Supporting Information

Co_3O_4@MWCNT nanocable as cathode with superior electrochemical performance for supercapacitors

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Experimental details

Commercial MWCNT (multiwall CNTs, outer diameter 10–20 nm) were treated in 6 M HNO_3 for 2 h with sonication to remove the impurities and endow the surface with hydrophilic groups such as –OH and –COOH. After being washed for several times, the as-treated MWCNT were filtered and collected as paper-like pieces.

Coating solution was prepared by dissolving 0.36 mmol $Co(Ac)_2.4H_2O$ into 30 ml distilled water. The MWCNT were dispersed into the aqueous solution, and then 4mL ammonia solution ($NH_3.H_2O$, 25%) was dropwise added into the mixture solution. The as-obtained mixture was transferred into a 40 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 5 h. After drying at 80 °C for 12 h, a hybrid of Co_3O_4 crystal coating layer on MWCNT was obtained and then calcined at 250 °C in air atmosphere for 2 h. Finally, the targeted Co_3O_4@MWCNT nanocable was achieved. Meanwhile, hydrothermally prepared nanostructured Co_3O_4 without MWCNT under the same reactive condition was also used for the comparison with the targeted material.

Both the prepared Co_3O_4@MWCNT nanocable and pristine Co_3O_4 were mixed with acetylene black and poly(tetrafluoroethylene) (PTFE) in a weight ratio of 8:1:1 with the help of ethanol. After drying, the mixture was pressed into a film with an active mass loading of about 6 mg/cm^2. Next, the film was cut into disks. These disks were pressed onto Ni-grid at a pressure of 10 MPa and then dried at 80 °C overnight to act as working electrodes.

The cyclic voltammetry (CV) data were collected at different scan rates on an electrochemical working station CHI440B (Chenhua). A three-electrode cell consisting of the above working electrode, Ni-grid as the counter electrode and SCE as the reference electrode was used to test the charge/discharge behaviors including rate capability and cycling behavior in 0.5 M KOH aqueous solution on a cell tester (Land).

1. Charge-discharge plot of the hybrid of pristine Co_3O_4 with MWCNT

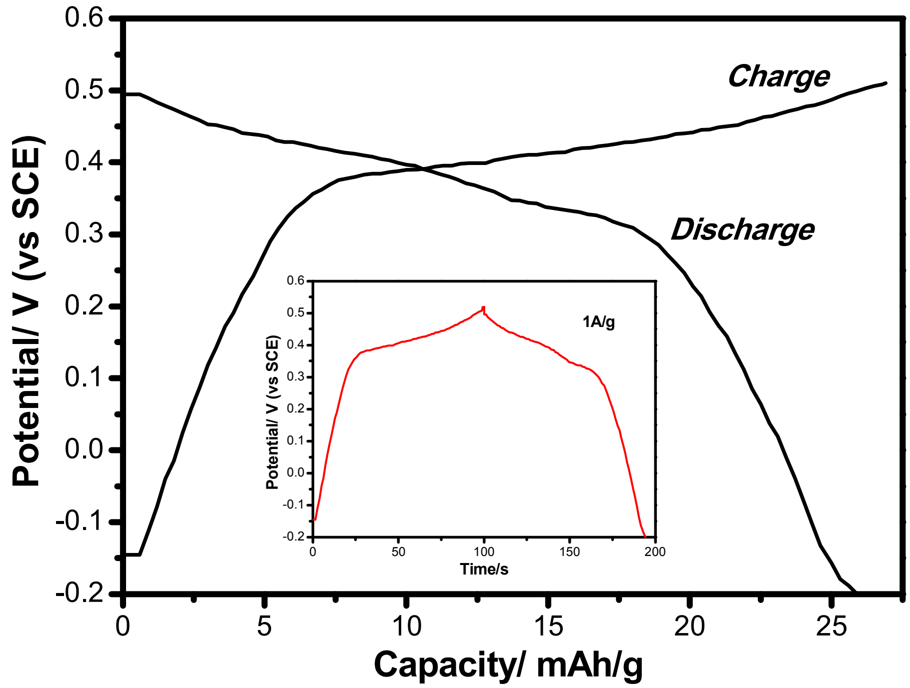

Figure S1 The charge-discharge plot of the hybrid of pristine Co_3O_4 with MWCNT.

The electrochemical performance of the hybrid containing pristine Co_3O_4 and MWCNT with the same weight amount of Co_3O_4 41.88 wt.% was measured under the same condition of 0.5 mol l^{-1} KOH within a smaller electrochemical window between -0.2 V and 0.52 V, compared with that of pristine Co_3O_4 -0.2 V and 0.56 V at a current density of 1 A g^{-1}. The fixed potential range even cannot reach the same level with pristine

Co_3O_4. The hybrid delivers a specific capacity of 25 mAh g^{-1} at a current density of 1 A g^{-1}, 125 F g^{-1} which is calculated in the same way with Co_3O_4@MWCNT nanocable in this paper, indicating that MWCNT plays very little part to the capacitance increase of the hybrid of Co_3O_4 with MWCNT. This means that the excellent capacitance of Co_3O_4@MWCNT nanocable is mainly derived from the Co_3O_4 while the MWCNT act as an adjuvant to construct a conductive core nanocable to promote the performance of the Co_3O_4@MWCNT nanocable. Also, as it is shown in the inset of **Figure S1,** the discharge time of the hybrid has been similar to pristine Co_3O_4 for less than 200 s. Moreover, the working electrode material is more and more difficult to be made into a film when the amount of MWCNT increases, so we measured the electrochemical performance of the hybrid containing pristine Co_3O_4 and MWCNT with the same weight amount of Co_3O_4 instead of MWCNT only.

2. Mean absolute deviation and Standard deviation of the capacitance of Co_3O_4@MWCNT nanocable and pristine Co_3O_4

Cell number / Current density	Charge capacitance(Discharge capacitance)/ F/g						Mean Absolute Deviation	Standard Deviation
	1	2	3	4	5	Mean		
Nanocable (15A/g)	584.30769 (583.41)	585.38462 (584.373)	590.85385 (589.12)	586.84615 (585.86)	586.15385 (585.15)	586.70923 (585.5826)	1.52592 (1.40308)	2.50135 (1.99585)
Nanocable (20A/g)	567.69231 (558.46154)	565.38462 (559.3077)	562.61538 (558.7692)	565.84615 (559.4615)	567.23077 (562.1534)	565.75385 (560.631)	1.99385 (1.71262)	2.85632 (2.17719)
Nanocable (30A/g)	548.30769 (543.6923)	542.30769 (536.7692)	543.69231 (539.0769)	548.76923 (538.1538)	547.84615 (536.7692)	546.18462 (538.89231)	4.34462 (2.54769)	5.09484 (2.96608)
Nanocable (50A/g)	552.46154 (538.53846)	560.76923 (543.6923)	550.46154 (536.3077)	561.69231 (546.4615)	553.61538 (539.3846)	555.8 (540.8769)	4.5415 (3.36)	5.31671 (4.11362)
Nanocable (80A/g)	515.07692 (510.76923)	510.92308 (505.6923)	508.84615 (502.6154)	509.76923 (505.8462)	515.53846 (505.3077)	512.03077 (506.0462)	2.62154 (1.8892)	3.08489 (2.9491)
Nanocable (100A/g)	513.23077 (512)	510.92308 (502.1538)	513.23077 (511.8462)	505.23077 (500.3077)	513.61538 (508.1538)	511.24615 (506.8923)	2.53538 (4.5292)	3.52774 (5.4321)
Pristine Co304(1A/g)	125.52632 (121.2632)	125.52632 (121.2632)	126 (120.3158)	125.05263 (121.2632)	125.05263 (121.2632)	125.43158 (121.0737)	0.30316 (0.30316)	0.39631 (0.4237)
Pristine Co304(3A/g)	109.42105 (108.4737)	109.42105 (106.579)	107.52632 (108.4737)	108.47368 (105.1579)	108 (108)	108.56842 (107.3368)	0.68211 (1.1747)	0.84735 (1.4445)
Pristine Co304(5A/g)	103.89474 (102.3158)	104.68421 (103.7368)	102.78947 (103.7368)	103.26316 (102.7895)	103.26316 (100.8947)	103.57895 (102.6947)	0.56842 (0.8716)	0.73213 (1.1795)
Pristine Co304(8A/g)	99 (98.5263)	98.05263 (93.7895)	98.10526 (97.0526)	99.57895 (97.4737)	98.52632 (97.579)	98.65263 (96.8842)	0.50947 (1.2379)	0.6431 (1.8119)
Pristine Co304(10A/g)	94.26316 (92.3684)	93.31579 (91.8947)	94.78947 (93.2632)	93.31579 (90.9474)	94.89474 (91.2632)	94.11579 (91.9474)	0.64 (0.6947)	0.76849 (0.9192)

Table S1 Mean absolute deviation (MAD) and Standard deviation (SD) of the capacitance of Co_3O_4@MWCNT nanocable and pristine Co_3O_4

Each datum was obtained with 5 cells, which is summerized in the above Table S1. In the case of pristine Co_3O_4, the highest mean absolute deviation and standard deviation of the charge and discharge capacitances are 0.6821 (1.2379) and 0.84735 (1.8119), respectively. As to

Co_3O_4@MWCNT nanocable, the highest mean absolute deviation and standard deviation of charge and discharge capacitances are 4.5415 (4.5292) and 5.3167 (5.4321). All the results imply the reliability and validity of the specific capacitance data.

3. Thermogravimetric analysis (TG) of Co_3O_4@MWCNT

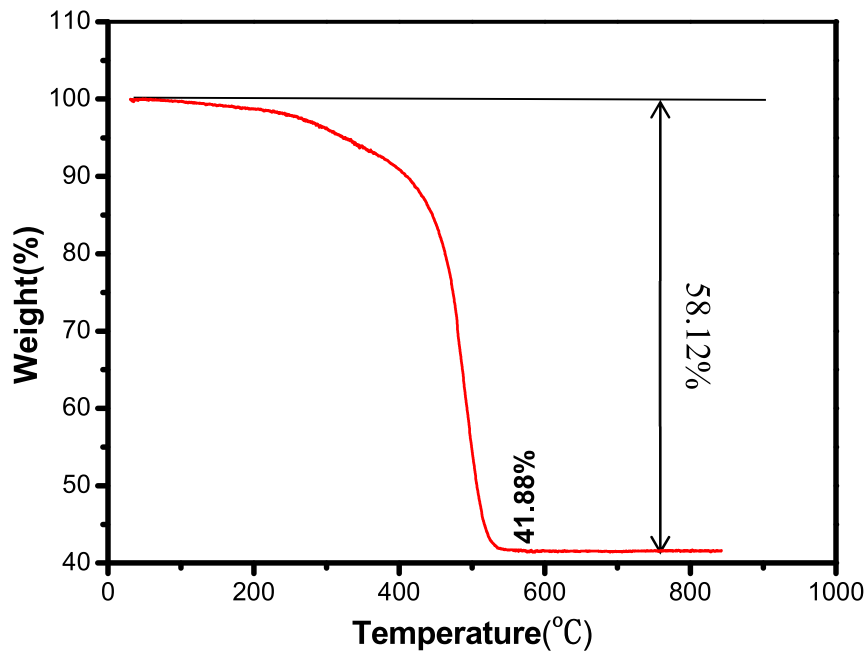

Figure S2 Thermogravimetric analysis (TG) of Co_3O_4@MWCNT in air atmosphere from 10 °C-800 °C at a rate of 10 °C/min.

The mass of Co_3O_4@MWCNT sample is 6.0370 mg. Along with the increase of temperature, Co_3O_4 is remained when MWCNT is completely burnt after 550 °C. Therefore, the mass ratio of Co_3O_4 in the prepared nanocable is determined (41.88%).

4. Nyquist plot of Co_3O_4@MWCNT and the pristine Co_3O_4

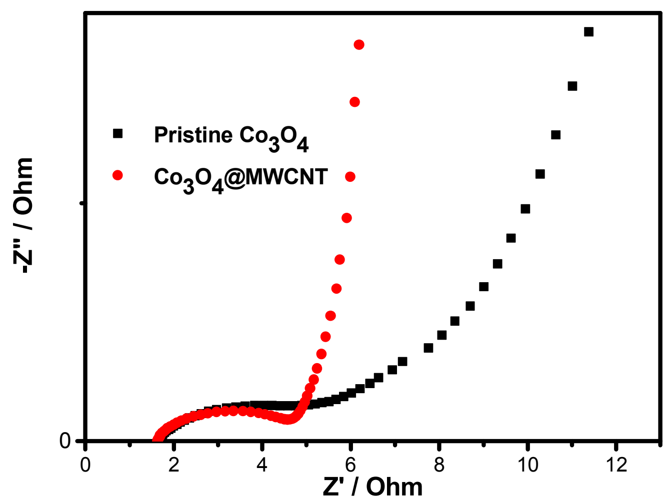

Figure S3. Nyquist plot of Co_3O_4@MWCNT and the pristine Co_3O_4 before charge in 0.5 M KOH aqueous solution. The mass loading is 6.33 mg/cm^2, which is the same as that of electrodes for cycling, and the frequency range is 0.01 Hz – 10000 Hz.