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Ultrafine Ternary Metal Oxide Particle with Carbon Nanotubes: Metal-Organic-Framework-Based Approach and Superior Lithium-Storage Performance

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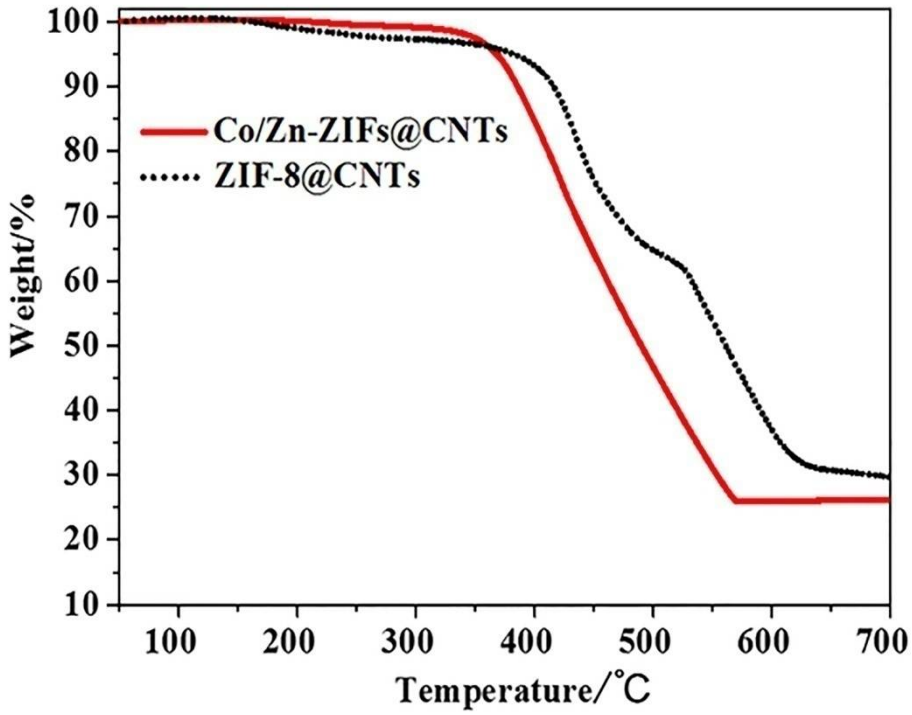

Fig. S1. TGA curves of ZIF-8@CNTs and Co/Zn-ZIFs@CNTs in air with 5 ^{o}C min^{-1}.

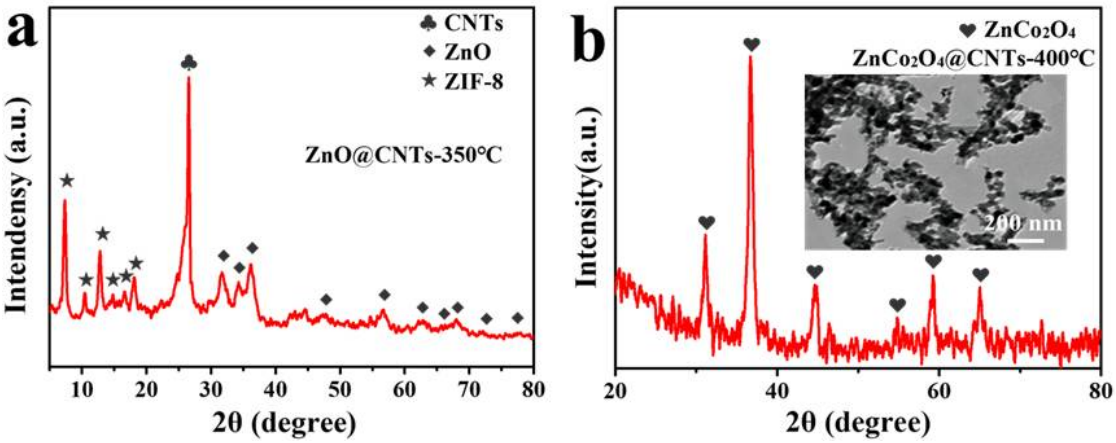

Fig. S2. XRD patterns for (a) ZnO@CNTs-350°C and (b) $ZnCo_2O_4$@CNTs-400°C (the insert is the SEM image of $ZnCo_2O_4$@CNTs-400°C).

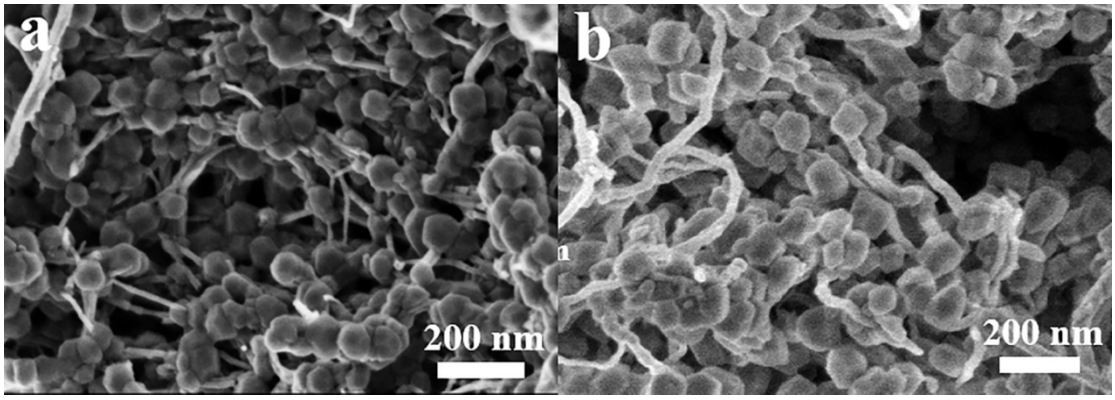

Fig. S3. SEM images of (a) ZIF-8@CNTs and (b) Co/Zn-ZIFs@CNTs.

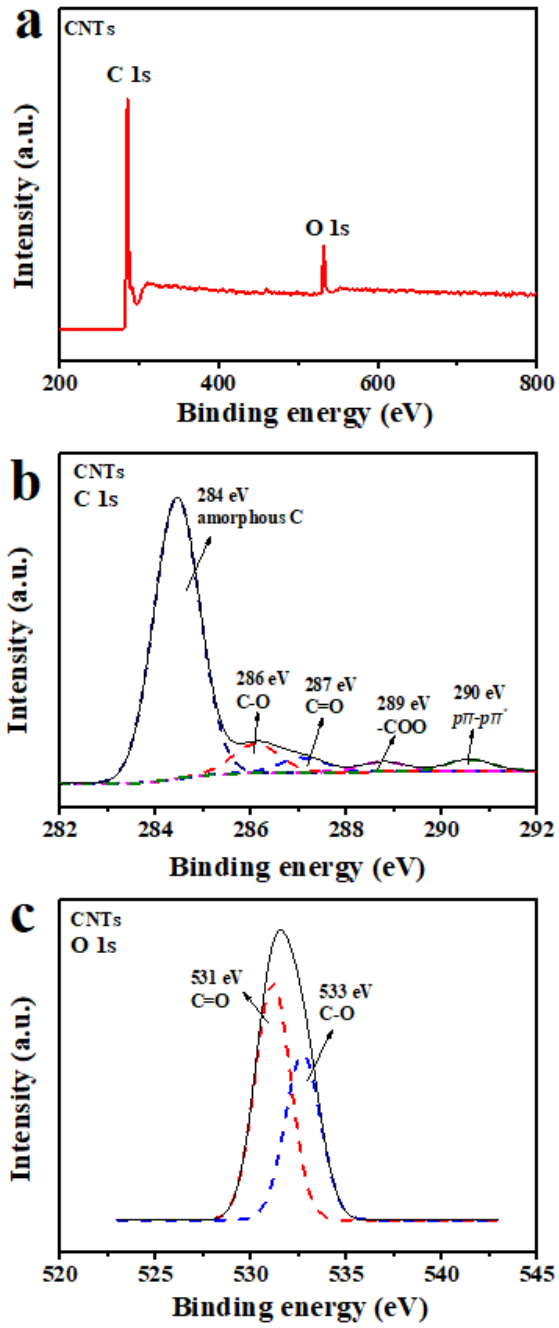

Fig. S4. (a) XPS survey spectrum of the CNTs. High-resolution XPS spectra of (b) C 1s and (c) O 1s for the CNTs.

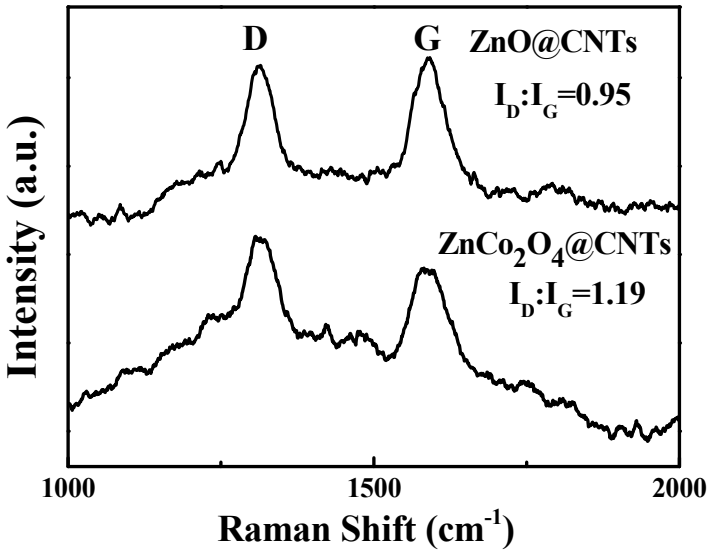

Fig. S5. Raman spectra of ZnO@CNTs and $ZnCo_2O_4$@CNTs composites

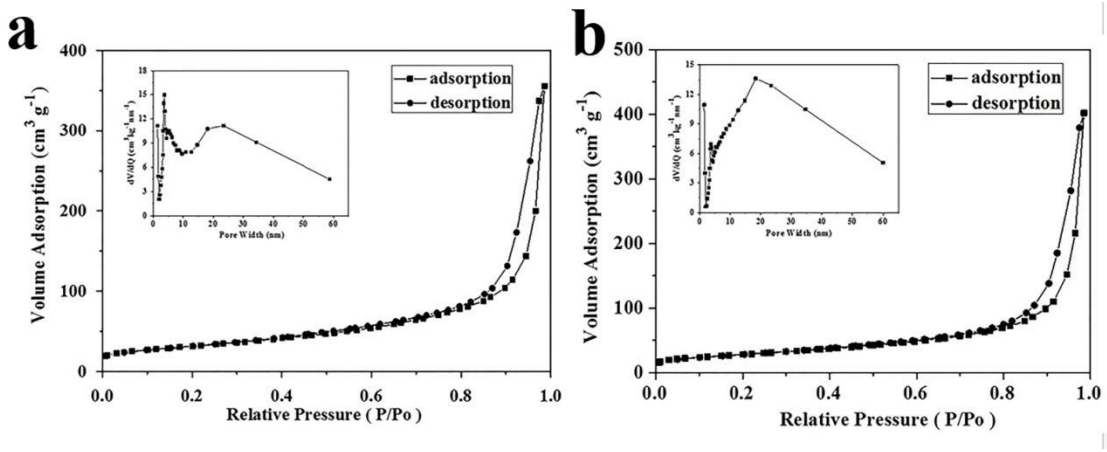

Fig. S6. Nitrogen adsorption-desorption isotherm and pore size distribution curves (a) ZnO@CNTs composite and (b) $ZnCo_2O_4$@CNTs composite

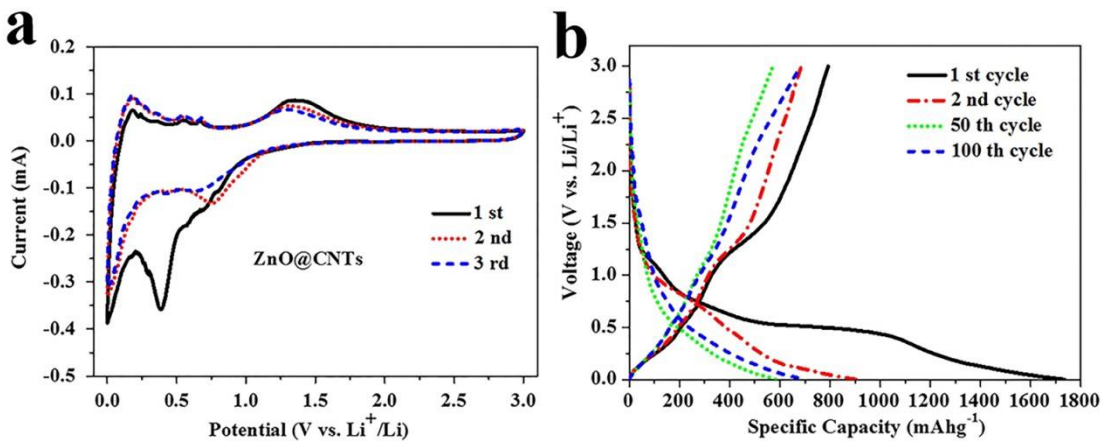

Fig. S7. (a) The first three cyclic voltammetry curves of ZnO@CNTs at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.005-3 V, (b) the discharge/charge curve of ZnO@CNTs at current density of 100 mA g^{-1} for the 1^{st}, 2^{nd}, 50^{th}, and 100^{th} cycles, A broad and strong cathodic peak located at 0.43 V can be observed in the lithium insertion scan of the first cycle CV curve, which can be assigned to the reduction of ZnO to metallic Zn and the formation of Zn-Li alloys together with the generation of solid electrolyte interphase (SEI) layers. In the first anodic sweep, some oxidation peaks in the potential range of 0.2-0.8 V, which can be attributed to the multistep dealloying process of Li-Zn alloy, The discharge/charge curves are in accordance with the results of CV.

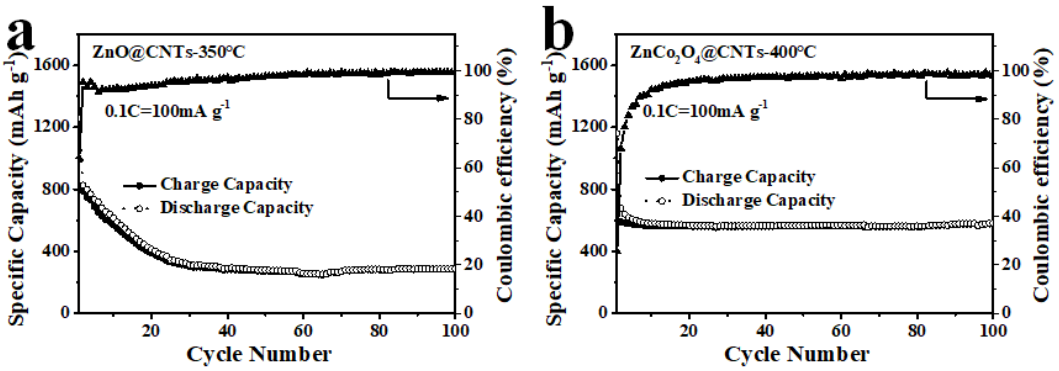

Fig. S8. Cycling performances of (a) ZnO@CNTs-350°C and (b) $ZnCo_2O_4$@CNTs-400 °C.

Table S1. CHN elemental analysis results of $ZnCo_2O_4$@CNTs and ZnO@CNTs

materials	**C (wt%)**	**N (wt%)**	**H (wt%)**	**S (wt%)**
$ZnCo_2O_4$@CNTs	39.56	0	0.121	0
ZnO@CNTs	50.02	0	0.35	0

Table S2 Compositions determination of $ZnCo_2O_4$@CNTs and ZnO@CNTs based on EDS and XPS results.

Samples	Compositions	XPS results
$ZnCo_2O_4$@CNTs	C (39.7 %)	Co-C/Zn-C (283.8 eV), C=C (285.1 eV), C-O (287.2 eV)
	Co (28.6 %)	Co $2p_{3/2}$ (641.3 eV), Co $2p_{1/2}$ (653.1 eV)
	Zn (16.3 %)	Zn $2p_{3/2}$ (1020.0 eV), Zn $2p_{1/2}$ (1043.0 eV)
	O (15.4 %)	Co-O (528.7 eV), Zn-O (530.8 eV), C-O (531.7 eV)
ZnO@CNTs	C (50.9 %)	Zn-C (283.4 eV), C=C (284.7 eV), C-O (286.3 eV)
	Zn (39.2 %)	Zn $2p_{3/2}$ (1020.0 eV), Zn $2p_{1/2}$ (1043.0 eV)
	O (9.8 %)	Zn-O (530.1 eV), C-O (531.6 eV)

Table S3. Electrochemical properties comparison between $ZnCo_2O_4$@CNTs and ZnO@CNTs electrodes in this work and previous reported $ZnCo_2O_4$-involved electrode materials.

Composite	morphology	IRC	RRC/CN	CD	Reference
$ZnCo_2O_4$@CNTs	Nanocrystal embedded into CNTs	1550	1507/200	100	This work
ZnO@CNTs	Polyhedron on CNTs	792	935/200	100	This work
$ZnCo_2O_4$/CNTs	Nanoparticle-assembled polyhedron with CNTs	1050	~870/150	100	1
$ZnCo_2O_4$@C	wrinkled-paper-like 3D structure	~810	~520/50	100	2
$ZnCo_2O_4$/CNFs	Nanocube on CNFs	~750	~600/300	500	3
$ZnCo_2O_4$/CNFs	Urchin on CNFs	~1150	~1100/100	180	4
$ZnCo_2O_4$/carbon cloth	Nanowire on carbon cloth	~1300	~1180/160	200	5
$ZnCo_2O_4$/ graphene	Nanoparticle on graphene	~950	~1100/90	90	6
$ZnCo_2O_4$/ graphene	Microsphere on graphene	854	~900/500	1000	7
$ZnCo_2O_4$/ graphene	Nanosheet on graphene	936	~930/100	90	8
$ZnCo_2O_4$/ graphene	Nanosheet on graphene	813	791/1000	1000	9
$ZnCo_2O_4$/graphene/CNTs	Peanut-like particle on graphene and CNTs	~902	1027/200	500	10
$ZnCo_2O_4$	Microsphere	1123	~1000/100	100	11
$ZnCo_2O_4$	Flower-like microsphere	~1110	~900/100	100	12
$ZnCo_2O_4$	Flower-like microsphere	1177	~1100/50	100	13
$ZnCo_2O_4$	Microsphere	869	~835/50	400	14
$ZnCo_2O_4$	Plum candy-like microsphere	950	~1000/110	200	15
$ZnCo_2O_4$	Microsphere	1205	~1200/100	100	16
$ZnCo_2O_4$	Yolk-shell microsphere	~1000	~910/100	200	17
$ZnCo_2O_4$	Twin microsphere	~1050	~800/100	1000	18
$ZnCo_2O_4$	Rose-like spherical particle	980	~1000/50	50	19
$ZnCo_2O_4$	Nanorod	1515	1663/200	500	20
$ZnCo_2O_4$	Nanorod	~1200	~800/50	100	21
$ZnCo_2O_4$	Nanowire	~1100	1220/20	100	22
$ZnCo_2O_4$	Nanowire	1068	~1000/100	100	23
$ZnCo_2O_4$	Nanotube	1200	1400/30	100	24
$ZnCo_2O_4$	Nanoflake	1020	750/25	80	25

$ZnCo_2O_4$	Nanosheet	~1086	~930/200	200	26
$ZnCo_2O_4$	Nanoribbon	1752	1422/80	200	27
$ZnCo_2O_4$	Microsphere	1388	~1297/200	100	28
$ZnCo_2O_4$	Nanoflake	~1639	~1138/500	1000	29
$ZnCo_2O_4$	Nanosheet	936	810/200	1000	30
$ZnCo_2O_4$	Nanorod	1118	1051/200	400	31
$ZnCo_2O_4$	Nanoparticle	2023	1243/80	100	32
$ZnCo_2O_4$	Nanoparticle	~880	1000/120	450	33
$ZnCo_2O_4$	Core-shell sphere	~585	511/400	1000	34
$ZnCo_2O_4$	Hollow octahedral nanocage	1131	1025/200	200	35
$ZnCo_2O_4$	Nanosheet	1274	1641/50	100	36
$ZnCo_2O_4$	Particle	1110	700/100	100	37

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