Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Metal hydroxides as conversion electrode for lithium-ion battery: A case study with $Cu(OH)_2$ nanoflower array

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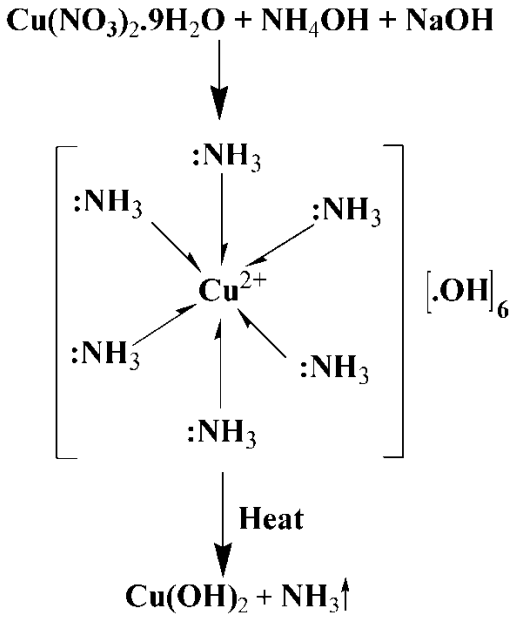
Reaction scheme for the synthesis of $Cu(OH)_2$

For synthesis, aqueous solutions of $[Cu(NO_3)_2.9H_2O]$, 25% ammonia and NaOH are used. The reaction proceeds through formation of an octahedral metal complex intermediate, $[Cu(NH_3)_6]^{2+}$ as shown below:



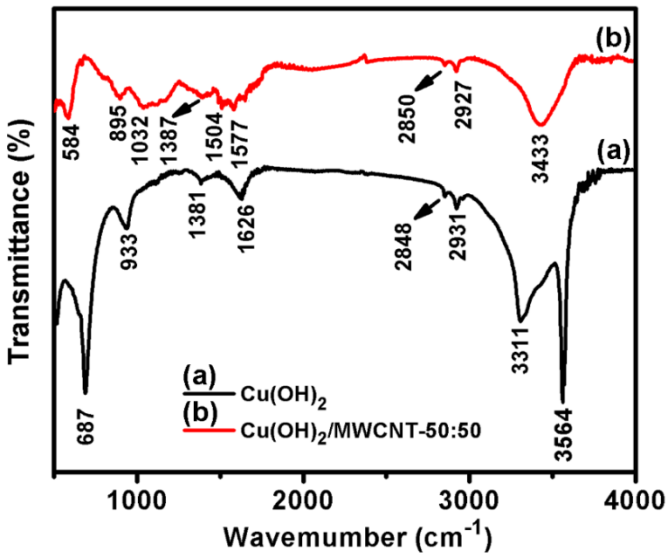


Figure S1: FTIR spectra of (a) as-synthesized $Cu(OH)_2$ and (b) $Cu(OH)_2$/MWCNT-50:50. In the as-synthesised $Cu(OH)_2$, presence of peaks at 3564 and 3311 cm^{-1} reflect stretching modes of hydroxyl groups in the $Cu(OH)_2$.[1] The peak at 1626 cm^{-1} reflects the bending mode of the absorbed water in the as synthesised $Cu(OH)_2$ powder.[2] C-O stretching vibration at 933 cm^{-1} can be assigned to the corresponding metal cation (Cu^{2+}) in $Cu(OH)_2$.[3,4] A new absorption band at 1032 cm^{-1} in the composite material is due to MWCNT. A broad peak at 3433 cm^{-1} appears instead of two separate peaks which were present in the bulk material and can be related to partial obliteration of hydrogen bonds.

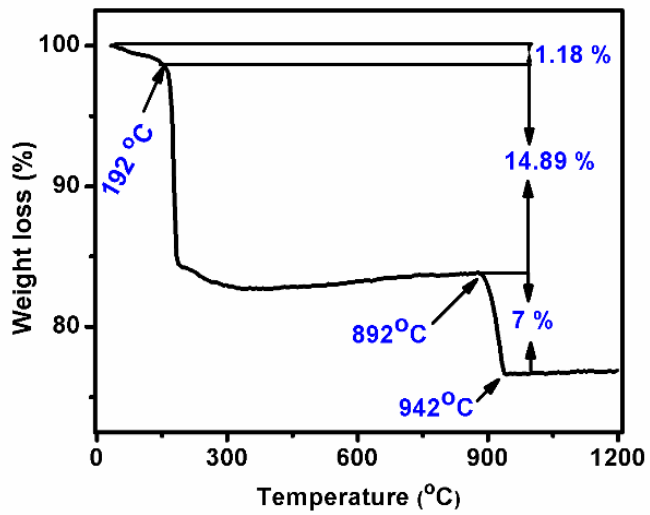


Figure S2: TGA curve for the as-synthesized $Cu(OH)_2$ nanoflowers at a heating rate of 10^o min^{-1} under argon flow. The observed weight losses can be divided into three steps: (i) ~1.2% weight loss occurs in the temperature range 30^o-192^oC due to the loss of physically absorbed water (ii) ~14.9% weight loss in the 192-892^oC range represents transformation from $Cu(OH)_2$ to CuO and finally, (iii) ~7.0% weight loss in the 892-942^oC range represents the formation of metallic Cu from CuO.

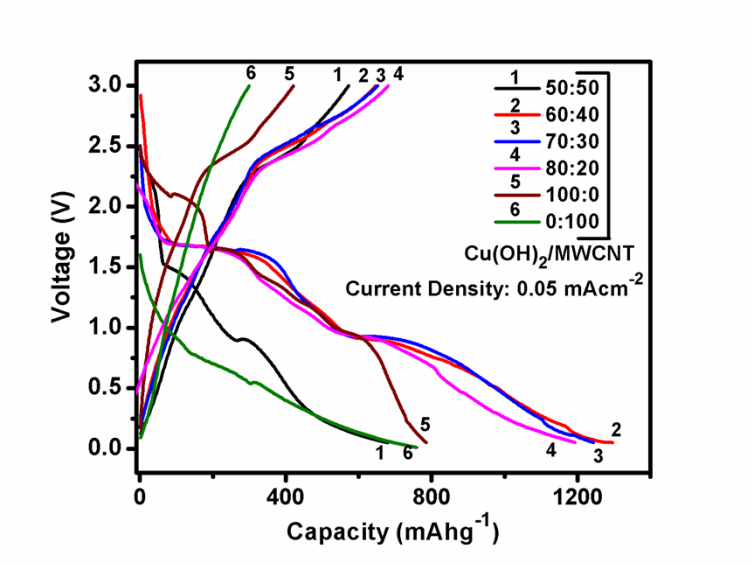


Figure S3: Initial discharge/charge voltage profiles for different composites of $Cu(OH)_2$ and MWCNT at a current density of 0.05 $mAcm^{-2}$. All composites except $Cu(OH)_2$/MWCNT-50:50 show a low Columbic efficiency of 50-57%. Surprisingly, $Cu(OH)_2$/MWCNT-50:50 composite shows a very high Columbic efficiency of 84% which may be attributed to synergic interaction with MWCNT and lower degree of structural disorder/defects.

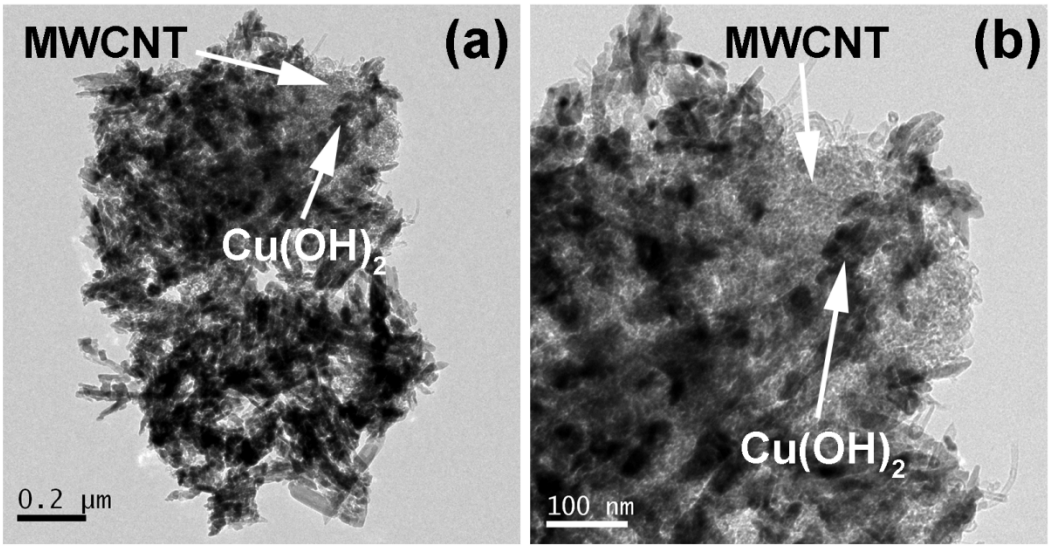


Figure S4: TEM images of $Cu(OH)_2$/MWCNT-50:50 composite. Clusters of short nanorod bundles of $Cu(OH)_2$ are formed from partial destruction of the flower like grains by hand grinding. An intimate attachment of MWCNT over $Cu(OH)_2$ is observed which would provide an enhanced intra-grain and inter-grain electron transport. At the same time, MWCNT would also act as a buffer matrix to absorb the volume changes associated with the conversion reactions.

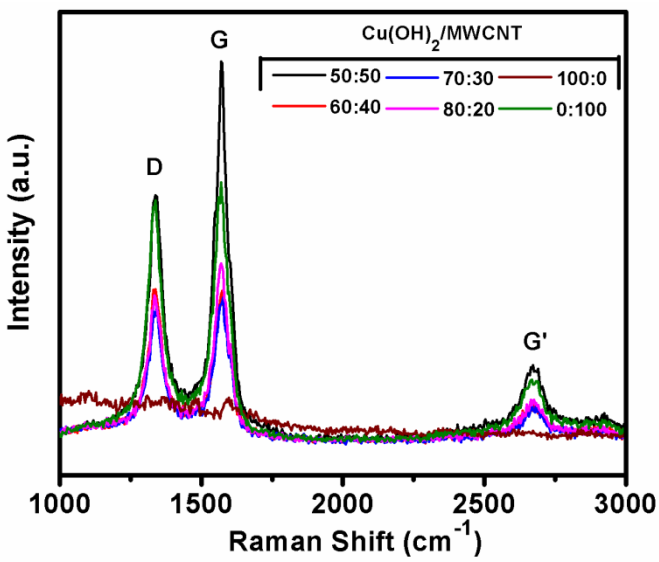


Figure S5: Raman spectra of $Cu(OH)_2$/MWCNT composites. The G band (1570 cm^{-1}) is related to the presence of sp^2-hybridized carbon and corresponds to the E_{2g} phonons. The D band (1340 cm^{-1}) is originated from disordered graphitic carbon due to the breathing modes of six-atom rings and requires a defect for its activation. The G′ band (2670 cm^{-1}) is actually the second order D peak. From the intensity ratio I_D/I_G and $I_{G'}/I_G$, the relative degree of crystallographic disorder/defects can be estimated[5,6]. $Cu(OH)_2$/MWCNT-50:50 shows the lowest I_D/I_G and $I_{G'}/I_G$ among all the composites indicating lowest concentration of structural disorder/defects.

Table S1: Raman spectroscopy data for $Cu(OH)_2$/MWCNT composites

Sample Name	I_D/I_G	I_G'/I_G
$Cu(OH)_2$/MWCNT-50:50	0.64	0.21
$Cu(OH)_2$/MWCNT-60:40	0.99	0.30
$Cu(OH)_2$/MWCNT-70:30	0.94	0.28
$Cu(OH)_2$/MWCNT-80:20	0.82	0.26
MWCNT	0.93	0.25

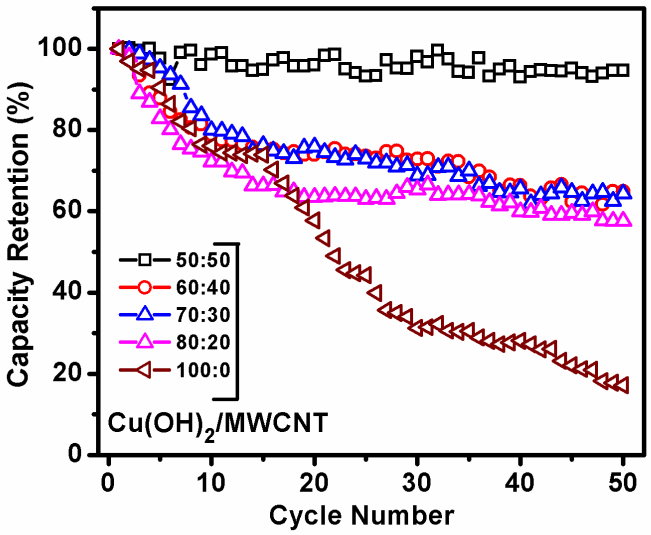


Figure S6: Capacity retention for different composites of $Cu(OH)_2$/MWCNT. Capacity retention increases with the increasing amount of MWCNT in the composite. The capacity retention is maximum (~ 95%) when $Cu(OH)_2$/MWCNT ratio is 50:50. Other composites of $Cu(OH)_2$/MWCNT (80:20, 70:30 and 60:40) show about 60-65% of capacity retention whereas, the pristine $Cu(OH)_2$ retains only 16 % capacity after 50 cycles.

Table S2: Impedance spectroscopy data of $Cu(OH)_2$/MWCNT-50:50 composite anode after different cycling intervals

$Cu(OH)_2$/MWCNT-50:50 (At different cycling intervals)	Rs (Ohm)	Rct (Ohm)	Q		W (mMho)	C (mF)
			Y_0 (μMho)	N		
As assembled state	1.3	70.5	12.4	0.851	20.0	22.5
After 1st cycle	1.4	101	32.0	0.753	11.1	19.1
After 20th cycle	1.9	50.1	86.2	0.65	12.0	17
After 40th cycle	3.1	34.9	98.2	0.59	13.3	16.5
After 60th cycle	3.5	37.3	103.2	0.44	9.96	15.8
After 80th cycle	4.0	42.8	144.4	0.37	11.3	12.8
After 100th cycle	4.9	41.9	142.7	0.39	10.2	14.7

References:

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