Supporting information

Synthesis and characterization of M$_3$V$_2$O$_8$ (M = Ni or Co) based nanostructures: a new family of high performance pseudocapacitive materials

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Fig. S1 (a) CV curves of NiCo$_2$O$_4$ and MnCo$_2$O$_4$ at a scan rate of 10 mV s$^{-1}$, (b) Specific capacitances of NiCo$_2$O$_4$ and MnCo$_2$O$_4$ at a controlled current densities. (c) CV curves of NiMoO$_4$ and CoMoO$_4$ at a scan rate of 10 mV s$^{-1}$, (d) Specific capacitances of NiMoO$_4$ and CoMoO$_4$ at a controlled current densities. (e) CV curves of NiWO$_4$ and CoWO$_4$ at a scan rate of 10 mV s$^{-1}$, (f) Specific capacitances of NiWO$_4$ and CoWO$_4$ at a controlled current densities. 

Figure S1a and S1b show the CV curves and specific capacitances of the NiCo$_2$O$_4$ and MnCo$_2$O$_4$ electrodes. When the Ni was replaced by Co, the CV curve was significantly changed and their specific capacitances were greatly decreased. The CV curve of the NiCo$_2$O$_4$ electrode shows a pair of strong redox peaks, and the
charges associated with the anodic and cathodic peaks are almost centred on the redox peaks, while that of MnCo$_2$O$_4$ electrode is equably distributed in the whole scan potential window. This means that for AB$_2$O$_4$ type binary metal oxides, the A element plays important roles in the generation of pseudo capacitance. This can further be confirmed by the much higher specific capacitances of NiCo$_2$O$_4$ (1128, 1068, 988, 937, 888 and 833 F g$^{-1}$ at the current densities of 0.625, 1.25, 2.5, 3.75, 5, and 6.25 A g$^{-1}$, respectively.) than MnCo$_2$O$_4$ electrodes (405, 384, 344, 309, 275 and 250 F g$^{-1}$ at the current densities of 0.625, 1.25, 2.5, 3.75, 5, and 6.25 A g$^{-1}$, respectively). In order to further study the contributions of both A and B elements on pseudocapacitive properties of the ABO$_4$ type binary metal oxides, the CV curves and specific capacitances of the NiMoO$_4$, CoMoO$_4$, NiWO$_4$, and CoWO$_4$ electrodes are shown in Fig. S1c-S1f. In the case of both NiMoO$_4$ and NiWO$_4$, when the Ni was replaced by Co, the CV curves were significantly changed. The specific capacitances of CoMoO$_4$ (286, 256, 229, 212, 202 and 193 F g$^{-1}$ at the current densities of 0.625, 1.25, 2.5, 3.75, 5, and 6.25 A g$^{-1}$, respectively.) and CoWO$_4$ (273, 254, 223, 202, 192, and 190 F g$^{-1}$ at the current densities of 0.625, 1.25, 2.5, 3.75, 5, and 6.25 A g$^{-1}$, respectively.) are greatly decreased compared with NiMoO$_4$ (1136, 960, 850,778, 725, and 688 F g$^{-1}$ at the current densities of 0.625, 1.25, 2.5, 3.75, 5, and 6.25 A g$^{-1}$, respectively.) and NiWO$_4$ (882, 809, 744, 638, 575, and 546 F g$^{-1}$ at the current densities of 0.625, 1.25, 2.5, 3.75, 5, and 6.25 A g$^{-1}$, respectively.). This indicates that for ABO$_4$ binary metal oxides, the A element also plays important roles in the generation of pseudo capacitance. Besides, it can be seen that the CV curves and specific capacitances of
NiMoO$_4$ and NiWO$_4$ are close to that of CoMoO$_4$ and CoWO$_4$ electrodes, this suggest that B elements has minor influence to the capacitances of the binary metal oxides. Therefore, it is concluded that the element located in A position with lower chemical valence plays important roles in the generation of pseudocapacitance, while the B element with higher chemical valence has minor influence to the capacitances of the binary metal oxides.

Fig. S2 (a) Overall XPS, (b) V2p, (c) Ni2p, (d) Co2p, and (e) O1s XPS spectra of the Ni$_3$V$_2$O$_8$ and Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ nanocomposite with a Ni/Co molar ratio of 1:1.
The overall XPS spectrum (Fig. S2a) shows the elements of the Ni$_3$V$_2$O$_8$ and Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ nanocomposite. The V2p corresponding to the and V$^{5+}$, and the Ni2p and Co2p are revealed to be Ni$^{2+}$ and Co$^{2+}$, respectively. O1s XPS shows a strong peak around 530.8 eV which can be regarded as characteristic peak of O1s in M$_3$V$_2$O$_8$.

Figure S3 Electrochemical characterizations of the Ni$_3$V$_2$O$_8$ and Co$_3$V$_2$O$_8$ electrodes. CV curves of (a) Ni$_3$V$_2$O$_8$ and (b) Co$_3$V$_2$O$_8$ electrodes at different scan rates. Charge-discharge curves of (c) Ni$_3$V$_2$O$_8$ and (d) Co$_3$V$_2$O$_8$ electrodes at controlled current densities.

Figure S3 shows the CV curves and charge-discharge curves of both Ni$_3$V$_2$O$_8$ and Co$_3$V$_2$O$_8$ electrodes. Though the CV curves of both Ni$_3$V$_2$O$_8$ and Co$_3$V$_2$O$_8$ electrodes show visible redox peaks, indicating their pseudo capacitance, the charges associated with the anodic and cathodic peaks are different. The charges of Co$_3$V$_2$O$_8$
electrode are equably distributed in the whole scan potential window, while that of 
Ni$_3$V$_2$O$_8$ electrode are almost centred on the redox peaks. This indicates that the 
faradaic reactions of Co$_3$V$_2$O$_8$ can take place in the whole potential window and will 
provide better rate capability, but that of Ni$_3$V$_2$O$_8$ can only occur around redox peaks 
and result in a poor rate capability. The shapes of the CV curves for both of the 
electrodes are not significantly influenced by the increase of the scan rates. This 
indicates the improved mass transportation and electron conduction in the host 
materials. The specific capacitances of the Ni$_3$V$_2$O$_8$ and Co$_3$V$_2$O$_8$ electrodes, 
calculated from the discharge times, are 1181, 1043, 847, 750, 692, 625 F g$^{-1}$ and 505, 
493, 470, 450, 430, 413 F g$^{-1}$ at the discharge current densities of 0.625, 1.25, 2.5, 
3.75, 5, and 6.25 A g$^{-1}$, respectively.

![Complex-plane impedance plots](image)

Fig.S4 Complex-plane impedance plots of Ni$_3$V$_2$O$_8$, Co$_3$V$_2$O$_8$, and Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ nanocomposite electrodes. The Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ nanocomposite has lower charge transfer resistance and ion diffusion resistance than Ni$_3$V$_2$O$_8$.

The pourbaix diagram (shown in Fig. S5) for Ni, Co and V reveals that V does 
not participate in any redox reaction and has no contribution to the capacitance of
M$_3$V$_2$O$_8$ (M = Ni or Co). The capacitance of M$_3$V$_2$O$_8$ is contributed by Ni and Co elements. This is in good accordance with the other reports about hierarchical MnMoO$_4$/CoMoO$_4$ heterostructured nanowires$^1$ and amorphous NiWO$_4$ nanostructure$^2$ as electrode materials for supercapacitors.

![Pourbaix diagram of (a) Ni, (b) Co and (c) V.](image)

Fig.S5 Pourbaix diagram of (a) Ni, (b) Co and (c) V.
Fig. S6 SEM images (a) Before 1000 cycles and (b) after 1000 cycles of the Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ electrodes. The microstructure and surface morphology are perfectly retained during the charge-discharge process.

Fig. S7 (a) CV curves and (b) Charge/discharge curves of AC and Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ nanocomposite based asymmetric supercapacitor. (c) Cycling performance of asymmetric supercapacitor.

A two electrode configuration (asymmetric supercapacitor) in which
Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ nanocomposite as positive electrode and activated carbon as negative electrode is assembled to measure the capacitive performance of the Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ electrode. For comparison, an activated carbon based symmetric supercapacitor is also assembled. The energy density ($E$) and power density ($P_{av}$) of the supercapacitor is calculated by:

$$E = \frac{1}{2} C V^2$$  \hspace{1cm} (1)
$$P_{av} = \frac{E}{t}$$  \hspace{1cm} (2)

where $t$ represent the discharge times, $C$ and $V$ represent the specific capacitance and the cell voltage of the supercapacitor, respectively. In asymmetric supercapacitor, the mass balancing between positive electrode ($m_+$) and negative electrode ($m_-$) follows the Equation:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+}$$  \hspace{1cm} (3)

The specific capacitance of the activated carbon and Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ are 187 and 1278 F g$^{-1}$. On the basis of potential windows found for the activated carbon and Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ electrodes, the mass of the activated carbon and Ni$_3$V$_2$O$_8$/Co$_3$V$_2$O$_8$ electrodes are 21.8 and 8 mg, respectively. After 1000 cycles, 95.2 % of the initial specific capacitance is remained.

References