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Hybrid supercapacitor based on flower-like Co(OH)$_2$ and urchin-like VN electrode materials

Rutao Wang, Xingbin Yan, Junwei Lang, Zongmin Zheng and Peng Zhang

A series of designed hybrid electrochemical capacitors have been firstly fabricated by using the flower-like cobalt hydroxide (Co(OH)$_2$) and urchin-like vanadium nitride (VN) as the positive and negative electrode materials, respectively. Both of Co(OH)$_2$ and VN electrode materials showed excellent electrochemical performance due to their unique structure and fast reversible Faradic reaction characteristics. With the different operation voltage window (OVW) and negative/positive mass ratios, the impacts on capacitance performance of hybrid supercapacitor were investigated thoroughly, which demonstrated that both mass ratio and OVW played the important role on their capacitance performance. Furthermore, theoretical modeling was performed and the simulation result was in agreement with the experimental results for the influence of negative/positive mass ratio on capacitance performance of hybrid supercapacitor. When an optimized negative/positive mass ratio was located 3, Co(OH)$_2$/VN hybrid supercapacitor could be cycled reversibly in the high-voltage region of 0-1.6 V and delivered an high energy density of 22 Wh kg$^{-1}$. Even at a large power density of 15.9 kW kg$^{-1}$, the hybrid supercapacitor still possessed a desirable specific energy density of 9 Wh kg$^{-1}$. Such an impressive hybrid supercapacitor was expected to be a highly promising candidate for application in high-performance energy storage systems.

**Introduction**

Energy storage devices, in particular supercapacitors, have attracted considerable attention in future energy storage applications. Currently, supercapacitors have been widely used in consumer electronics, memory back-up systems, hybrid electrical vehicles and industrial power/energy management due to high power density (> 10 kW kg$^{-1}$), long cycle life (> 10$^5$ cycles) and fast charge/discharge processes (within seconds). However, they still suffer from a lower energy density compared with rechargeable batteries. Therefore, it is urgent to develop advanced supercapacitors with enhanced energy density without sacrificing the power delivery and cycle stability to meet the future energy demands.

Aqueous hybrid supercapacitors, combining an energy-type Faradaic electrode and a power-type electrode, have been paid extensive attention as an alternative or supplement to batteries in energy storage field. Aqueous electrolytes endow hybrid supercapacitor with the advantages of ionic conductivity, low cost, non-flammability, environmentally robust, and easy to handle. Furthermore, the energy density of hybrid capacitor can increase through full use of the difference in the potential windows of two electrode materials to maximize operating voltage in the cell system. Therefore, hybrid supercapacitors are able to fill the gap between batteries and conventional capacitors without sacrificing energy/power delivery and cycle life. Various electrode materials such carbon, transition metal oxides, metal hydroxides, and electronically conducting polymer materials have been widely investigated for potential applications in hybrid supercapacitor. Among that, studies on hybrid supercapacitor with metal oxides/hydroxides and activated carbon (AC) as positive and negative electrodes in aqueous electrolyte, respectively, are becoming the hot topic. AC based hybrid supercapacitor, such as PbO$_2$/AC, NiO//AC, Co(OH)$_2$/AC, Ni(OH)$_2$/AC, MnO$_2$/AC, MoO$_3$/AC, Li insertion materials (LiMn$_2$O$_4$, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, LiFe$_{0.5}$Mn$_{0.5}$PO$_4$, and LiFePO$_4$)/AC, have been widely reported, and they all exhibit high work potential region of 1.2-2 V and much improved energy density ranging from 10 to 50 Wh kg$^{-1}$. For negative materials aspect, AC is characterized by a high hydrogen evolution overpotential, considerable specific capacitance, and impressive rate capability. However, the low volume density and high surface area (>$1000$ m$^2$/g) of AC limit the volume energy performance in this hybrid supercapacitor system. This is majorly attributed to the increased volume percentage of the
negative electrode and extra electrolyte within these hybrid supercapacitors. Therefore, it is necessary to explore other electro-active negative materials with a large specific capacitance instead of the activated carbon to form a hybrid cell.

To our knowledge, only a few of metal oxides are considered to be qualified candidates as the negative electrode materials in hybrid supercapacitors, such as RuO$_2$, FeOOH, MoO$_3$, V$_2$O$_5$, TiO$_2$, and MnFe$_2$O$_4$. RuO$_2$ is the most prominent negative materials due to its considerable electrical conductivity and high specific capacitance, however, the high cost of Ru is a limitation for practical application. Though FeOOH and MnFe$_2$O$_4$ can be used as negative materials for hybrid supercapacitors, the hybrid systems are suffer from their low energy and power delivery. Metal nitride, especially vanadium nitride (VN), is considered to be good candidates as negative materials in hybrid supercapacitor due to their large theoretical capacity (> 500 F g$^{-1}$), reversible and fast redox Faradic response, and high hydrogen evolution overpotential.$^{20,31}$ Up to now, there are rare reports on VN based hybrid supercapacitors only of V$_2$O$_5$/VN and NiO/VN systems.$^{21,23,22}$ Considerable energy density and power delivery can be achieved in these VN based hybrid systems, which is comparable to AC based hybrid supercapacitors.

Herein, we have successfully designed a series of hybrid supercapacitor consisting of the urchin-like VN negative and flower-like Co(OH)$_2$ positive electrode materials. The experimental and theoretical results prove that the negative/positive mass ratio plays an important role in determining the capacitance of Co(OH)$_2$/VN hybrid supercapacitor. The optimal hybrid supercapacitor thus shows a high energy density of 22 Wh kg$^{-1}$ at a power density of 0.16 kW kg$^{-1}$, and a high power density of 15.9 kW kg$^{-1}$ at an energy density of 9 Wh kg$^{-1}$, all with a 1.6 V cell voltage operating in 2 M KOH aqueous electrolyte. This strategy for the choice of metal oxide or nitride provided a promising route for new-type supercapacitor with high energy and power densities.

**Experimental section**

**2.1 Synthesis of flower-like Co(OH)$_2$**

Flower-like Co(OH)$_2$ was synthesized by a facile precipitation method. In a typical experiment, 0.01 M of CoCl$_2$$\cdot$6H$_2$O was dissolved in 10 ml of distilled water under magnetic stirring. NH$_4$OH solution (5 wt%) was slowly added into the CoCl$_2$$\cdot$6H$_2$O solution until the pH values reached 9. The reaction mixture was stirring vigorously for 3 h at room temperature. Then the solid was filtered and washed with a copious amount of distilled water. The obtained product was dried at a temperature of 60 °C in air for 12 h.

**2.2 Synthesis of urchin-like VN**

The urchin-like VN were firstly fabricated through a two-step approach. First, we used a modified method according to Lou' work.$^{22}$ Typically, commercial V$_2$O$_5$ (4.8 g) and H$_2$C$_2$O$_4$$\cdot$H$_2$O in a molar ratio of 1:3 were dissolved in 160 ml of distilled water under vigorous stirring at 80 °C for 5 h. A blue clear solution (VOC$_2$O$_4$) was formed. 5 ml of VOCI$_2$O$_4$ (about 0.33 M) solution was then added into a 50 ml Teflon container, followed by addition of 1 ml of H$_2$O (35 wt.%) under stirring. After 10 min, 15 ml of ethanol was added and the obtained solution was stirred for another 5 min. Then the container was sealed in an autoclave and transferred to an electrical oven and kept at 180 °C for 24 h. After cooling down naturally, the precipitates were collected by filtering with distilled water for several times and dried at 60 °C for 12 h. Second, as-made precipitate was directly annealed in the NH$_3$ (flow rate 40 cc min$^{-1}$) at 600 °C for 2 h with a heating rate of 5 °C min$^{-1}$ to obtain the urchin-like VN micro-flowers.

**2.3 Structural characterization**

Field emission scanning electron microscopy (FESEM, JSM 6701F) and transmission electron microscopy (TEM, JEOL 2100 FEG) were employed to investigate the morphology and microstructure of as-prepared electrode materials. Powder X-ray diffraction (XRD, Rigaku D/Max-2400) was performed using Cu-K$_\alpha$ radiation to investigate the structure and composition of the samples. The nitrogen adsorption-desorption isotherm measurements were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. The total pore volume was estimated from the amount adsorbed at a relative pressure of P/P$_0$ = 0.99.

**2.4 Electrode preparation and electrochemical measurements.**

The working electrodes were prepared as follows: 90 wt% of sample was mixed with 5 wt% of acetylene black in an agate mortar until a homogeneous black powder was obtained. To this mixture, 5 wt% of poly(tetrafluoroethylene) was added with a few drops of ethanol. After briefly allowing the solvent to evaporate, the resulting paste was pressed at 10 MPa to the nickel gauze with a nickel wire for an electric connection. The assembled electrodes were dried for 12 h at 60 °C in air. Each electrode contained about 5 mg of electro-active material and had a geometric surface area of about 1 cm$^2$.

Electrochemical measurements were performed using an electrochemical working station (CHI660D, Shanghai, China) in a three-electrode system in 2 M KOH aqueous electrolyte at room temperature. A platinum gauze electrode and a saturated calomel electrode served as the counter electrode and the reference electrode, respectively. The average specific capacitance values were calculated from the galvanostatic discharge curves, using the following equation:

$$ C = \frac{I}{(dE/dt) \times n} \times \frac{1}{[(\Delta E/\Delta t) \times m]} \left[\text{F g}^{-1}\right] \quad (1) $$

Where $I$ is constant discharge current, $\Delta t$ is the time period for a full discharge, $m$ indicates the mass of the corresponding active electrode material, and $\Delta E$ represents the voltage change after a full discharge.

A two-electrode cell configuration was used to measure the performance of asymmetric supercapacitor in 2 M KOH aqueous electrolyte solution. The working electrodes were prepared by the as above-stated method. After drying, the two identical electrodes were pressed at 10 MPa, and they were placed together and separated by a porous nonwoven cloth separator. And then, the assemble two-electrode cell was infiltrated with 2 M KOH solution. Finally, the assemble two-electrode cell was sealed by plastic film and tightly clamped by two poly(tetrafluoroethylene) plates. The energy density ($E$) of aqueous asymmetric supercapacitor can be achieved by the specific capacitance ($C$) and the cell voltage ($V$) according to the following equation:

$$ E = 0.5 CV^2 \quad (2) $$
The power density \( P \) of asymmetric supercapacitor can be achieved by the energy density \( E \) and the discharging time \( t \) according to the following equation:

\[
P = \frac{E}{t} \quad (3)
\]

### Results and discussion

#### 3.1 Flower-like Co(OH)\(_2\) positive materials

The typical low-magnification scanning electron microscope (SEM) image (Fig. 1a) clearly illustrates that the as-synthesized Co(OH)\(_2\) samples are composed of many well-defined microflowers with interconnected nanoflakes. The high-magnification SEM image (Fig. 1a inset) reveals that these nanoflakes have the ultrathin structure with the thickness below 10 nm. The TEM image (Fig. 1b) also proves the flower-like structure of as-synthesized Co(OH)\(_2\) which composed of interconnected and ultrathin nanoflakes. In the corresponding selected-area electron-diffraction pattern (Fig. 1b inset), the broad and diffused halo rings are observed, indicating a polycrystalline structure of Co(OH)\(_2\) flowers. No sharp peaks have been observed in the powder X-ray diffraction (XRD) pattern (Fig. 1c), and which is corresponding to the layered \( \alpha\)-Co(OH)\(_2\) structure (PDF, card no. 46-0605) with low crystallinity. Furthermore, the profile of the adsorption-desorption hysteresis loop is characteristic of porous structure for the layered \( \alpha\)-Co(OH)\(_2\) (Fig. 1d). The wide capillary condensation step toward higher relative pressure indicates the wide distribution of pore sizes, which can also be observed in the Barrett-Joyner-Halenda (BJH) mesopore-size-distribution curves. The Brunauer-Emmet-Teller (BET) specific surface area of as-synthesized Co(OH)\(_2\) are calculated to be 85 m\(^2\) g\(^{-1}\) along with a large pore volume of 0.33 cm\(^3\) g\(^{-1}\). Such flower-like structure of Co(OH)\(_2\) could benefit the penetration of the electrolyte OH\(^-\) to Co(OH)\(_2\) active material, which is crucial for surface redox reactions.

Electrochemical characterization of the specific pseudocapacitance of porous Co(OH)\(_2\) hydroxides microflowers were investigated by cyclic voltammetry (CV) and galvanostatic test in a three-electrode beaker cell with a 2 M KOH electrolyte. The typical pseudocapacitive behavior of flower-like Co(OH)\(_2\) is present in the form of one pair of strong redox peaks in CV curves (Fig. 2a). The redox peaks of CV curves correspond to the conversion between different cobalt oxidation states. The two sequential reactions are described as follows:\(^{13,33}\)

\[
\begin{align*}
\text{Co(OH)}_2 + \text{OH}^- & \rightarrow \text{CoOOH} + \text{H}_2\text{O} + e^- \\
\text{CoOOH} + \text{OH}^- & \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^-
\end{align*}
\]

The capacitive response comes from as above-stated Faradic redox reactions, which is very distinct from that of electric double layer capacitors that commonly produce a CV curve close to an ideal rectangular shape. Fig. 2b shows the galvanostatic charge/discharge curves at the different current densities. The observation of nearly symmetric potential-time curves at all current densities implies the high charge-discharge columbic efficiency and low polarization of our electrode. The specific capacitance values calculated from the discharge curves are 429, 405, and 369 F g\(^{-1}\) at the current densities of 1, 2, and 5 A g\(^{-1}\), respectively, as shown in Fig. 2c. Even at a relatively high current density of 10 A g\(^{-1}\), the specific capacitance is still maintained at 337 F g\(^{-1}\), thereby exhibiting the high capacitance performance and good rate capability of flower-like Co(OH)\(_2\). The Nyquist plot (Fig. 2d) ranging from 100 kHz to 0.01 Hz features a high phase-angle (exceeding 45°) impedance plot and a low Faradic charge transfer resistance, indicating the fast ion transfer behavior of flower-like Co(OH)\(_2\).

#### 3.2 Urchin-like VN negative materials

As shown in Fig. 3a and b, uniform urchin-like VN micro flowers with an average diameter of about 3-5 \( \mu \)m are composed of one-dimensional (1D) nanorods. High-resolution SEM image reveals that 1D nanorods with overall diameter of around 100 nm which are composed of closely stacked nanoparticles with a diameter of around 20 nm. TEM image (Fig. 3c and 3d) also reveals the urchin-like morphology of VN microflowers. Selected area electron diffraction (SAED) pattern (Fig. 3d inset) shows that each diffraction spot is converted into an arc, which is the
porous VN microflowers are cubic phase crystallized where the VN microflowers is also verified by N2 like VN can be interpreted as porous nanorods which built with interconnected nanoparticles. XRD analysis (Fig. 3e) proves that evidence of texture in the polycrystalline structure. The urchin-like VN electrode exhibits excellent rate capability, and the retention rate of VN is 71.6% when the discharging current density increases from 0.5 to 20 A g\(^{-1}\)), which is higher than other VN nanoparticles and still comparable to other VN nanostructures.\(^{21,23,34,35}\) The superior electrochemical performance of VN microflowers can be attributed to the porous structure with large accessible surface area.

**3.3 Hybrid supercapacitor based on flower-like Co(OH)\(_2\) and urchin-like VN**

Considering the high pseudocapacitance of flower-like Co(OH)\(_2\) and the excellent rate capability of the urchin-like VN, VN/Co(OH)\(_2\) hybrid supercapacitor was fabricated as shown in Fig. 5a. Fig. 5b show that the VN electrode was measured at a scan rate of 20 mV s\(^{-1}\) with a potential window of -0.1 V to -1.2 V (vs. SCE), while Co(OH)\(_2\) was measured within a potential window of -0.4 V to +0.5 V (vs. SCE). By expressing the total cell voltage as the sum of the potential range of VN and Co(OH)\(_2\), the hybrid supercapacitor can be operated up to 1.6 V. When the hybrid supercapacitor work with in a potential range of 0-1.6 V, it can reach a safe performance of both electrodes during long cycling. Fig. 5c exhibits the CV curves of the optimized hybrid supercapacitor (VN/Co(OH)\(_2\)) mass ratio: 3) measured at different scan rates of 5, 10, 20, 50, and 100 mV s\(^{-1}\) between 0 and 1.6 V in 2 M KOH solutions. A couple of symmetric redox peaks, derived from the fast redox reactions on the VN and Co(OH)\(_2\) electrode.
Microflower electrode, are observed in each CV curves even at the high scan rates. The shapes of all these curves are almost the same, indicating the excellent rate capability of as-fabricated hybrid supercapacitor. The high specific capacitance and rate capability of the hybrid supercapacitor are revealed by galvanostatic measurements (Fig. 5c). The specific capacitance is 62.4 F g\(^{-1}\) at a current density of 0.2 A g\(^{-1}\). At a high current density of 10 A g\(^{-1}\), a useful capacitance of 34.4 F g\(^{-1}\) is measured. The high performance of our hybrid supercapacitor can be attributed to the individual properties of electrode materials and their synergistic effects between the positive and negative electrodes. Both Co(OH)\(_2\) and VN are pseudo-capacitive materials with high theoretical specific capacitance values. The micro-flower morphology and porous structure of Co(OH)\(_2\) and VN are able to enrich in electrolyte ions and shorten the diffusion paths for both electrons and ions, resulting in the increase of specific capacitance and rate capability of hybrid supercapacitor.

In addition, operation voltage window (OVW) and mass ratio of Co(OH)\(_2\)/VN play the important roles in enhancing the electrochemical properties of hybrid supercapacitor— as demonstrated below.

In a control experiment, an Co(OH)\(_2\)/VN hybrid supercapacitor with mass ratio of 3 works at different potential windows in 2 M KOH aqueous solution at a scan rate of 50 mV s\(^{-1}\) as shown in Fig. 6a. When OVW is located at 1.0 V, a triangular CV curve implies an incomplete pseudocapacitive response from the hybrid supercapacitor. By increasing the OVW to 1.2 V, oxidation and reduction humps appear in the CV curves, showing the pseudocapacitive properties. Further increased OVW to 1.6 V, some distinct redox peaks arise in these CV curves, indicating the moredeep redox reactions on the surface of positive Co(OH)\(_2\) and negative VN electrode. Fig. 6b shows the galvanostatic charge–discharge curves under the different OVWs ranging from 1.0 V to 1.6 V at the current density of 1 A g\(^{-1}\). It can be clearly seen that as-fabricated hybrid supercapacitor shows a good capacitative behavior with quasi-symmetrical triangular charge-discharge curves, even at voltages up to 1.6 V. Fig. 6b inset image depicts the specific capacitance of the hybrid supercapacitor as a function of the OVW and discharging time. It is found that the specific capacitance increase from 34.4 F g\(^{-1}\) to 48.9 F g\(^{-1}\) as the OVW range increases from 1.0 V to 1.6 V, but there is no significant change in internal resistance (from IR drop, Fig. S2). It means that the stored energy and delivered power density could be improved at least by 263%, according to equation 2 and 3. The capacitance performance of VN/Co(OH)\(_2\) hybrid supercapacitor improves gradually with the elevated OVW, which is related to the continually in-depth redox reactions of electrode materials from less to more.\(^{12,22}\) The OVW range of hybrid supercapacitor is higher than that of symmetrical supercapacitor fabricated by VN (Fig. S8) or Co(OH)\(_2\)-based electrodes (less than 1.2 V, Fig. S9). When the optimal OVW of 1.6 V is selected, the overall performance of the hybrid supercapacitor could be remarkably improved in 2 M KOH aqueous electrolyte.

In order to further develop an optimal VN/Co(OH)\(_2\) hybrid supercapacitor, the charges at positive (\(q_+\)) and negative (\(q_-\)) electrodes should be balanced (\(q_+ = q_-\)). The charge stored by each electrode depends on the specific capacitance (C), the charge/discharge potential range (V) and the mass electrode (m) following Equation 4:\(^{26}\)

\[
q = C \times V \times m \quad (4)
\]

In order to obtain \(q_+ = q_-\), it is necessary to balance the mass ratio between the two electrodes. The mass balancing will be
expressed as follows:

\[ m_2/m_1 = (C_e \times V_e)/(C_p \times V_p) \]  

(5)

Based on \( C \) and \( V \) for \( \text{Co(OH)}_2 \) and VN micro-flowers, the optimal mass ratio between the negative and positive electrodes should be \( m_{\text{VN}}/m_{\text{Co(OH)}_2} = 3.6 \). Whether the mass ratio \( (m_{\text{VN}}/m_{\text{Co(OH)}_2} : 3.6) \) is a optimal choice decided by equation (5). Recently, Zheng and Wilson et al. predicted that the maximum electrochemical capacitive value was obtained at the low positive/negative mass ratio (less than the \( q \) balance value) through two types of mathematical models. In order to determine the optimal \( \text{VN}/\text{Co(OH)}_2 \) mass ratio, hybrid supercapacitors was fabricated by using different negative/positive mass ratio, 0.25, 0.5, 0.75, 1, 2, 3, 3.5, 4, and 5. Fig. S3 shows that the CV curves of hybrid supercapacitors under the different mass ratios. Interestingly, under the low \( \text{VN}/\text{Co(OH)}_2 \) mass ratios (below 2), the CV profiles of the as-fabricated supercapacitor show the quasi-rectangular shapes at the low voltage range. The quasi-rectangular shape may be related to the incomplete redox reaction of the \( \text{Co(OH)}_2 \) electrode. However, significant increment in the positive current (positive polarization) at the high voltage is noticed. This may be due to imbalanced \( q \) between \( \text{Co(OH)}_2 \) and VN electrode leads to \( \text{H}_2 \) evolution at the negative VN electrode. Nevertheless, the degree of positive polarization falls gradually as the increment of \( \text{VN}/\text{Co(OH)}_2 \) mass ratio. Less positive polarization is found at the high \( \text{VN}/\text{Co(OH)}_2 \) mass ratio. As the \( \text{VN}/\text{Co(OH)}_2 \) mass ratios of hybrid supercapacitor over 2, a pair of redox humps arise near the 0.8 V. Especially, an obvious redox peaks appears under the high \( \text{VN}/\text{Co(OH)}_2 \) mass ratio of 5, which indicates a battery-like behavior dominates in this hybrid cell.

Fig. S4 show the typical galvanostatic charge-discharge curves of hybrid supercapacitors under the different \( \text{VN}/\text{Co(OH)}_2 \) mass ratios. At the low \( \text{VN}/\text{Co(OH)}_2 \) mass ratios (below 1), a non-capacitive behavior with asymmetric charge-discharge lines is found around 1.2-1.6 V, indicating the low cumblic efficiency of hybrid supercapacitor. This behavior is probably related with the fact that hydrogen produced during the negative polarization of the VN electrode. The non-symmetric charge-discharge lines gradually disappeared with the increase of the \( \text{VN}/\text{Co(OH)}_2 \) mass ratio. When the \( \text{VN}/\text{Co(OH)}_2 \) mass ratio is set to or over 3, a symmetric charge-discharge line can be obtained. However, oversized VN mass (\( \text{VN}/\text{Co(OH)}_2 \) mass ratio over 4) in the negative electrode leads to the discharge line distort. Fig. S5 shows the specific capacitance values of hybrid capacitors at the different discharging current densities. The rate capability of hybrid supercapacitors increases at the higher \( \text{VN}/\text{Co(OH)}_2 \) mass ratio, which indicate that more VN addition is in favor of the reducing over current and improving the efficiency of charge-discharge. It is worth noting that the higher specific capacitance values of hybrid capacitors can be obtained at the lower \( \text{VN}/\text{Co(OH)}_2 \) mass ratios (0.75-3). Fig. S6 shows the cycle stabilities of the hybrid supercapacitor under the different \( \text{VN}/\text{Co(OH)}_2 \) mass ratios. A stable cycling stability (> 80% of initial capacitance after 4000 cycles) can be obtained as the \( \text{VN}/\text{Co(OH)}_2 \) mass ratio is over to 2, which suggests that a gravimetrically oversized VN negative electrode is possibly to extend the hybrid supercapacitor cycle-life by reducing the swing potential across the positive electrode.

Furthermore, we used the Wilson’ mathematical model to find the region of optimal positive/negative mass ratio which corresponded to the maximum capacitive value of hybrid supercapacitor (more details in reference 39 and supporting information). Simulation result (Fig. 6 and Fig. S7) suggests that...
the higher capacitive performance can be obtained at the lower range of VN/Co(OH)$_2$ mass ratios about 1-3, which is approaching to the our experimental results (about 0.75-3). Especially, the highest capacitive performance of hybrid supercapacitor can be obtained as the VN/Co(OH)$_2$ mass ratio is about 2. This value is less than the optimal mass ratio about 3.6 calculated from equation 5. The different is attributed to that Wilson mathematical model is not considered to the positive and negative swing voltages.

In our experimental results, the higher capacitance can be obtained at VN/Co(OH)$_2$ mass ratios about 0.75-3. The low VN percentage in total hybrid capacitance can bring about the high capacitive performance. But the corresponding hybrid supercapacitors have the limited cycling stability, so far being well below expectations. As shown in Fig. S5, the hybrid capacitor with a VN/Co(OH)$_2$ mass ratio of 0.75 possesses the highest capacitance value of 88.3 F g$^{-1}$ at 0.2 A g$^{-1}$, however, the capacitance value drops by 18% after only 1000 cycles. Under the lower VN/Co(OH)$_2$ mass ratios, the extra Faradic current from water splitting at the high OVW region (Fig. S3 and Fig. S4) can introduce the additional charges. These additional charges are included in the capacitance calculation and leads to the high but untrue capacitance values. As the VN/Co(OH)$_2$ mass ratio is 2, closer to the optimal mass ratio from simulated result, the corresponding hybrid supercapacitor shows a high capacitance value of 76.7 F g$^{-1}$ and a relatively lower cycle-life about 71% of initial capacitance. At the hybrid capacitor with the mass ratio of 3.5, closer to the value calculated from equation 5, shows the high cycle stability (86.6% of initial capacitance value), whereas the capacitance value is down to 54.6 F g$^{-1}$. Base on the stated above, the experimental and simulation results show that operating hybrid supercapacitor at the low optimal mass ratios can deliver the higher specific capacitance values but involve a trade-off in cycle-life. Under these conditions to obtain the maximum capacitance, severe redox reactions and fast voltage swing may occur in the positive Co(OH)$_2$ electrode, as well as the negative polarization from hydrogen evolution happens on the VN electrode. A gravimetrically oversized VN electrode can reduce the proportion of voltage swing across the positive electrode and eliminate the hydrogen evolution experienced at the negative electrode. This is well suited to long-term cycling, but will lead to a less-than- optimum specific capacitance value of the hybrid supercapacitor. Thus, considering the specific capacitance, OVW, and cycling stability, the optimal VN/Co(OH)$_2$ mass ratio of the hybrid supercapacitor is 3. Under the optimal mass ratio, hybrid supercapacitor has the specific capacitance of 62.4 F g$^{-1}$, a long cycling-life (86% of initial specific capacitance, Fig. S8a), and the high rate capability, which is much higher than that of symmetrical Co(OH)$_2$//Co(OH)$_2$, VN//VN, and the commercial AC//AC supercapacitor (Fig. S8-10). Importantly, the optimal hybrid supercapacitor exhibits a high energy density of 22 Wh kg$^{-1}$ at a power density of 0.16 kW kg$^{-1}$, and a high power density of 15.9 kW kg$^{-1}$ at an energy density of 9 Wh kg$^{-1}$ (Fig. 8b).

Conclusions

A novel and durable asymmetric hybrid supercapacitor based on flower-like Co(OH)$_2$ and urchin-like VN materials as the positive and negative electrodes, respectively, has been fabricated in aqueous KOH electrolyte. After optimization of OVW and VN/Co(OH)$_2$ mass ratio, the as-assembled hybrid supercapacitor can be cycled reversibly in the voltage range of 0-1.6 V, and exhibits the maximum specific capacitance of 62.4 F g$^{-1}$. In addition, it delivers an energy density of 22 Wh kg$^{-1}$ and has an excellent rate capability. Even at a power density of 15.9 kW kg$^{-1}$, it still has a specific energy of 9 Wh kg$^{-1}$. Moreover, the hybrid supercapacitor exhibits good long cycle-life along with 86% specific capacitance retained after 4000 cycles. This is the first time that Co(OH)$_2$ and VN electrode materials have been paired up to produce supercapacitors with excellent electrochemical performance. The impressive results presented here show great potential in designing new type of hybrid supercapacitor for promising applications in the high performance energy storage systems.

Acknowledgments

This work was supported by the Top Hundred Talents Program of Chinese Academy of Sciences, the National Nature Science Foundations of China (21203223) and the Youth Science Foundations of Gansu Province (1107RJYA274)

Notes and references


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A new hybrid supercapacitor with excellent electrochemical performance is fabricated by using the flower-like Co(OH)$_2$ and urchin-like VN.