Supporting Information

An asymmetric supercapacitor with both ultra-high gravimetric and volumetric energy density based on 3D $Ni(OH)_2/MnO_2$@carbon nanotube and activated polyaniline-derived carbon

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The detailed synthetic procedure of APDC powder

Synthesis of APDC was realized by carbonization of PANI precursor followed by a KOH activation process. The PANI precursor was synthesized via an oxidative polymerization route. Typically, 10 g of aniline and 10 g of citric acid were mixed together in 1000 ml of distilled water under vigorous stirring. Then, an aqueous solution of ammonium persulfate was poured into the above mixture solution. After continuously stirring for 30 s, the resulting solution was placed into a refrigerator at 4 ^{o}C. After 24 h, dark green PANI nanorods were collected by filtering and rinsed with copious water, and finally dried in freezing- dryer for 48 h. As-prepared PANI nanorods precursor was pyrolyzed at 800 ^{o}C for 1 h under Ar atmosphere to obtain PANI-derived carbon (PDC). The activation process was performed by impregnating PDC powder with KOH (PDC: KOH = 1:6, wt%) in aqueous solution and then heated at 80 ^{o}C to remove residual water followed by heating at 700 ^{o}C for 1 h under Ar atmosphere. After being cooling down to room temperature, the resulting product was neutralized by 5% HCl solution followed by repeatedly washing with copious deionized water, and finally dried at 60 ^{o}C in air for characterization.

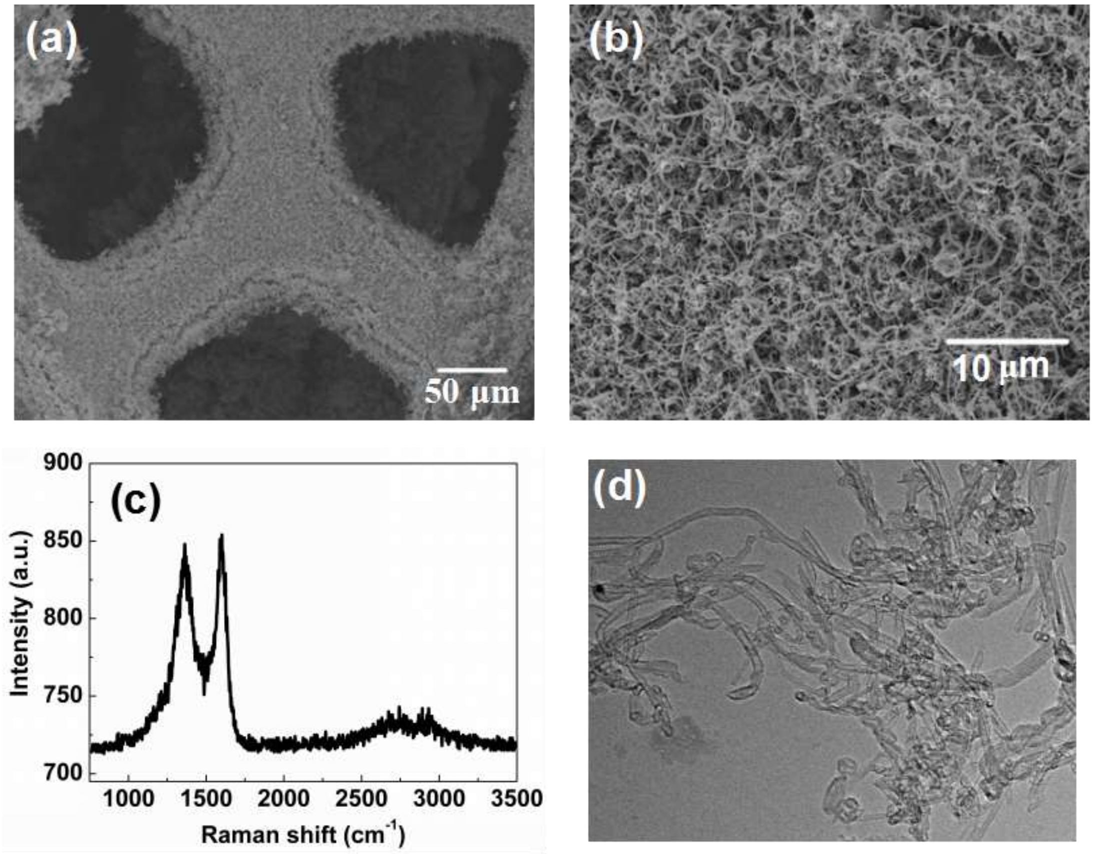

Figure S1. (a)-(b) SEM images of CNTs under different magnifications. (c) Raman spectrum and (d) HRTEM of CNTs.

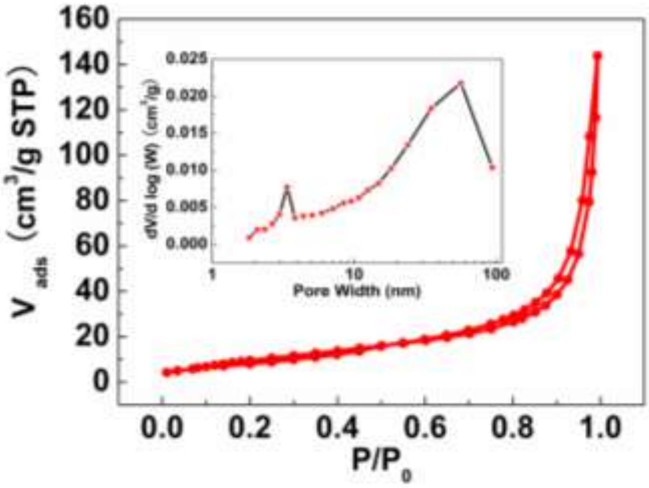

Figure S2. Nitrogen adsorption-desorption isotherms and pore size distribution (inset) of $Ni(OH)_2/MnO_2$ powder.

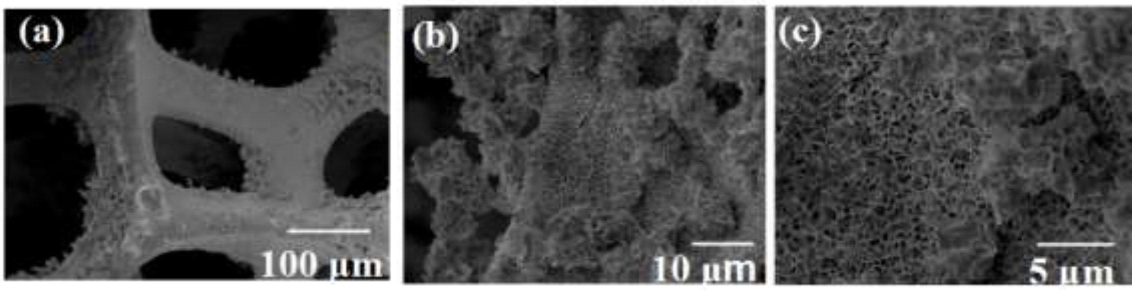

Figure S3. (a)-(c) SEM images of $Ni(OH)_2/MnO_2$ composite loaded on NF at different magnifications.

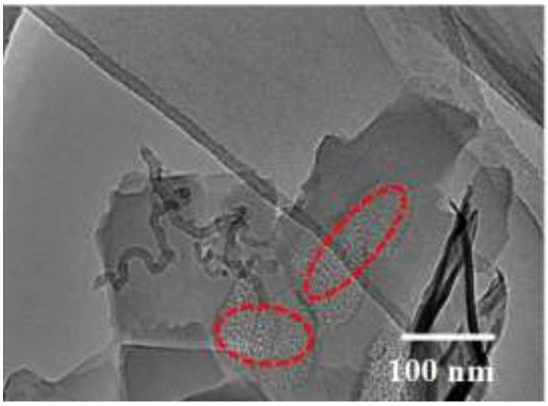

Figure S4. HRTEM image of $Ni(OH)_2/MnO_2$ nanosheets.

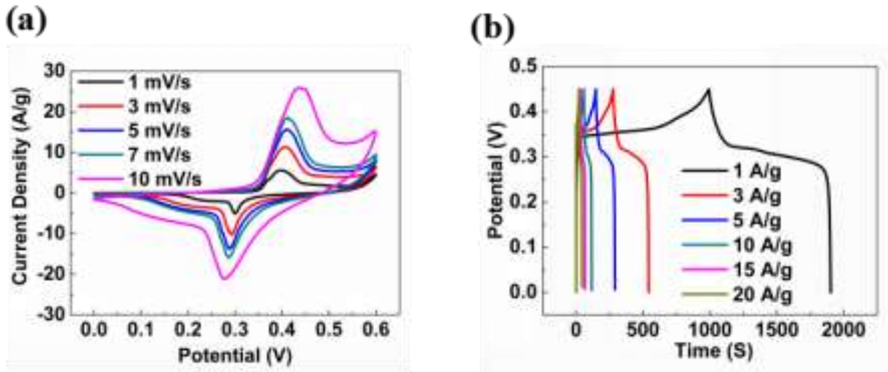

Figure S5. (a) CV curves at different scan rates and (b) GCD curves under varies of current densities of $Ni(OH)_2/MnO_2/NF$ electrode.

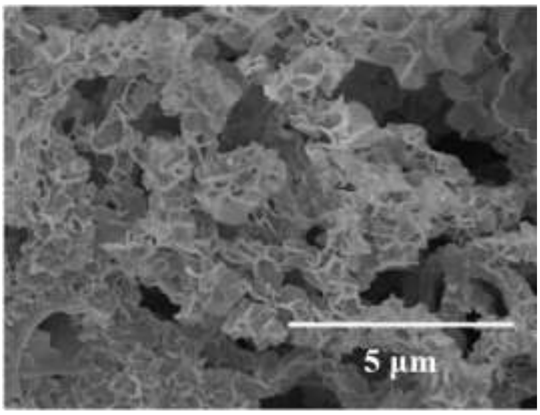

Figure S6. SEM images of $Ni(OH)_2/MnO_2$@CNT/NF electrode after 3000 cycles at a current density of 0.5 A/g.

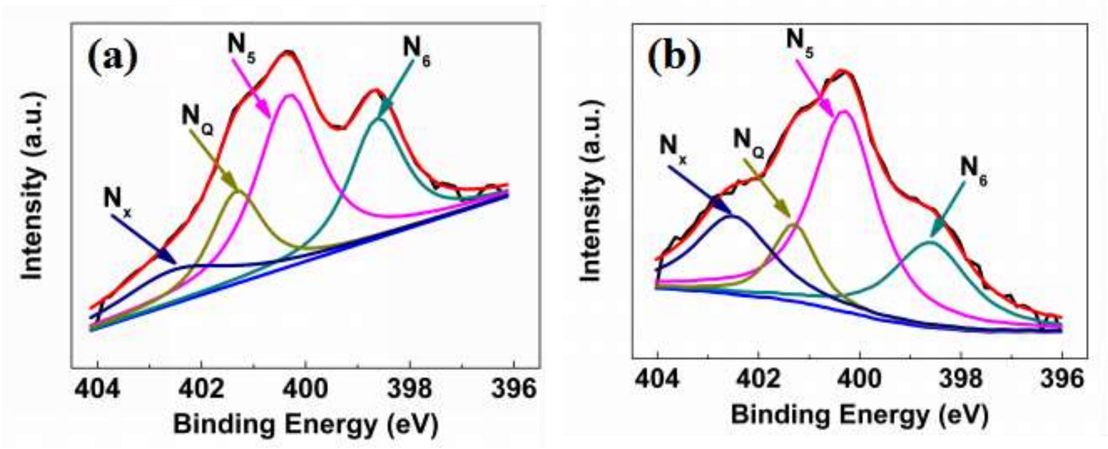

Figure. S7 High-resolution XPS spectra for N 1s of APDC: (a) before and (b) after electrochemical cycling test.

The XPS spectra for N 1s of APDC can be deconvoluted into four subpeaks located at 398.6, 400.3, 401.5 and 402.5 eV, corresponding to N-6 (pyridinic N), N-5 (pyrrodic N), N-Q (quaternary N) and N-X (oxidized N) groups, respectively. As shown in Figure S7, N-6 group decreased and N-5, N-X groups increased after electrochemical cycling test.

The gravimetric energy density (*E*) and corresponding power density (*P*) of the ASC device were calculated by using the equations (1) and (2):

$$E = \frac{C \times U^2}{2 \times 3.6} \tag{1}$$

$$P = \frac{E \times 3600}{\Delta t} \tag{2}$$

Where *C* is the specific capacitance, *U* is the working potential window, *Δt* is the discharge time.

Table S1. Comparison of electrochemical performance of similar aqueous asymmetric supercapacitor

Positive//Negative	m positive + m negative (mg)	Operation Potential (V)	Energy Density (Wh kg^{-1})	Power Density (kW kg^{-1})	Ref
Co-Ni DH//FeOOH	1.28 + 1.23	1.6	86.4 (@1.83 kW kg^{-1})	11.6 (@22.8 Wh kg^{-1})	1
Co_3O_4@$Ni(OH)_2$//AC	2.9 + 9.1	1.6	49.8 (@801 W kg^{-1})	16.1(@28.1 Wh kg^{-1})	2
$MnCo_2O_4$@$Ni(OH)_2$//AC	6.3 + 16	1.6	48 (@1.4 kW kg^{-1})	7.26 (@14.9 Wh kg^{-1})	3
CuO@MnO_2//AG	4.5 +5.5	1.8	29.9(@269.9Wkg^{-1})	-	4
Ni-Co DH/rGO//HPC	2 + 4.16	1.6	56.1 (@76 W kg^{-1})	7.12 (@37.5Wh kg^{-1})	5
Fe_3O_4/GNS//Fe_3O_4/GNS	-	1.0	11.0 (@200 W kg^{-1})	9.0 (@3.0 Wh kg^{-1})	6
NiO/$Ni(OH)_2$/PEDOT//CMK-3	-	1.5	1.1 mWh cm^{-3} (@33 mW cm^{-3})	780 mW cm^{-3} (@0.61 mWh cm^{-3})	7
MnO_2/GCF//N-GCF	-	1.8	5 mWh cm^{-3} (@929 mW cm^{-3})	-	8
$Ni(OH)_2$-MnO_2@CNT/ NF//APDC	6.52 + 19.5	1.7	126.4 (@424.1 W kg^{-1}) 10.9 mWh cm^{-3} (@36.7 mW cm^{-3})	8.4 (@46.9 Wh kg^{-1}) 730 mW cm^{-3} (@4.06 mWh cm^{-3})	This work

Abbreviations: DH double hydroxide, AC activated carbon, AG activated graphene, rGO reduced graphene oxide, HPC hierarchical porous carbon. CNT carbon nanotube, APDC activated polyamine-derived carbon. GNS graphene nanosheet, PEDOT poly(3,4-ethyl-enedioxythiophene), CMK-3 ordered mesoporous carbon. GCF dried rGO/SWCNT, SWCNT single-walled carbon nanotube. N-GCF nitrogen doped rGO/SWCNT.

REFERENCES:

(1) Chen, J. Z.; Xu, J. L.; Zhou, S.; Zhao, N.; Wong, C. P. Amorphous Nanostructrured FeOOH and Co-Ni Double Hydroxides for High-Performance Aqueous Asymmetric Supercapacitor. *Nano Energy* **2016**, 21, 145-153.

(2) Zhang, X. D.; Xiao, J. L.; Zhang, X. Y.; Meng, Y.; Xiao, D. Three-Dimensional Co_3O_4 Nanowires@Amorphous $Ni(OH)_2$ Ultrathin Nanosheets Hierarchical Structure for Electrochemical Energy Storage. *Electrochim. Acta* **2016**, 191, 758-766.

(3) Zhao, Y.; Hu, L. F.; Zhao, S. Y.; Wu, L. M. Preparation of $MnCo_2O_4$@$Ni(OH)_2$ Core–Shell Flowers for Asymmetric Supercapacitor Materials with Ultrahigh Specific Capacitance. *Adv. Funct. Mater* **2016**, 26, 4085-4093.

(4) Chen, H.; Zhou, M.; Wang, T.; Li, F.; Zhang, Y. X. Construction of Unique Cupric Oxide–Manganese Dioxide Core–Shell Arrays on a Copper Grid for High-Performance Supercapacitors. *J. Mater. Chem. A* **2016**, 4, 10786-10793.

(5) Ma, H.; He, J.; Xiong, D. B.; Wu, J.; Li, Q.; Dravid, V.; Zhao. Y. Nickel Cobalt Hydroxide@Reduced Graphene Oxide Hybrid Nanolayers for High Performance Asymmetric Supercapacitors with Remarkable Cycling Stability. *ACS Appl. Mater. Interfaces* **2016**, 8, 1992-2000.

(6) Karthikeyan, K.; Kalpana, D.; Amaresh, S.; Lee, Y. S. Microwave Synthesis of Graphene/Magnetite Composite Electrode Material for Symmetric Supercapacitor with Superior Rate Performance. *RSC Adv.* **2012**, 2, 12322-12328.

(7) Yang, H. L.; Xu, H. H.; Li, M.; Zhang, L.; Huang, Y. H.; Hu, X. L. Assembly of $NiO/Ni(OH)_2$/PEDOT Nanocomposites on Contra Wires for Fiber-Shaped Flexible

Asymmetric Supercapacitors. *ACS Appl. Mater. Interfaces* **2016**, 8, 1774-1779.

(8) Yu, D. S.; Goh, K. L.; Zhang, Q.; Wei, L.; Wang, H.; Jiang, W. C.; Chen, Y. Controlled Functionalization of Carbonaceous Fibers for Asymmetric Solid-State Micro-Supercapacitors with High Volumetric Energy Density. *Adv. Mater.* **2014**, 26, 6790-6797.