ Fe$_2$O$_3$/NiO (105 W h kg$^{-1}$),$^{44}$ and VACNTs//NiO/VACNTs (90.9 W h kg$^{-1}$).$^{45}$ Even at a high power density of 39.3 kW kg$^{-1}$ (1.8 W cm$^{-3}$), the assembled device still retains an energy density of 102.2 W h kg$^{-1}$ (4.6 mW h cm$^{-3}$), highlighting the superior power capacity of our asymmetric supercapacitor. More details on volume energy/power densities of the asymmetric supercapacitor are presented in Table S6.$^{†}$ Furthermore, the NiO/VACNTs//Fe$_2$O$_3$/VACNT asymmetric supercapacitor also expresses excellent cycling ability. Fig. 6f shows the capacitance retention of the NiO/VACNTs//Fe$_2$O$_3$/VACNT asymmetric supercapacitor.

![Fig. 6](image_url)
asymmetric supercapacitor as a function of the cycle number at a current density of 8 A g\(^{-1}\) for 5000 charge/discharge cycles. About 89.2\% of its initial capacitance could be maintained after 5000 cycles, suggesting good cycling stability of the assembled supercapacitor.

The remarkable energy and power densities of the present NiO/VACNTs/Fe\(_2\)O\(_3\)/VACNT asymmetric supercapacitor can be attributed to the unique electrode design and the good cathode–anode coupling. Compared with other electrodes, the TMOs/VACNT composites exhibit high specific capacitance and excellent rate performance due to the synergetic effects of the highly conductive CNT arrays and well-dispersed TMO nanoparticles. Firstly, the ordered pores or channels in the VACNTs may promote fast electrolyte ion diffusion into the composite arrays and fast faradaic reactions. Secondly, the nanometer-sized TMO particles along with their good dispersion and the compact contact between CNTs and TMO nanoparticles maximize the specific capacitance of the composite electrode. What’s more, the high specific capacitance of our Fe\(_2\)O\(_3\)/VACNT anode matches well with that of the NiO/VACNT cathode, and the desirable anode–cathode coupling builds a high-performance asymmetric supercapacitor, with both high energy density and high power density.

4. Conclusion

In summary, a facile synthesis method for Fe\(_2\)O\(_3\)/VACNT composites featuring well-distributed Fe\(_2\)O\(_3\) nanoparticles in VACNTs has been presented. With the high conductivity and ordered pore structure of VACNTs and the high pseudocapacitance of metal oxide made full use of, the Fe\(_2\)O\(_3\)/VACNT composites exhibit high specific capacitance and good rate capability. A 1.8 V asymmetric supercapacitor is built by using Fe\(_2\)O\(_3\)/VACNTs as the anode and NiO/VACNTs as the cathode in a 2 M KOH aqueous electrolyte. The asymmetrical supercapacitor obtains an energy density of 137.3 W h kg\(^{-1}\) at the power density of 2.1 kW kg\(^{-1}\) and retains 102.2 W h kg\(^{-1}\) at 39.3 kW kg\(^{-1}\), indicating excellent energy density, high power density and excellent rate capability. Besides, it also exhibits good cycling stability with 89.2\% of the initial capacitance retained at 8 A g\(^{-1}\) after 5000 cycles. The low-cost Fe\(_2\)O\(_3\)/VACNT anode with such a remarkable supercapacitive performance holds great promise for practical applications in high performance energy storage systems.

Acknowledgements

The authors gratefully acknowledge the financial support from the Natural Science Foundation of Shanghai (16ZR1423500) and The Program for Associate Professor of Special Appointment (Young Eastern Scholar) at Shanghai Institutions of Higher Learning (QD2016013).

References