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# High performance solid state asymmetric supercapacitor device based upon NiCo<sub>2</sub>O<sub>4</sub> nanosheets//MnO<sub>2</sub> microspheres

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High performance solid state asymmetric supercapacitor (SSASCs) device is successfully fabricated by combining the NiCo<sub>2</sub>O<sub>4</sub> as the positive and MnO<sub>2</sub> as the negative electrode materials. Herein, we also report the facile strategy to synthesize the mesoporous layered NiCo<sub>2</sub>O<sub>4</sub> nanosheets and 3D hierarchical MnO<sub>2</sub> microspheres by simple microwave heating method. Both materials exhibit excellent electrochemical performance due to their unique morphological features along with nanocrystallite size, high specific surface area, narrow pore size distribution and large pore volume. The SSASCs device operates within the potential window of 1.5 V and exhibits high volumetric capacity and energy density of 0.954 mAh cm<sup>-3</sup> (2.3 F cm<sup>-3</sup>) and 0.715 mWh cm<sup>-3</sup> at 1 mA cm<sup>-2</sup> respectively. The device also demonstrates excellent cyclic stability with capacity retention of 83 % by the end of 10000 cycles at the current density of 2 mA cm<sup>-2</sup>. This work constitutes the first demonstration of using 3D hierarchical MnO<sub>2</sub> microspheres as high energy negative electrode for SSASCs device. SSASCs device with high volumetric capacity and energy density has significant potential applications in portable electronics and electrical vehicles.

#### Introduction

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Recently, research has focused extensively on the development of light weight, flexible and environmental benign solid state energy storage devices for portable electronics, roll up displays and miniature medical applications.<sup>1-2</sup> Supercapacitors are the class of energy storage devices which deliver high power density with sustainable energy density and are being considered as the most promising solution for various emerging energy applications.<sup>1-3</sup> The main objective is to fabricate such solid state devices which must be capable to deliver high power, high energy, higher rate capability and a long cycle life.<sup>4</sup> It is also important to fabricate these devices into more smaller scale for their futuristic implementation in flexible and portable microscale electronics appliances.<sup>5</sup> Supercapacitors are basically divided into electrical double layer capacitors (EDLCs) and redox capacitors or pseudocapacitors based upon their charge storage mechanism.<sup>6-10</sup> EDLCs based on the carbonaceous materials deliver high power density but limited energy density upto 3-4 Wh kg<sup>-1</sup> which hinders its practical device application.<sup>11</sup> Energy density of supercapacitor is basically governed by equation  $(E = 0.5CU^2)$ , so it can be enhanced either by utilizing pseudocapacitive or battery-type faradaic electrode materials which have higher specific capacitances or

capacities than carbonaceous material.<sup>11</sup> Secondly, the enhancement in operating voltage window also increases tremendously the energy density of supercapacitor. The voltage window of aqueous electrolyte based hybrid supercapacitor can be enhanced up to 2.0 V by utilizing the pseudocapacitive or battery-type faradaic material as the cathode and carbonaceous material as an anode.<sup>12</sup> It is also important to differentiate between pure pseudocapacitive and battery-type faradaic materials. In case of pseudocapacitive materials, reversible faradaic reactions occur at or near the surface of an electrode and are fast enough that cyclic voltammgram (CV) curves are analogues to that of capacitive carbon electrode material.<sup>13-14</sup> Whereas for battery-type materials, CV curves are characterized by strong faradaic redox peaks and these peaks are often accompanied with large voltage separation (greater than 0.1 to 0.2 V) as a result of phase transitions.<sup>13, 15</sup>

Further kinetic information obtained from CV curves can also be used to determine the charge storage behavior of electrode material. <sup>15</sup> In CV curves, the relationship  $(I = a \gamma^b)$  between the peak current intensity (I) and scan rate ( $\gamma$ ) signifies the charge storage phenomena, for pseudocapacitive materials b  $\approx$ 1, whereas b  $\approx$  0.5 for faradaic redox material.<sup>15</sup> So it is also very important to define the true metrics to characterize the electrochemical performance of electrode materials. The concept of capacitance (F) cannot be applied to battery-type electrode materials, in such case the true metric "capacity" (Coulomb C or mAh) is most appropriate parameter to report their electrochemical performance.<sup>13</sup> So electrochemical performance of battery-type faradaic materials are characterized by areal capacity (mAh cm<sup>-2</sup>), discharge capacity

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(mAh g<sup>-1</sup>), volumetric capacity (mAh cm<sup>-3</sup>), volumetric energy density (mWh cm<sup>-3</sup>) and volumetric power density (W cm<sup>-3</sup>).

It is also worthwhile to note that in most of the asymmetric supercapacitor (ASCs) devices, carbonaceous material such as active carbon, carbon nanotube and graphene are being utilized as the anode material.<sup>16-18</sup> Although these carbonaceous materials offer much higher specific surface area but their specific capacitances are much smaller than the battery-type faradaic materials.<sup>19</sup> So it is also one of the most important key research area to develop high performance negative electrode material for SSASCs devices. The main objective is to fabricate SSASCs devices with high volumetric energy density for portable and miniaturized electronics applications. SSASCs devices also have few advantages in comparison with the conventional ASCs devices such as light weight, higher degree of flexibility, operationally safer, wider operating temperature range, and higher cyclic stability.<sup>2, 20</sup> Secondly the robust encapsulation is also not required for the fabrication of SSASCs devices.<sup>2</sup>

Recently few papers have been published on the development of negative electrode material for SSASCs devices such as  $Fe_2O_3$ ,<sup>21</sup> VN,<sup>22</sup> Mn<sub>3</sub>O<sub>4</sub>,<sup>23</sup> hydrogenated TiO<sub>2</sub>@C,<sup>24</sup> CoSe<sub>2</sub>,<sup>25</sup> and Co<sub>3</sub>O<sub>4</sub>@RuO<sub>2</sub>.<sup>26</sup> The volumetric energy density reported for Co<sub>9</sub>S<sub>8</sub> nanorods//Co<sub>3</sub>O<sub>4</sub>@RuO<sub>2</sub> nanosheet based solid state device is superior than the mostly reported SSASCs devices.<sup>26</sup> But the potential of such device cannot be realized for large scale application due to very high cost, rareness and toxic nature of Ru element.<sup>27</sup> However the low volumetric energy density is still the area of great concern for most of the reported SSASCs devices.<sup>21-25, 28</sup> So it is still a challenge to look for novel combination of cost effective cathode and anode materials to achieve the enhanced volumetric energy density of SSASCs device.

In the present work we synthesize unique nanostructures of 3D hierarchical MnO<sub>2</sub> microspheres (3DHM-MnO<sub>2</sub>) and mesoporous layered NiCo<sub>2</sub>O<sub>4</sub> nanosheets (MLNS-NiCo<sub>2</sub>O<sub>4</sub>) using microwave assisted method. This technique has already been utilized to synthesize various porous inorganic nanostructures due to its reduced synthesis time and environmental friendly aspect.<sup>29-34</sup> MnO<sub>2</sub> microspheres are composed of ultrathin nanosheets (2.0 nm) and are endowed with high specific surface area (184.3  $m^2 g^{-1}$ ), large pore volume (0.416  $\mbox{cm}^3\mbox{ g}^{\mbox{-1}}\mbox{)}$  and an average pore diameter (5.158 nm). As-synthesized 3DHM-MnO<sub>2</sub> demonstrates the well defined faradaic redox peaks in the potential window of 0.2 to -0.8 V in three electrode configuration. It is an indicative of its strong potential to be used as the negative electrode material for the asymmetric supercapacitor device. 3DHM-MnO<sub>2</sub> demonstrates an areal capacity of 276.7  $\mu$ Ah cm<sup>-2</sup> (101.7 mAh  $g^{-1}$ ) at 5 mV  $s^{-1}$ . The attained capacity value is much higher than to most of the reported anode materials of asymmetric devices.<sup>21-26</sup> The few major advantages are also associated with the use of  $MnO_2$  as electrode material such as its natural abundance, low cost, environmental benign and non toxicity.<sup>3,</sup>

Although the various transition metal oxides ( $MnO_2$ ,  $Co_3O_4$ , NiO, NiCo<sub>2</sub>O<sub>4</sub>, etc) have been reported as the positive

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electrode material.<sup>11, 36-38</sup> Among them, nickel, cobaltite (NiCo<sub>2</sub>O<sub>4</sub>) has been considered as more: electrochemically favorable due to its higher electrical conductivity in comparison with the monometallic oxides of Ni or Co.<sup>39</sup> The variety of morphologies of NiCo<sub>2</sub>O<sub>4</sub> such as microspheres,<sup>11</sup> nanosheets,<sup>39</sup> nanowires,<sup>40</sup> and nanorods,<sup>41</sup> have been reported so far. In the present work we report the synthesize of novel mesoporous layered nanosheets structure of NiCo2O4 (MLNS-NiCo2O4) by using microwave heating method followed by the calcination of as-prepared precursor. This kind of mesoporous layered nanosheets structure for NiCo<sub>2</sub>O<sub>4</sub> is never reported before by any method. As-synthesized MLNS-NiCo<sub>2</sub>O<sub>4</sub> possess high specific surface area (100.03 m<sup>2</sup> g<sup>-1</sup>), large pore volume (0.2489 cm<sup>3</sup> g<sup>-1</sup>) and an average pore diameter (8.28) nm). MLNS-NiCo<sub>2</sub>O<sub>4</sub> exhibits very high areal capacity of 344.7  $\mu$ Ah cm<sup>-2</sup> (221.0 mAh g<sup>-1</sup>) at 5 mV s<sup>-1</sup>. The obtained capacity value is higher than many previously reported positive electrode materials.<sup>22-24, 26, 35, 38</sup> The layered nanosheets structure is considered to be more electrochemically favorable due to their enhanced structural tolerance during electrolyte insertion-deinsertion process.<sup>42-43</sup> This kind of structure also provides the maximum utilization of electroactive material despite being high mass loading by providing the tremendous ease for electrolyte ions to penetrate inside the electroactive material. Consequently such nanostructures are also capable to deliver outstanding discharge capacity retention even at higher scan rate.

In this work the novel SSASCs device based on MLNS-NiCo<sub>2</sub>O<sub>4</sub> as cathode and 3DHM-MnO<sub>2</sub> as an anode material is successfully fabricated. Further we have made use of the gel like electrolyte (PVA-KOH) to obtain all solid component supercapacitor with compact design. SSASCs device exhibits high volumetric capacity and energy density of 0.954 mAh cm<sup>-3</sup> & 0.715 mW h cm<sup>-3</sup> at 1 mA cm<sup>-2</sup> respectively which are much higher than most of the reported asymmetric devices.<sup>21-25, 28, 44</sup> The superior device performance along with its simple fabrication strategy also holds its great promise for futuristic energy storage devices.

#### Experimental

#### Synthesis of 3D hierarchical MnO<sub>2</sub> microspheres

All the reagents used in the experiments were of analytical grade and used as received without further purification. In a typical synthesis 6 mmole of manganese chloride tetrahydrate (MnCl<sub>2</sub>.4H<sub>2</sub>O) and 4 mmole of potassium permanganate (KMnO<sub>4</sub>) were dissolved in 100 ml of de-ionized water with constant magnetic stirring. After vigorous stirring of 60 minutes at room temperature, the resulting homogenous solution was transferred to 500 ml, 3 necked flask. The 3 necked flask was then transferred to microwave heating oven (MAS II, SINEO) equipped with water cooled condenser. The solution was then heated at 100°C in a microwave oven under medium high mode power of 700 watt for 10 minutes. After reaction, the solution was allowed to cool down naturally and standing for 24 hrs. The solution was centrifuged several times at 12000 rpm for 4 minutes using de-ionized water and

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absolute ethanol to collect the precipitates. The precipitates were then dried at 90°C in air environment overnight.

#### Synthesis of mesoporous layered NiCo2O4 nanosheets

In a typical synthesis, 5 mmol of nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O), 10 mmol of cobalt nitrate hexahydrate  $(Co(NO_3)_2.6H_2O)$  and 120 mmole of carbamide  $(CO(NH_2)_2)$ were dissolved into a 100 ml of de-ionized water with constant magnetic stirring at room temperature to form a homogeneous solution. After 15 minutes, 3 ml of triethanolamine ( $C_6H_{15}NO_3$ ) was added to the above solution under constant magnetic stirring. After vigorous stirring for further 60 minutes, the solution was poured into 500 ml, 3 necked flask. The 3 necked flask was then transferred to microwave heating oven (MAS II, SINEO) equipped with water cooled condenser. The solution was then heated at 100°C in a microwave oven under medium high mode power of 500 watt for 15 minutes. The solution was allowed to cool down naturally and let the precipitates to be settled for 24 hrs. The precipitates were washed several times at 12000 rpm for 4 minutes with de-ionized water & absolute ethanol and then dried at 90°C in air environment overnight. Finally the calcination of as-prepared precursor was carried out at 300° C for 210 minutes in air environment, to transform it into mesoporous layered NiCo<sub>2</sub>O<sub>4</sub> nanosheets.

#### Characterization

The phase analysis of as-synthesized MLNS-NiCo<sub>2</sub>O<sub>4</sub> and 3DHM-MnO<sub>2</sub> were investigated by X-ray diffraction (XRD; X'Pert Philips Pro MPD). using Cu- $K_{\alpha}$  radiation source ( $\lambda = 0.15148$  nm) with 20 ranging from 10° to 80° at a scanning speed of 0.02°s<sup>-1</sup>. Field emission microscopy (FESEM, Hitachi electron S-4800) scanning was used to obtain the surface morphologies of uncalcined and calcined samples. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) investigations were carried out on (HRTEM, JEOL-JEM-2100F) to harness in more detail the morphological and structural features of as-synthesized products. N2 adsorption-desorption isotherms were performed on a COULTER SA 3100 apparatus at 77 K. The specific surface area was calculated through Brunauer-Emmett-Teller (BET) method whereas pore volumes and pore size distributions were derived from the desorption branches of isotherms employing the Barrett- Joyner- Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) was performed on (XPS, PHI Quanteral II, Japan, with an Al  $K_{\alpha}$ excitation source) to determine the valence states of assynthesized samples.

#### Fabrication & electrochemical characterization of solid state asymmetric supercapacitor device

Ni foam is being used as the current collector for fabrication of SSASCs devices. Prior to use, Ni foam was thoroughly cleaned using ultrasonication by acetone and 1M HCl solution for 30 minutes each. Finally the Ni foam was washed thoroughly using deionized water, absolute ethanol and then dried at

100°C for 24 hrs. For cathode or anode preparation active materials (80 wt %), acetylene black (04 10wt 3%) C6RA15 and polytetrafluoroethylene (PTFE) (6 wt %) are homogeneously mixed in ethanol, and then the mixture is deposited on Ni foam (1 cm<sup>2</sup>). All prepared electrodes are dried at 80°C for 24 hrs, then pressed under 10 MPa pressure for 30 seconds and finally dried at 80°C for 10 hrs. The electrochemical performance of both materials were initially investigated using standard three electrode cell configuration. The mass balance between cathode and anode materials was calculated on the basis of their capacitances values attained in three electrode cell configuration. SSASCs device was fabricated by assembling MLNS-NiCo2O4/Ni foam as the positive electrode and 3DHM-MnO<sub>2</sub>/Ni foam as the negative electrode face to face with polypropylene membrane (TF 45 NKK) as separator with PVA-KOH as electrolyte. PVA-KOH gel electrolyte was prepared as follows: PVA(6 g) was dissolved in 60 ml of DI water under vigorous stirring and heated at 85°C for 3 hrs. KOH (6 g) was dissolved in 20 ml DI water with constant magnetic stirring at room temperature for 30 minutes. Finally the above two solutions were mixed together under vigorous stirring with constant heating maintained at 85°C until the formation of homogeneous solution. The prepared electrodes (exposed surface area ; 1 cm<sup>2</sup>) and separators were immersed in the above prepared PVA-KOH electrolyte for 10 minutes. After that electrodes and separators were taken out and allowed to solidify at room temperature for 60 minutes. Finally the SSASCs device was assembled and its electrochemical testing was carried out after 12 hrs of its fabrication. Cyclic voltammetry (CV), and electrochemical impedance spectra (EIS) measurements were conducted by employing a CHI660D electrochemical workstation (Chenhua, Shanghai). It was measured over a frequency range from 100 KHz to 0.01 Hz at open circuit potential with AC perturbation of 5 mV. Chronopotentiomerty (CP) measurements were carried out on a LAND CT-2001A battery tester setup (Wuhan, China). The areal capacity & discharge capacity were calculated on the basis of CV and CP curves using equations (1&2) and (3&4) respectively.<sup>23, 38</sup> It is also very important to mention that the we reported the modified formulas in equations (1-4) in order to calculate areal and discharge capacities instead of areal and specific capacitances.<sup>23, 38</sup>

$$C_{a} = \frac{S}{2 \times 3.6 \times \gamma \times A} \text{ (mAh cm}^{-2}\text{)}$$
(1)

$$C_{s} = \frac{S}{2 \times 3.6 \times \gamma \times m} \text{ (mAh g}^{-1}\text{)}$$
(2)

where S , Y(V s<sup>-1</sup>), A (cm<sup>2</sup>) and m(g<sup>-1</sup>) are the area under the curve of CV loop, scan rate, area of electrode and mass of active material in the working electrode respectively.

$$C_{a} = \frac{I \times \Delta T_{d}}{3.6 \times A} \text{ (mAh cm}^{-2}\text{)}$$
(3)

$$C_{\rm V} = \frac{I \times \Delta T_{\rm d}}{3.6 \times V} \,\,(\text{mAh cm}^{-3}) \tag{4}$$

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where I(A),  $\Delta T_d(s) A(cm^2)$ , and V(cm<sup>3</sup>) are the constant discharge current, discharge time, area of electrode, and volume of whole device respectively. The volumetric capacity was calculated taking into account the volume of the device stack ( area and thickness of our SSASCs device are 1 cm<sup>2</sup> & 0.06 cm; 0.06 cm<sup>3</sup>) which includes the active material, substrate and the separator with electrolyte. Volumetric energy and power densities were calculated from the CP curves using equations (5) and (6) respectively.<sup>22, 26</sup>

$$E = \frac{C_V \times U^2}{2} \text{ (mW h cm}^{-3}\text{)}$$
 (5)

$$P = \frac{U^2}{4 \times V \times R_{ir}} (W \text{ cm}^{-3})$$
 (6)

Where 
$$R_{ir} = \frac{\Delta U_{ir}}{2 \times I}$$
 ( $\Omega$ )

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where  $R_{ir}$  is the internal resistance of device which is determined from the voltage drop at the beginning of discharge cycle, while the  $\Delta U_{ir}$  represents the voltage drop during discharge cycle which corresponds to IR drop, I(mA) is the constant discharge current and V(cm<sup>3</sup>) is volume of whole device.

#### **Results and discussion**

#### Structural and morphological characterizations

X-ray diffraction (XRD) patterns of as-synthesized 3DHM-MnO<sub>2</sub> and MLNS-NiCo<sub>2</sub>O<sub>4</sub> are demonstrated in Fig. 1a and b respectively. The diffraction peaks (Fig. 1a and b) are considerably broadened due to nanocrystalline nature of as-synthesized materials. All observed peaks (Fig. 1a) are well indexed as (211), (301), (600) and (002), which corresponds to crystal planes for tetragonal phase of pure MnO<sub>2</sub> (JCPDS 44-0141).<sup>42</sup> This kind of crystallographic structure of MnO<sub>2</sub> is extremely feasible for the intercalation/deintercalation of protons or cations during charging-discharging process.<sup>3, 42</sup> It is due to highly desirable tunnel size (4.6 Å) offered by this kind of crystallographic structure of MnO<sub>2</sub> which favors for insertion/extraction to alkali cations.<sup>42</sup> As-prepared precursor of cathode material is initially characterized by XRD (Fig. S1(ESI<sup>+</sup>)) which indicates the presence of both Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub> according to JCPDS card No. 01-0147 and JCPDS card No. 02-0925 respectively. XRD pattern (Fig. 1b) of calcinated sample at 300°C for 210 minutes indicates the complete transformation of as-prepared precursor to pure NiCo $_2O_4$  according to JCPDS card # 20-0781. All observed peaks (Fig. 1b) are assigned to (111), (220), (311), (400), (422), (511), (440) and (533) which corresponds to typical diffraction planes of cubic spinel NiCo<sub>2</sub>O<sub>4</sub> (JCPDS 20-0781). It also indicates 300°C is the appropriate temperature to convert asprepared precursor to pure nanocrystalline NiCo<sub>2</sub>O<sub>4</sub> phase. The nanocrystalline NiCo2O4 is highly favorable for supercapacitor application due to its higher electrochemical activity and structural stability in alkaline media.<sup>45</sup> No peaks corresponding to any unidentified phases are detected (Fig. 1a and b), indicating the high purity of as-synthesized



Figure 1. XRD patterns of (a) 3D hierarchical  $\mathsf{MnO}_2$  microspheres and (b) mesoporous layered  $\mathsf{NiCo}_2\mathsf{O}_4$  nanosheets.

materials. The average crystallite size of the as-synthesized 3DHM- $MnO_2$  and MLNS-NiCo<sub>2</sub>O<sub>4</sub> are measured to be 8.8 nm and 7.32 nm respectively according to Scherrer's formula (equation (7)). (Table S1 and S2(ESI<sup>+</sup>)) also depict the crystallite sizes of as-synthesized materials along different orientations. The nanocrystalline nature of both electrode materials along with electrochemically favorable crystallographic structure will endow excellent electrochemical properties.<sup>42, 45</sup>

$$D = \frac{K\lambda}{\beta Cos(\theta)}$$
(7)

where D is the crystallite size in Angstroms,  $\beta$  is the half-maximum line width, K = 0.9,  $\Theta$  is the Bragg's angle and  $\lambda$  is the wavelength of X-rays.

The chemical composition and valence states of the asprepared 3DHM-MnO<sub>2</sub> & MLNS-NiCo<sub>2</sub>O<sub>4</sub> are further examined by XPS and the results are shown in Fig. 2 and 3 respectively. Fig. 2a, illustrates typical XPS survey spectrum from the asprepared 3DHM-MnO<sub>2</sub>, which confirms the existence of only O, Mn and C (as reference). The high resolution XPS spectra (Fig. 2b and c) further indicates all the possible valence states of Mn 2p, and O 1s. The observed peaks (Fig. 2b) at 641.95 eV (Mn  $2p_{3/2}$ ) and 653.55 eV (Mn  $2p_{1/2}$ ), with spin energy separation of 11.6 eV further confirms the existence of MnO<sub>2</sub>.<sup>35</sup> The O 1s spectrum (Fig. 2c) include a strong peak at 529.55 eV and a relatively weak peak at 531.05 eV, which corresponds to existence of oxygen in the lattice of [MnO<sub>6</sub>] octahedral, and in the interlayer H<sub>2</sub>O respectively.<sup>46</sup> The survey spectrum (Fig. 3a) shows the high purity of as-synthesized MLNS-NiCo<sub>2</sub>O<sub>4</sub> with the presence of only O, Ni, Co and C (as reference). The high resolution XPS spectra (Fig. 3b-d ) of Ni 2p, Co 2p and O 1s indicate the electrochemically favorable valence states in the as-synthesized material. By using a Gaussian fitting method, Ni 2p spectrum (Fig. 3b) is best fitted considering two spin orbit doublets, characteristic of Ni<sup>2+</sup> and Ni<sup>3+</sup> and two shakeup satellites (indicated as 'Sat.'). Similarly the Co 2p spectrum (Fig. 3c) is best fitted considering two spin orbit doublets, characteristic of Co<sup>2+</sup> and Co<sup>3+</sup> and two shakeup satellites. In the Ni 2p spectrum (Fig. 3b), the fitting peaks at (853.52 eV, 870.45 eV) and (855.5 eV, 873.0 eV) are ascribed to valence states corresponding to Ni<sup>2+</sup>and Ni<sup>3+</sup> respectively.<sup>39</sup>

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Figure 2. XPS spectra of as-synthesized 3D hierarchical  $MnO_2$  microspheres (a) survey spectrum; (b) Mn 2p and (c) O



Figure 3. XPS spectra of as-synthesized mesoporous layered  $\rm NiCo_2O_4$  nanosheets (a) survey spectrum; (b) Ni 2p; (c) Co 2p and (d) O 1s

Whereas the fitting peaks at (860.3 eV, 878.3 eV) are assigned as shakeup satellites (indicated as 'Sat.') at the high binding energy side of Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$  respectively.<sup>39</sup> In the Co 2p spectrum (Fig. 3c), the fitting peaks at (778.47 eV, 793.65 eV) and (780.25 eV, 797.15 eV) are assigned to valence states corresponding to Co<sup>3+</sup> and Co<sup>2+</sup> respectively.<sup>39</sup> Similarly the fitting peaks at (787.85 eV, 802.15 eV) are assigned as shakeup satellites (Sat.) at the high binding energy side of Co  $2p_{3/2}$  and Co  $2p_{1/2}$  respectively.<sup>39</sup> The fitting peaks of O 1s spectrum (Fig. 3d) at 529.15 eV, 530.0 eV, 530.74 eV and 532.0 eV are attributed to a typical metal–oxygen bond, oxygen in hydroxyl group, high number of defect sites with a low oxygen



Figure 4. N2 adsorption-desorption isotherms and corresponding pore size distribution of (a & b) 3D hierarchical  $MnO_2$  microspheres and (c & d) mesoporous layered  $NiCo_2O_4$  nanosheets calculated by Barrette-Joynere-Halenda (BJH) method from desorption branch.

coordination in the material with small particle size and a multiplicity of physically and chemically bonded water on and within the surface respectively.<sup>39</sup> XPS spectra also indicate that the as-obtained products are well equipped with all possible oxidation states with no evident detectable impurities in the sample.

The N<sub>2</sub> adsorption-desorption isotherm are performed in order to determine the porosity of the as-synthesized 3DHM-MnO<sub>2</sub> (Fig. 4a and b) and MLNS-NiCo<sub>2</sub>O<sub>4</sub> (Fig. 4c and d). The typical Langmuir type IV isotherms (Fig. 4a and c) are observed for both materials with obvious hysteresis loop in the relative pressure range of (0.45-1.0) and (0.55-1.0) respectively, which are the characteristics of mesoporous materials.<sup>11</sup> The specific surface area of 3DHM-MnO<sub>2</sub> is found to be 184.325 m<sup>2</sup> g<sup>-1</sup> as determined by BET method (Fig. 4a). Its pore size distribution and pore volume are calculated using BJH method from desorption part of the isotherm (Fig. 4b). It indicates that assynthesized material consists of a narrow distribution of mesopores mainly centers at 4.04 nm with average pore diameter (5.158 nm) and large pore volume (0.416 cm<sup>3</sup> g<sup>-1</sup>). Specific surface area and pore volume of 3DHM-MnO<sub>2</sub> are also higher than most of the previous reports (Table S3(ESI<sup>+</sup>)). Similarly MLNS-NiCo<sub>2</sub>O<sub>4</sub> possess high BET specific surface area  $(100.15 \text{ m}^2 \text{ g}^{-1})$ , large pore volume  $(0.2489 \text{ cm}^3 \text{ g}^{-1})$  and narrow pore size distribution mainly centres at 3.77 nm with average pore diameter (8.280 nm) (Fig. 4c and d). Actually such mesoporous microstructures are considered as highly favorable for electrochemical application by providing the enhanced electrode-electrolyte interfacial contact area and by facilitating the high speed ion transfer within the mesopores.

FESEM, TEM, HRTEM and SAED investigations are carried out to understand the detailed morphological and structural features of 3DHM-MnO<sub>2</sub> (Fig. 5) & MLNS-NiCo<sub>2</sub>O<sub>4</sub> (Fig. 6). FESEM images (Fig. 5a and b) indicate that as-prepared MnO<sub>2</sub> has uniform microsphere structure with each microsphere is composed of numerous ultrathin nanosheets which creates

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Figure 5. FESEM (a & b); TEM(c-f); HRTEM (g) and SAED (h) images of 3D hierarchical  $MnO_2$  microspheres

porous nanostructure with adequate empty spaces between them. TEM images (Fig. 5c and d) further reveals that the numerous ultrathin nanosheets reach far from interior are interconnected each other to form each microsphere which is in accordance with the SEM findings. The edges of microspheres also indicate the loose packed structure with abundant open spaces between them (Fig. 5d). TEM image (Fig. 5e) further reveals that the surface of nanosheets consist of folding silk like morphology with transparent features. It also indicates that the lateral size of nanosheets is much larger than its thickness. The thickness of nanosheets as indicated by TEM measurements is around 2.0 nm (Fig. 5f). As a result of ultrathin nature of nanosheets the bending and curling are also clearly visible (Fig. 5e). The numerous pin holes are clearly visible on the surface of nanosheets which further confirms the mesoporous nature of synthesized material as already evidenced by BET measurements (Fig. 5f). These mesopores mainly originate from the aggregation of small nanoparticles while the large mesopores correspond to void space between the sheets. HRTEM image (Fig. 5g) taken from individual MnO<sub>2</sub> nanosheets reveals a lattice spacing of 0.244 nm, corresponding to the distance of two neighbouring (211) crystal plane in MnO2. Selected area electron diffraction (SAED) pattern (Fig. 5h) shows broad and diffused polycrystalline rings indexed as (211), (301) and (600). The broad and diffused rings are also an indicative of



Figure 6. FESEM (a & b) images of as-prepared precursor. FESEM (c & d); TEM (e & f); HRTEM (g) and SAED (h) images of mesoporous layered NiCo<sub>2</sub>O<sub>4</sub> nanosheets.

nanocrystalline structure which is well coordinated with the XRD findings. The high specific surface area as evidence from the BET measurement is due to ultrathin nanosheets building blocks of  $3DHM-MnO_2$  as evidence from FESEM and TEM findings. So  $3DHM-MnO_2$  will endow tremendous electrochemical performance owing to its ultrathin nanosheets building blocks, very high specific surface area, narrow pore size distribution and large pore volume.

As-prepared precursor of cathode material (Fig. 6a) shows long chains of layered morphology with well defined nanosheets structure along with uniform size distribution. High magnification SEM image (Fig. 6b) further reveals the abundant open spaces between the layered nanosheets structure. FESEM image (Fig. 6c) shows that morphological features of assynthesized NiCo<sub>2</sub>O<sub>4</sub> are well preserved after calcination at 300 °C. In fact after calcination the abundant space between the ultrathin nanosheets is enhanced which will provide more electroactive sites for penetration of electrolyte (Fig. 6d). The long chains of layered nanosheets structure are also clearly evident even in low magnification TEM image (Fig. 6e). TEM image (Fig. 6f) further indicates the long chain of layered nanosheets are also equipped with mesoporous porosity. The high magnification TEM image (Fig. 6f) shows that the thickness of nanosheets is much smaller than its lateral length

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and numerous interparticle mesopores are visible on the surface of nanosheets. These mesoporous are formed as a result of annealing during thermal decomposition of hydroxides. The gaseous species produced during the calcination process and recrystallization at low temperature are also the main contributing factors in the development of mesopores on the surface of nanosheets. The well resolved lattice fringes spacing are measured to be 0.28 nm and 0.244 nm as indicated by HRTEM image (Fig. 6g) which are well consistent with the crystallographic orientations of cubic NiCo<sub>2</sub>O<sub>4</sub> (JCPDS# 20-781). SAED pattern (Fig. 6h) further demonstrates the polycrystalline nature of the mesoporous layered nanosheets and can be readily indexed to (111), (220), (311), (400), (511), and (440) crystal planes of the pure NiCo<sub>2</sub>O<sub>4</sub> phase, which correlates well with the XRD findings. This kind of long chains of layered nanosheets with mesoporous porosity are highly beneficial for electrolyte to penetrate deepen inside the electroactive material despite being high mass loading. This kind of structure will deliver higher specific capacitance and its retention even at higher rates owing to its special morphological features.

#### **Electrochemical analysis**

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The electrochemical capacitive behavior of 3DHM-MnO<sub>2</sub> and MLNS-NiCo<sub>2</sub>O<sub>4</sub> are first measured in standard three electrode cell configuration by using cyclic voltammetry (CV) method. A standard three electrode cell consists of Pt foil as the counter electrode, Hg/HgCl (Saturated KCl solution) as the reference electrode and  $NiCo_2O_4/Ni$  or  $MnO_2/Ni$  foam as the working electrode in 2.0 M KOH electrolyte. CV curves (Fig. 7a) of 3DHM-MnO<sub>2</sub> are measured at various scan rates ranging from 5-100 mV s<sup>-1</sup> in the potential window of -0.8 to 0.25 V. CV curves (Fig. 7a) demonstrate the well defined typical faradaic redox behavior of anode material. It also indicate that the peak current intensity increases with the increasing scan rate which is also an indicative of high rate capability. It can be observed that redox couple is situated at -0.428 V/-0.153 V (vs saturated calomel electrode SCE) at 5 mV s<sup>-1</sup> (Fig. S2(ESI<sup>+</sup>)) which is almost consistent with the previous reports such as -0.4 V/-0.06 V at 5 mV s  $^{\text{-1}}$  and -0.35V/-0.01V at 10 mV s  $^{\text{-1}}$  .  $^{47\text{-}48}$ The slight difference in observed redox peak potential is mainly due to different morphology of nanostructure material.49 The most importantly the presence of oxidation and reduction peaks in the potential window of -0.8 to 0.25 V further signifies the potentialities of as-synthesized 3DHM- $MnO_2$  that can be used as an anode of asymmetric supercapacitor. The possible faradaic redox reaction (equation (8)) involves the surface adsorption of electrolyte cations ( $C^+$  =  $H^{+}$ ,  $Li^{+}$ ,  $Na^{+}$  and  $K^{+}$ ) on the manganese oxide.<sup>46</sup> The redox reaction is basically governed by the reversible transformation of III and IV oxidation states of Mn.<sup>46</sup>

$$MnO_2 + C^+ + e^- \longleftrightarrow MnOOC$$
(8)

The areal and discharge capacities of 3DH-MnO<sub>2</sub> are calculated from CV curves (Fig. 7a) by using equations (1) and (2) respectively. 3DH-MnO<sub>2</sub> exhibits areal and discharge capacities of 276.7  $\mu$ Ah cm<sup>-2</sup> and 101.7 mAh g<sup>-1</sup> (MnO<sub>2</sub> loading ~ 2.72 mg cm<sup>-2</sup>) respectively at scan rate of 5 mV s<sup>-1</sup> (Fig. 7b).



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Figure 7. (a) CV curves and (b) areal & discharge capacities of  $3DHM-MnO_2$  at various scan rates. (c) CV curves and (d) areal & discharge capacities of MLNS-NiCo2O4 at various scan rates

The detailed values at various scan rates (5-100 mV s<sup>-1</sup>) are also provided in Table S4(ESI<sup>+</sup>). It is not possible to compare directly the achieved areal and discharge capacities with most of the reported data of anode materials. Because most of the literature data are reported the areal and specific capacitances of the electrode materials. So in order to compare with the reported data, we have converted areal capacity (276.7  $\mu$ Ah cm<sup>-2</sup>) and discharge capacity (101.7 mAh g<sup>-1</sup>) in to areal capacitance (949 mF cm<sup>-2</sup>) and specific capacitance (348.89 F  $g^{-1}$ ) at 5 mV  $s^{-1}$ . The areal and specific capacitances are much higher than or comparable to most of the reported anode materials of asymmetric devices such as N- $Fe_2O_3$  nanorods (277.3 mF cm<sup>-2</sup> & 64.5 F g<sup>-1</sup> at 10 mV s<sup>-1</sup>),<sup>21</sup> VN (298.5 F  $g^{-1}$  at 10 mV  $s^{-1}$ ),<sup>22</sup> Mn<sub>3</sub>O<sub>4</sub> (432 mF cm<sup>-2</sup> & 432 F  $g^{-1}$ at 5 mV s<sup>-1</sup>), <sup>23</sup> H-TiO<sub>2</sub> @C (253.4 F g<sup>-1</sup> at 10 mV s<sup>-1</sup>), <sup>24</sup> CoSe<sub>2</sub>  $(332 \text{ mF cm}^{-2} \text{ at } 1 \text{ mA cm}^{-2})$ ,<sup>25</sup> Co<sub>3</sub>O<sub>4</sub>@RuO<sub>2</sub> nanosheet (750 mF  $cm^{-2}$  & 375 F  $g^{-1}$  at 5 mV  $s^{-1}$ ,<sup>26</sup> carbon nanotube (30-150 F  $g^{-1}$  $^{1}$ ),  $^{50}$  graphene (50-250 F g<sup>-1</sup>),  $^{51}$  and active carbon (30-250 F g<sup>-1</sup>) <sup>1</sup>).<sup>52</sup>

As-synthesized 3DHM-MnO<sub>2</sub> demonstrates good rate capability with capacity retention of 37 % at 100 mV s<sup>-1</sup> (Fig. 7b) which is comparable to most of the reported negative electrode of asymmetric devices such as N-Fe<sub>2</sub>O<sub>3</sub> nanorods (35.3 % at 400 mV s  $^{-1}$  ),  $^{21}$  Mn\_3O\_4 (46 % at 100 mV s  $^{-1}$  ),  $^{23}$ CoSe<sub>2</sub>(30.4 % at 10 mA cm<sup>-2</sup>),<sup>25</sup> Co<sub>3</sub>O<sub>4</sub>@RuO<sub>2</sub> nanosheet (24.5 % at 200 mV s<sup>-1</sup>), <sup>26</sup> and Graphene/MoO<sub>3</sub> nanosheets (40 % at 50 mV s<sup>-1</sup>).<sup>53</sup> The outstanding discharge capacity and its retention even at higher scan rates despite being high mass loading further enhances its potential to be used as negative electrode material. The superior electrochemical performance can be attributed to its high surface area, large pore volume, mesoporous porosity and nanocrystalline nature of ultrathin nanosheets.

CV curves (Fig. 7c) of MLNS-NiCo<sub>2</sub>O<sub>4</sub> are measured at various scan rates (5-100 mV  $s^{-1}$ ) in the potential window of -0.2 to 0.6V. CV curves consist of well defined strong redox peaks which indicates that the material exhibits typical faradaic

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behavior consistent with the battery-type electrode. The well defined redox couple is situated at 0.161 V/0.278 V (vs saturated calomel electrode SCE) at 5 mV s<sup>-1</sup> (Fig. S2(ESI<sup>+</sup>)) which is in accordance with the previous report. <sup>40</sup> The area of CV curves and peak current intensity increases linearly with the increase of scan rate. The linear behavior between the peak current intensity and square root of scan rate (Fig. S3(ESI<sup>+</sup>)) also indicates the redox reaction is diffusion controlled which is typical characteristic of faradaic material.<sup>15</sup> The presence of well defined pair of redox peaks (Fig. 7c) even at higher scan rates indicates its high rate capability. The plausible reaction mechanism (equations (9) and (10)) which control the redox process is governed by valence state transformation of  $Co^{3+}/Co^{4+}$  as well as  $M^{2+}/M^{3+}$  transitions (where M represents Ni or Co) on the surface of the electrode materials.45

$$NiCo_2O_4 + OH + H_2O \longleftrightarrow NiOOH + 2CoOOH + 2e^-$$
(9)

$$CoOOH + OH \longleftrightarrow CoO_2 + H_2O + e^{-1}$$
(10)

The areal and discharge capacities of MLNS-NiCo<sub>2</sub>O<sub>4</sub> are calculated from CV curves (Fig. 7c) by using equations (1) and (2). MLNS-NiCo<sub>2</sub>O<sub>4</sub> exhibits an excellent areal and discharge capacities of 344.7  $\mu$ Ah cm<sup>-2</sup> and 221.0 mAh g<sup>-1</sup> (NiCo<sub>2</sub>O<sub>4</sub> loading ~ 1.56 mg cm<sup>-2</sup>) at scan rate of 5 mV s<sup>-1</sup> (Fig. 7d). The detailed values at various scan rates (5-100 mV s<sup>-1</sup>) are also reported in Table S5(ESI<sup>+</sup>). As-synthesized MLNS- $NiCo_2O_4$  also demonstrates better rate capability with capacity retention of 42 % at 100 mV s<sup>-1</sup> (Fig. 7d). Similarly to compare with the reported data we have converted the areal capacity (344.7  $\mu$ Ah cm<sup>-2</sup>) and discharge capacity (221.0 mAh g<sup>-1</sup>) in to areal capacitance (1551.29 mF cm<sup>-2</sup>) and specific capacitance (994.41 F  $g^{-1}$  ) at 5 mV  $s^{-1}$ . The obtained capacity values and rate capability are comparable to or higher than many previously reported positive electrode materials.<sup>22-24, 26, 35, 38</sup> Its excellent electrochemical performance can be attributed to its unique morphological features with mesoporous porosity and high specific surface area which enables fast faradaic reaction even at higher scan rate.

To achieve optimum performance of SSASCs device, prior to its fabrication, the mass ratio between the positive and negative electrode should be determined. According to the charge balance theory ( $q^* = q^-$ ),<sup>11</sup> the mass ratio between the electrodes is found to be ( $m_+/m_- = 0.46$ ) at 5 mV s<sup>-1</sup> calculated by using (equation (11)).<sup>11</sup> This mass ratio is determined on the basis of specific capacitances calculated from the CV curves (Fig. 7b and d) for both negative and positive electrode materials.

$$\frac{\mathbf{m}_{+}}{\mathbf{m}_{-}} = \frac{\mathbf{C}_{-} \times \Delta \mathbf{U}_{-}}{\mathbf{C}_{+} \times \Delta \mathbf{U}_{+}} \tag{11}$$

where C<sub>+</sub> & C<sub>-</sub> and  $\Delta U_+ \& \Delta U_-$  are the specific capacitances and operating voltage windows of positive and negative electrodes at 5 mV s<sup>-1</sup> respectively.

# All SSASCs devices are fabricated according to the above mass

balance between the positive and negative1021ectrodes20A PVA/KOH gel electrolyte. The schematic illustration of assembled structure of SSASCs device is shown in Fig. 8a. Prior to assembly, the electrodes (exposed surface area; 1 cm<sup>2</sup>) and separators are immersed in the PVA-KOH gel electrolyte for 10 minutes. After that the electrodes and separators are taken out and allowed to solidify at room temperature for 60 minutes. Finally the SSASCs device are assembled according to schematic illustration (Fig. 8a). The bare part of Ni foam serve as the electrical contact between the electrodes and alligator clips of electrochemical work station (Fig. 8a). The electrochemical testing of SSASCs device are carried out after 12 hrs of its fabrication. CV measurements of SSASCs device are carried out to understand its capacitive behavior and to identify the desirable potential limit for the charge-discharge analysis. The well defined oxidation and reduction peaks (Fig. 8b) are observed and the peak current increases with the increase of scan rate which demonstrates excellent reversibility of fabricated device. The desirable potential limit for the charge-discharge measurements is 0 to 1.5 V as evidenced from CV measurements. The most importantly linear relationship between the peak current intensity as a function of square root of scan rate indicates that the redox reaction is diffusion controlled process (Fig. S4(ESI<sup>+</sup>)).<sup>15</sup> The main reason of obtaining the dominating faradaic behavior (Fig. 8b) is by combining faradaic materials as both cathode and anode which is also in accordance with few reports such as Co<sub>9</sub>S<sub>8</sub> nanorods//Co<sub>3</sub>O<sub>4</sub>@RuO<sub>2</sub> nanosheet,<sup>26</sup> MnO<sub>2</sub>//Bi<sub>2</sub>O<sub>3</sub> nanoflowers,<sup>54</sup> and VO<sub>x</sub> nanowires//VN nanowires.<sup>22</sup> The shape of CV curves (Fig. 8b) of our fabricated device is also similar to few reported asymmetric devices which also shows the dominance of faradaic redox behavior. <sup>22, 26, 54</sup> It is also important to mention that in most of the reported asymmetric devices electrical double layer capacitive behavior plays the major role due to the presence of carbonaceous material such as active carbon, carbon nanotube and graphene as their anode material.<sup>16-18, 38</sup> Chronopotentiomerty (CP) measurements are conducted to determine the electrochemical performance of SSASCs devices at different current densities (Fig. 8c). SSASCs devices (Fig. 8c) demonstrate electrochemical reversibility within the potential window of 0 to 1.5 V. The non linearity in the CP curves (Fig. 8c) further confirms the contribution of redox reaction from metal oxides as already evidenced by CV measurements (Fig. 8b). CP curves (Fig. 8c) are also in good symmetry in comparison to many reported CP curves of asymmetric devices which can be attributed to its kinetic reversibility due to its dominant faradaic characteristic.<sup>21, 23, 25-26, 28, 44, 54</sup> CP curves for few cycles at current densities 1, 2, 3 & 5 mA cm<sup>-2</sup> are also presented in Fig. S5(ESI<sup>+</sup>). The areal and volumetric capacities (Fig. 8d) of SSASCs device are calculated from CP curves by using equations (3) and (4) respectively. SSASCs device exhibit areal & volumetric capacities of 57.2 µAh cm<sup>-2</sup> & 0.954 mAh cm<sup>-3</sup> at 1 mA cm<sup>-2</sup> (Fig. 8d). So for comparison with the reported data, we have converted volumetric capacity (0.954 mAh cm<sup>-3</sup>) in to volumetric capacitance (2.3 F cm<sup>-3</sup>) at 1

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Figure 8. (a) Schematic illustration of the SSASCs device. (b) CV curves of the SSASCs device collected at different scan rates. (c) CP curves of the SSASCs devices collected at different current densities. (d) Areal & Volumetric capacities of SSASCs device collected from CP curves as a function of current density.(e) Cycling performance of SSASCs device at the current density of 2 mA cm-2 for 10000 cycles.(f) Ragone plot of SSASCs device, the values reported for other SSASCs devices are added for comparison. <sup>21-25, 28, 44</sup>

mA cm<sup>-2</sup>.The volumetric capacitance is much higher than most of the reported SSASCs devices (Table 1).<sup>21-25, 28, 44</sup> It can be observed that device capacitance decreases (Fig. 8d) with the increase of current density which also reflects that capacitance is mainly associated with the redox reaction. It is due to the fact that at lower current density both inner and outer surfaces of materials participated in the redox reaction whereas at higher current density the diffusion of ions more likely happen on the outer surface which results in decrease of capacity. However, SSASCs device still demonstrates excellent rate capability with capacity retention of 54.34 % at much higher current density of 8 mA cm<sup>-2</sup> (Fig. 8d). It also indicates that even at higher current density both anode & cathode materials act as a ion buffering reservoir which results in shortening the ionic transport path and reduce the fading of capacity. The device capacity retention is also much higher

than or comparable to most of the reported SSASCs (Table 1).<sup>21-25, 28, 44</sup> Cycling stability of SSASCs is elaborated by using CP & CV measurements at 2 mA cm<sup>-2</sup> & 100 mV s<sup>-1</sup> in the potential window of 0 to 1.5 V for 10000 cycles as shown in Fig. 8e & Fig. S6(ESI<sup>+</sup>) respectively. SSASCs device maintains capacity retention of 83 % & 80 % after 10000 cycles at current density of 2 mA cm<sup>-2</sup> & scan rate of 100 mV s<sup>-1</sup> which indicates its electrochemical stability for long time practical usage. The cyclic capacity retention is also comparable to most of the reported SSASCs devices (Table 1).<sup>21-25, 28, 44</sup>

The cyclic stability test also indicate the long term stability of such devices which can be attributed to the use of solid state electrolyte. Actually the solid state electrolyte suppressed the dissolution of MnO<sub>2</sub> which results in the significant cyclic stability for long time usage.<sup>24, 44</sup> The Ragone plot (Fig. 8f) summarizes the volumetric energy and power densities of the

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#### System Volumetric capacitance Energy density Rate capacity retention Cycling capacity retention Ref. $(mWh cm^{-3})$ (F cm<sup>-3</sup>) 0.715 at 1 mA cm<sup>-2</sup> 54.34 % at 8 mA cm<sup>-2</sup> 83 % (10000 cycles) at 2 mA cm<sup>-2</sup> This 2.3 at 1 mA cm<sup>-2</sup> NiCo<sub>2</sub>O<sub>4</sub>//MnO<sub>2</sub> 0.388 at 8 mA cm<sup>-2</sup> 80 % (10000 cycles) at 100 mV s<sup>-1</sup> 72.72 % at 5 mA cm<sup>-2</sup> work 21 1.21 at 0.5 mA cm<sup>-2</sup> 0.41 at 0.5 mA cm<sup>-2</sup> 81.6 % (6000 cycles) at 100 mV s<sup>-1</sup> MnO<sub>2</sub> //Fe<sub>2</sub>O<sub>3</sub> 85 % at 6 mA cm<sup>-2</sup> 22 87.5 % (10000 cycles) at 100 mV s<sup>-1</sup> VO<sub>x</sub> //VN 1.35 at 0.5 mA cm<sup>-2</sup> 0.61 at 0.5 mA cm<sup>-2</sup> 74 % at 5 mA cm<sup>-2</sup> 23 83 % (12000 cycles) at 100 mV s<sup>-1</sup> Mn<sub>3</sub>O<sub>4</sub>//Ni(OH)<sub>2</sub> 2.07 at 1 mA cm<sup>-2</sup> 0.30 at 1 mA cm<sup>-2</sup> 38.64 % at 5 mA cm<sup>-2</sup> TiO<sub>2</sub> @MnO<sub>2</sub> 24 91.2 % (5000 cycles) at 100 mV s<sup>-1</sup> 0.7 at 0.5 mA cm<sup>-2</sup> 0.30 at 0.5 mA cm<sup>-2</sup> 37 % at 4 mA cm<sup>-2</sup> //TiO₂ @C 25 94.8 % (2000 cycles) at 3 mA cm<sup>-2</sup> MnO<sub>2</sub> //CoSe<sub>2</sub> 1.77 at 1 mA cm<sup>-2</sup> 0.588 at 1mA cm<sup>-2</sup> 7.85 % at 10 mA cm<sup>-2</sup> 28 95.5 % (5000 cycles) at 200 mV s<sup>-1</sup> H-MnO<sub>2</sub>//RGO 0.55 at 2 mA cm<sup>-2</sup> 0.25 at 2 mA cm<sup>-2</sup> 42 % at 800 mV s<sup>-1</sup> ZnO@MnO<sub>2</sub> 44 0.52 at 5 mV s<sup>-1</sup> 0.234 at 0.5 mA cm<sup>-2</sup> 70 % at 400 mV s<sup>-1</sup> 98.4 % (5000 cycles) at 0.5 mA cm<sup>-2</sup> //graphene

Table 1. Comparison of the performance metrics of as-fabricated (NiCo<sub>2</sub>O<sub>4</sub>//MnO<sub>2</sub>) SSASCs device with previously reported SSASCs devices 0.1039/C6RA15420D

SSASCs device together with other reported devices for comparison. It indicates that volumetric energy density is significantly higher than most of the reported SSASCs devices (Fig. 8f and Table 1). <sup>21-25, 28, 44</sup> The detail values of volumetric energy and power densities of SSASCs device at different current densities are also summarized in Table S6(ESI+). SSASCs device exhibits volumetric energy and power densities of 0.715 mWh cm<sup>-3</sup> and 353.7 mW cm<sup>-3</sup> at 1 mA cm<sup>-2</sup> respectively. Even at higher current density (8 mA cm<sup>-2</sup>) device still retains energy density of 0.388 mWh cm<sup>-3</sup> and power density of 750 m W cm<sup>-3</sup>. SSASCs device exhibits superior rate capability with energy density retention of 53 % at 8 mA cm<sup>-2</sup> (Fig. 8f) which is itself quite significant regarding its practical application. More specifically the achieved maximum volumetric energy density at 1mA cm<sup>-2</sup> is around 138 % higher than that of latest paper at the same current density.<sup>23</sup> It is worthwhile to note that even at higher current density of 8 mA  $cm^{-2}$ , volumetric energy density (0.388 mWh cm<sup>-3</sup>) is still higher than maximum attained energy density of many reported asymmetric devices at low current density (Fig. 8f and Table 1).<sup>23-24, 28, 44</sup> But the achieved volumetric energy density is lower than the highest value (1.44 mWh cm<sup>-3</sup>) reported for  $Co_9S_8$  nanorods//Co\_3O\_4@RuO\_2 nanosheet based solid state device.  $^{\rm 26}$  But the potential of device based on  ${\rm RuO}_2$  is much limited for practical application due to its high cost, rareness and toxicity of Ru element.<sup>27</sup> The overall results indicate that SSASCs device has superior electrochemical performance in comparison with most of the reported SSASCs devices which also indicates its futuristic practical applicability due to its low fabrication cost and environmental friendly aspect. Electrochemical impedance spectroscopy (EIS) is employed to harness the origin of superior electrochemical performance of both materials and SSASCs device. EIS measurements of anode and cathode materials are carried out in three electrode cell configuration (Fig. S7 and S8(ESI<sup>+</sup>)). Whereas EIS measurements of SSASCs device are carried out in fresh and

after 10000 CV cyclic test at 100 mV s<sup>-1</sup> in two electrode configuration (Fig. S9). The Nyquist plots (Fig. S7-S9(ESI<sup>+</sup>)) indicate a semicircle in the high frequency region and sloping line deviating 90° in the low frequency region which is an indication of well defined typical capacitive behavior. Both materials and SSASCs device (Fig. S7-S9(ESI<sup>+</sup>)) demonstrate a more vertical line leaning to an imaginary axis of more than 45°, which is an indicative of more facile electrolyte ions diffusion to the active materials. The intercept of semicircle along x-axis represent the equivalent series resistance (Rs) whereas its width determines the charge transfer resistance  $(R_{ct})$ .<sup>11, 39</sup> R<sub>s</sub> values for 3DHM-MnO<sub>2</sub> and MLNS-NiCo<sub>2</sub>O<sub>4</sub> are measured to be 0.748  $\Omega$  and 0.504  $\Omega$  respectively (Fig. S6 and S7(ESI<sup>+</sup>)) which indicates high conductivities for both materials. It is also important to note that the width of semicircles are very small (Fig. S7 and S8(ESI<sup>†</sup>)) which also indicates low charge transfer resistance (R<sub>ct</sub>) for both materials. The Nyquist plot (Fig. S9(ESI<sup>+</sup>)) also demonstrates the comparison between fresh and after 10000 CV cycles used SSASCs device. It is worthwhile to note that there is no much difference between the impedance profile of fresh and used devices except a declined line deviating 90° in the low frequency region exhibits more deviation for used device associating with the larger electrochemical polarization due to excessive cyclic operation (Fig. S9). The values of R<sub>s</sub> as indicated by the Nyquist plots for fresh and used SSASCs devices are 1.576  $\Omega$  & 1.717  $\Omega$  respectively (Fig. S9(ESI<sup>+</sup>)). The most importantly SSASCs device also exhibit very small charge transfer resistance in the fresh and even after 10000 CV cyclic test at 100 mV s<sup>-1</sup> (Fig. S9). These lower values of R<sub>s</sub> and R<sub>ct</sub> for both materials and SSASCs devices are also the strong indicative of the increased diffusion and transport pathways for electrolyte ions during charge/discharge processes which are responsible for high performance characteristics. The lower value of R<sub>ct</sub> further indicates that the charge transfer resistance mainly caused by faradaic reaction and contribution

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from electrochemical double layer capacitance is very small . The SSASCs device outstanding performance can be attributed the following reasons (1) 3D hierarchical MnO<sub>2</sub> to microspheres which consists of ultrathin nanosheets (~ 2nm) with mesoporous porosity facilitate extremely facile charge transfer (2) long chains of interconnected mesoporous layered NiCo<sub>2</sub>O<sub>4</sub> nanosheets provide extensive path for transporting charges despite being high mass loading (3) nanosheets structure of both anode & cathode materials shorten the ion diffusion path within the electrode material (4) nanocrystallite size, high surface area & large pore volume of both anode & cathode materials provide enhanced accessible sites for electrolyte (5) its charge storage phenomena is mainly governed by faradaic redox behavior (6) low interfacial and charge transfer resistances are also an indicator of increased diffusion and transport pathways for electrolyte ions due to the dominance of faradaic redox behavior.

#### Conclusions

Novel SSASCs device is successfully fabricated by using 3D hierarchical MnO<sub>2</sub> microspheres as an anode and mesoporous layered NiCo<sub>2</sub>O<sub>4</sub> nanosheets as cathode. In particular, the device operates successfully within a potential window of 1.5 V, giving rise to higher volumetric capacity and energy density of 0.95 mAh cm<sup>-3</sup> (2.3 F cm<sup>-3</sup>) and 0.715 mWh cm<sup>-3</sup> at 1 mA cm<sup>-2</sup>. In addition, the SSASCs device also exhibits high volumetric energy & power densities of 0.388 mWh cm<sup>-3</sup> and 750 m W cm<sup>-3</sup> respectively at 8 mA cm<sup>-2</sup>. The attained SSASCs device performance is much better than most of the reported SSASCs devices. SSASCs device also demonstrates superior cyclic stability with capacitance retention of 83 % after 10000 cycles at 2 mA cm<sup>-2</sup>. The well-defined faradic redox behavior of SSASCs device enabled fast charge storage/release processes even at higher current density which is responsible for good rate capability and superior cyclic stability. The enhanced solid state device performance along with its simple fabrication strategy further indicates its strong potential for a variety of energy storage futuristic applications.

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Volumetric energy density and power density of novel solid state device  $(NiCo_2O_4 //MnO_2)$  are much higher than mostly reported devices.