A New Approach to Facilely Synthesize Crystalline $Co_2(OH)_3Cl$ Microstructures in Eggshell Reactor Systems

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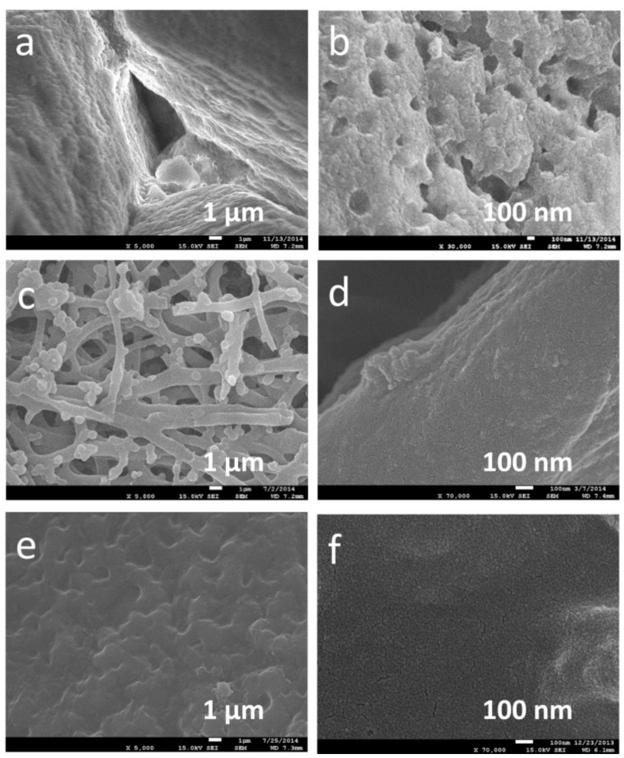
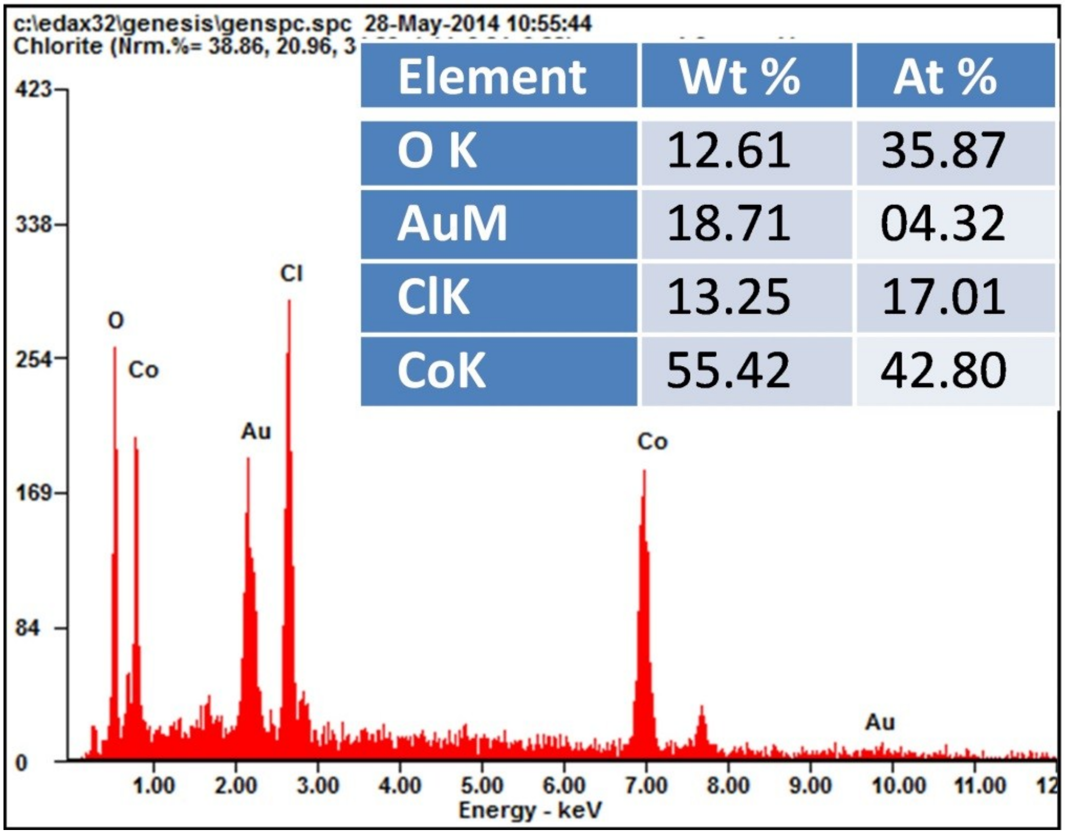


Figure S1. Eggshell characterization: FESEM images of (a, b) porous eggshell with pores visible; (c, d) outer layer eggshell membrane; (e, f) inner layer eggshell membrane at (a, c, e) high and (b, d, f) low magnification views, as previously observed.[1]



Element	Wt %	At %
O K	12.61	35.87
AuM	18.71	04.32
ClK	13.25	17.01
CoK	55.42	42.80

Figure S2. EDS analysis of typical $Co_2(OH)_3Cl$ microparticles obtained from the eggshell reactor system. Reaction time was 3 days; other experimental conditions unchanged.

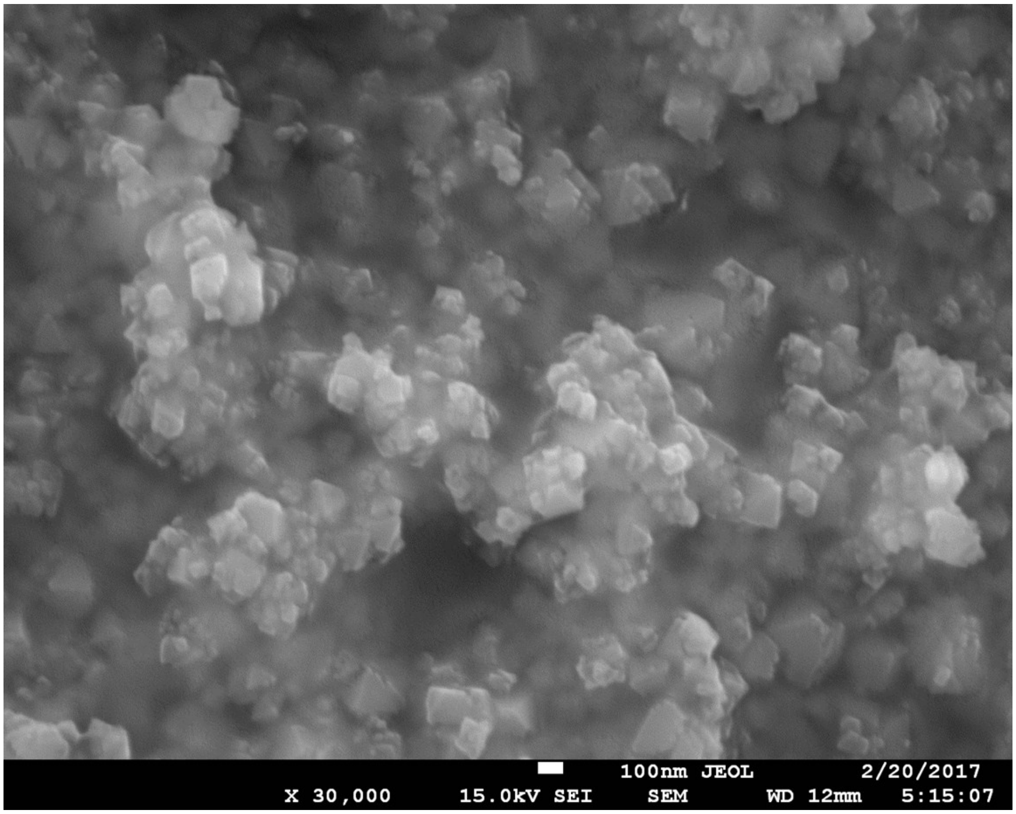


Figure S3. FESEM image of the particles obtained from a control experiment where the aqueous solutions of 30 ml 1 M $CoCl_2$ with 10 mM surfactant CTAB and 30 ml 1 M NaOH were directly mixed and stirred in a beaker and then kept at 50 ^oC for 5 days without stirring. Note, the $Co_2(OH)_3Cl$ nanoparticles obtained in the control experiment are significantly smaller as compared to those crystalline $Co_2(OH)_3Cl$ microparticles obtained in our eggshell reactor system, indicating the important role played by eggshell reactor system in facilitating the formation and growth of crystalline $Co_2(OH)_3Cl$ microstructures.

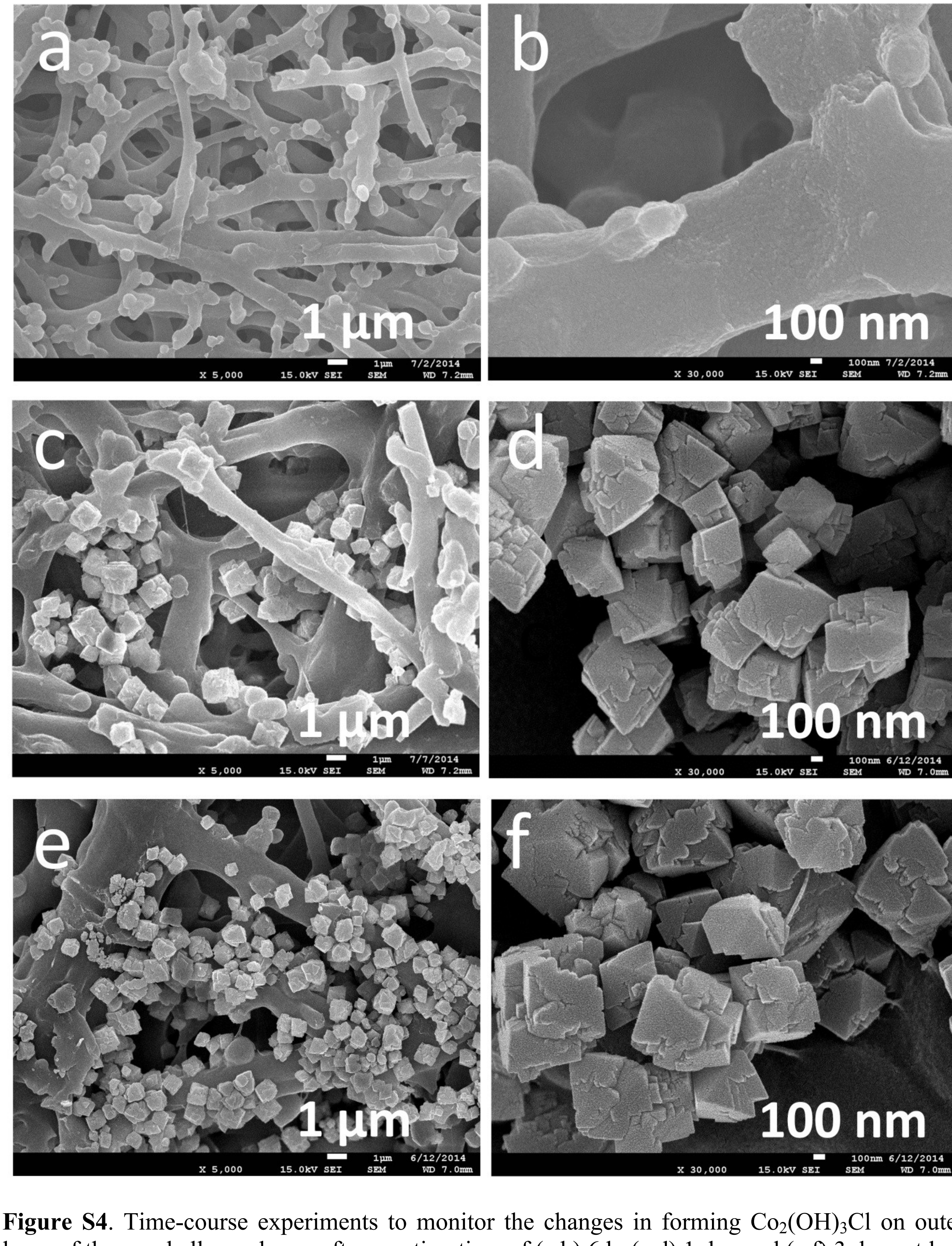


Figure S4. Time-course experiments to monitor the changes in forming $Co_2(OH)_3Cl$ on outer layer of the eggshell membrane after reaction time of (a,b) 6 h, (c,d) 1 day and (e,f) 3 days at low (a,c,e) and high (b,d,f) magnification views.

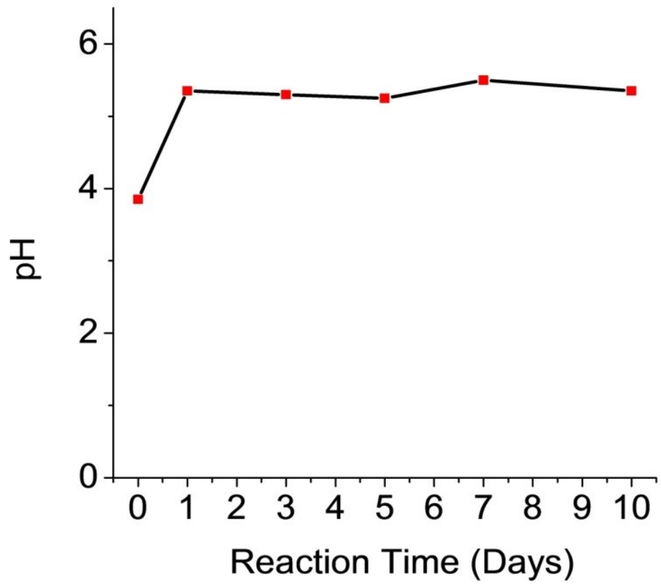


Figure S5. The pH measured along with time inside of the eggshell reactor.

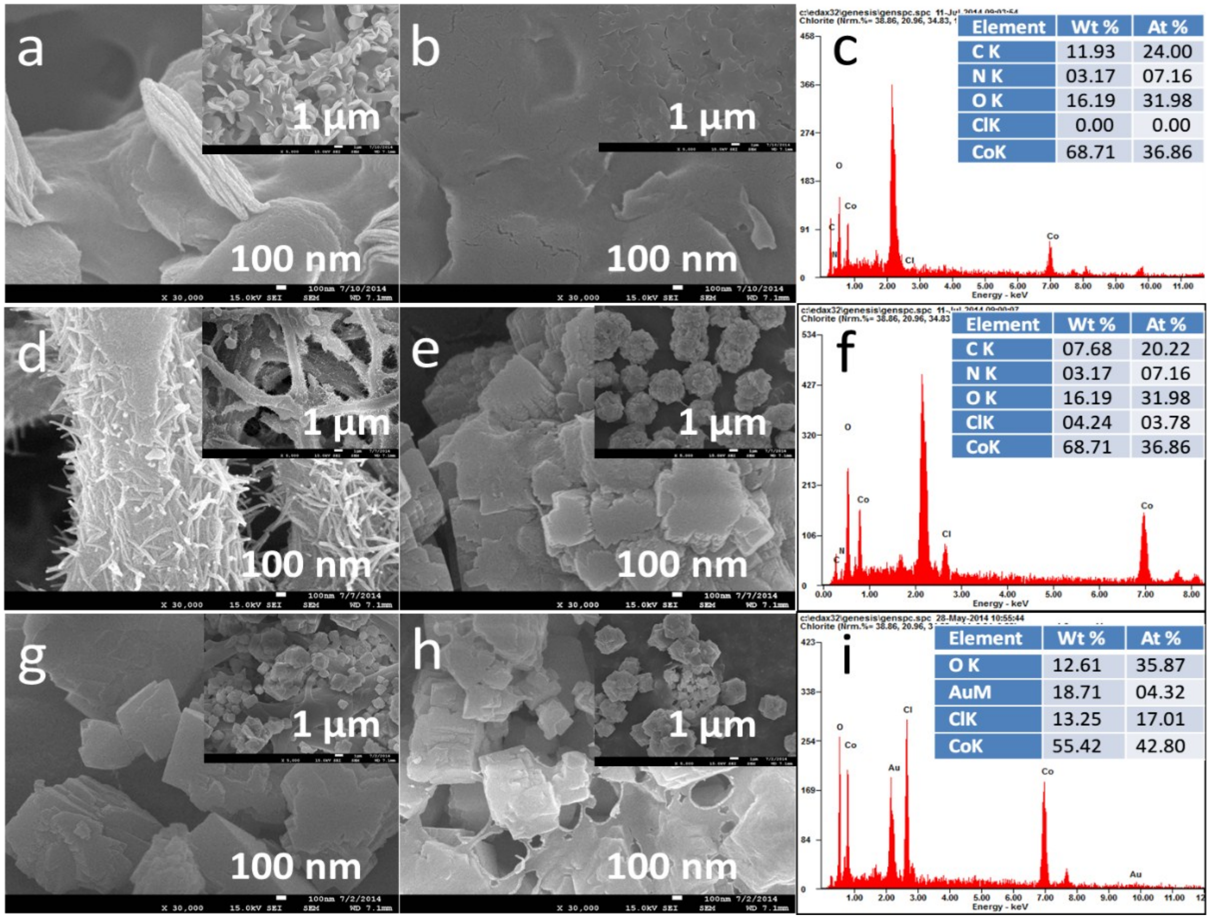


Figure S6. FESEM images and EDS results of solid products obtained from the eggshell reactor systems after 3 days of reaction where the concentration of $CoCl_2$ solution was changed while kept other experimental parameter unchanged: (a, b, c) 0.01 M $CoCl_2$, (d, e, f) 0.25 M $CoCl_2$, and (g, h, i) 1 M $CoCl_2$ solution. To be noted here, the concentration of $CoCl_2$ inside the eggshell reactor is critically important which could determine the morphology and composition of the products obtained.

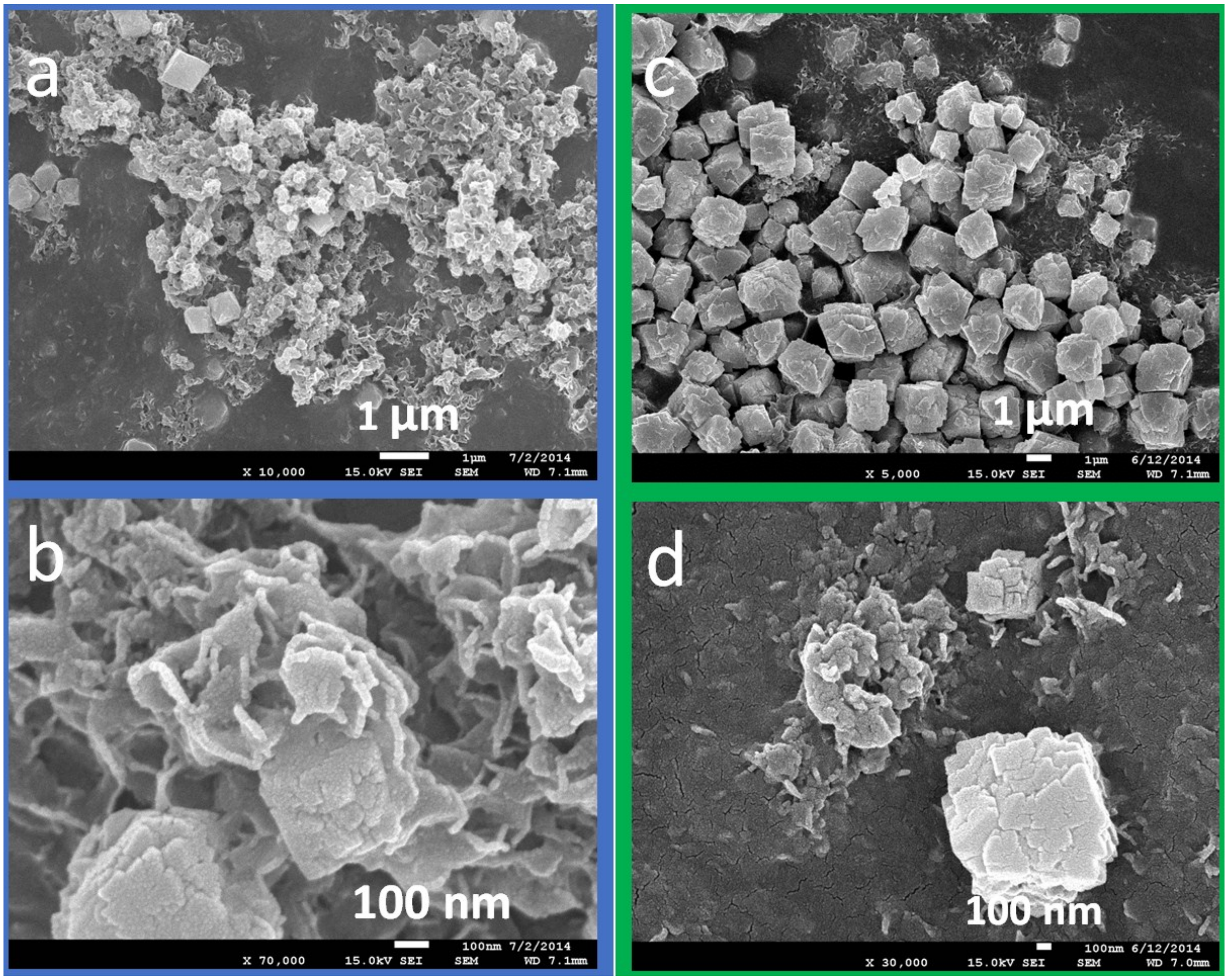


Figure S7. Additional FESEM images for the samples obtained after different reaction time inside the eggshell reactor system at various degrees of magnification: (a,b) after 12 hours; (c,d) after 24 hours at low (a,c) and high (b,d) magnification views.

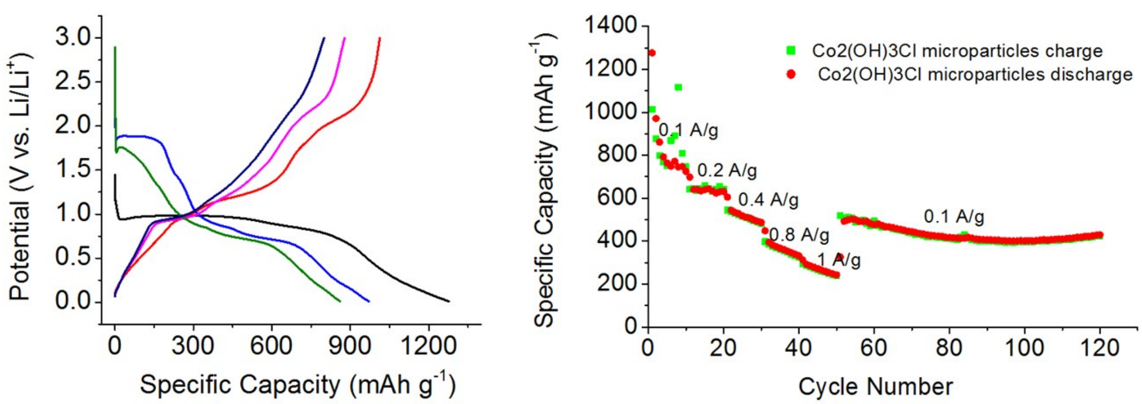


Figure S8. Electrochemical performance of the as-prepared $Co_2(OH)_3Cl$ microstructures collected from the eggshell reactor system: (left) first three cycle charge-discharge profiles; (right) capacity vs cycle number plots tested at various current conditions.

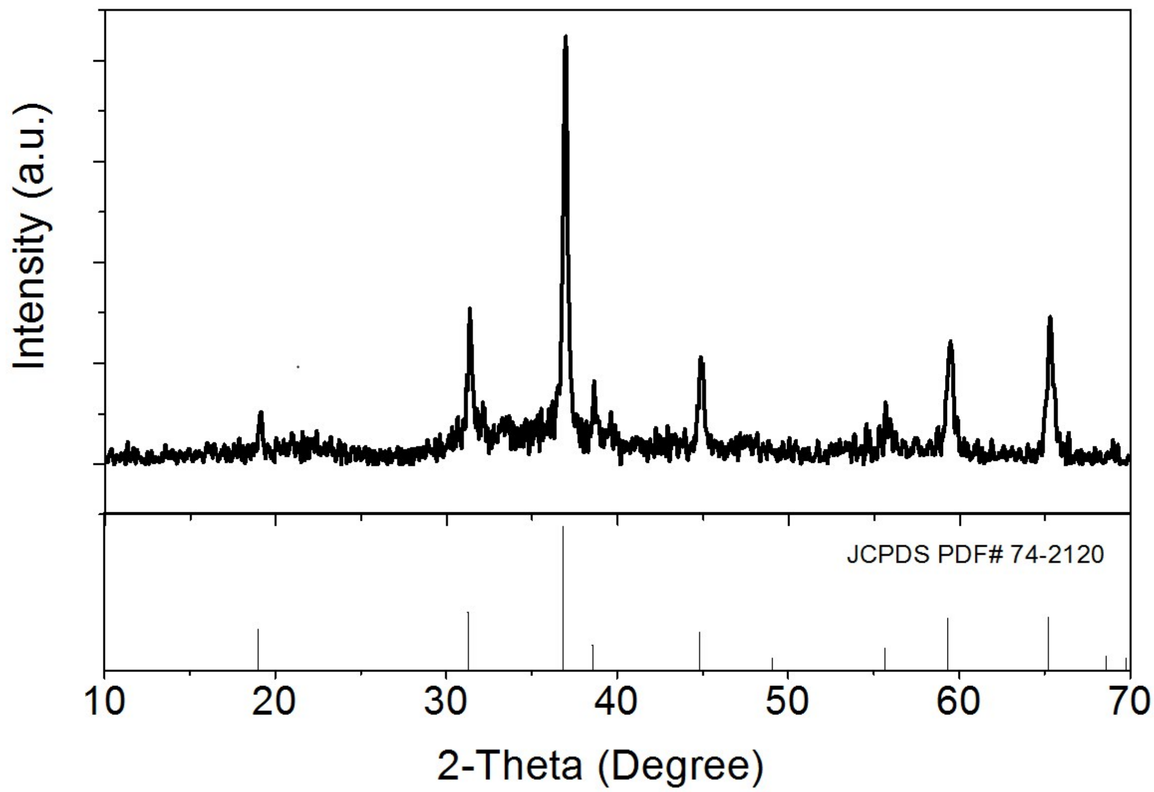


Figure S9. XRD pattern of Co_3O_4 derived from $Co_2(OH)_3Cl$ microstructures after calcination at 450 ^oC in air for 2 h.

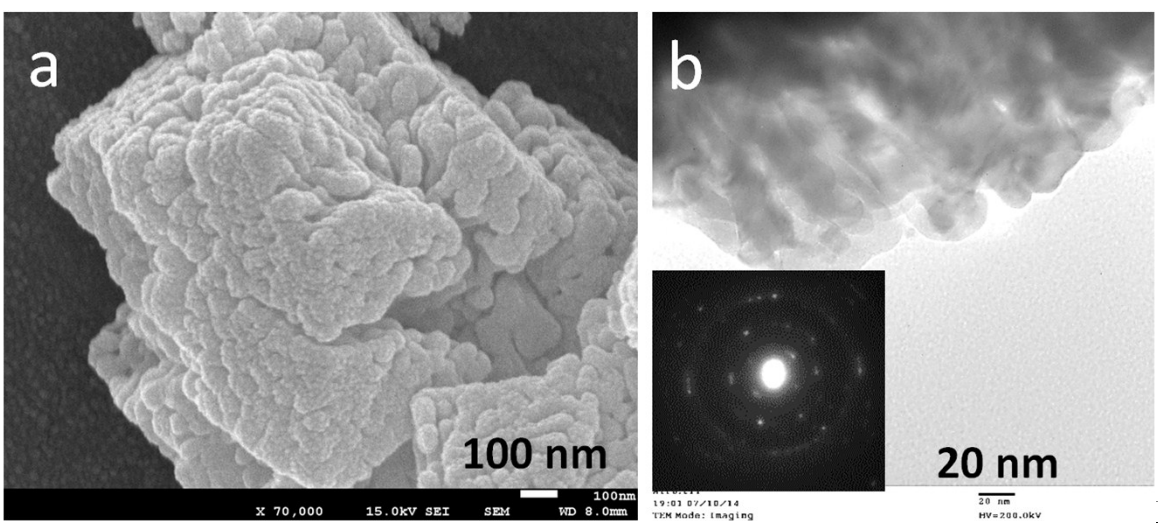


Figure S10. (a) SEM and (b) TEM characterization of the Co_3O_4 microstructures derived from $Co_2(OH)_3Cl$ microparticles after calcination at 450 ^oC in air for 2 h. Inset of (b) is SAED which agrees with XRD analysis.

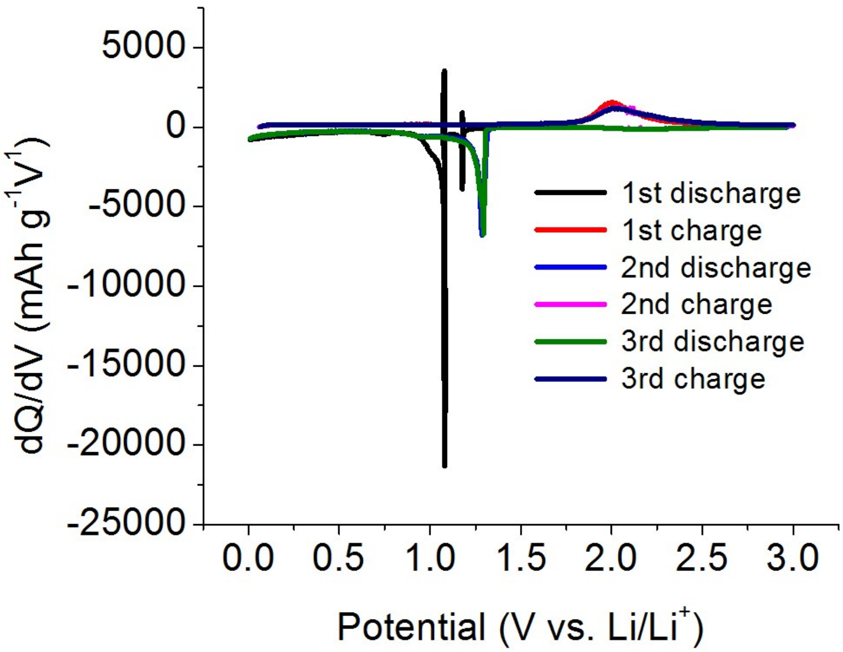


Figure S11. The dQ/dV vs V plots for the first three cycles of the as-derived nanoporous Co_3O_4 microstructures with nanopores.

Table S1. *Summaries of reported battery performances of Co_3O_4 reported in the literature.*

Morphologies	**Methods**	**Specific capacities**	**Current densities**	**Cycles**	**Ref**
nanofibers	Hydrothermal	937 mAh/g	100 mA/g	150	[2]
mesoporous cubes	Hydrothermal	1010 mAh/g	0.1 C	60	[3]
nanoparticles with C	Hydrothermal	888.8 mAh/g	0.2 C	80	[4]
mesoporous nanoflakes	Microwave assisted	806 mAh/g	0.1 C	300	[5]
mesoporous flakes	Hydrothermal	1115 mAh/g	0.05 C	100	[6]
mesoporous particles	Hydrothermal	913 mAh/g	200 mA/g	60	[7]
nanowire arrays	Hydrothermal	1031 mAh/g	100 mA/g	100	[8]
hierarchical star-like	Hydrothermal	1200 mA h/g	50 mA/g	100	[9]
High-order microstructured	*Eggshell reactor and calcination*	*900 mAh/g*	*100 mAh/g*	*110*	*This work*

References:

1. (a) Meng, X.; Deng, D., Trash to Treasure: Waste Eggshells as Chemical Reactors for the Synthesis of Amorphous $Co(OH)_2$ Nanorod Arrays on Various Substrates for Applications in Rechargeable Alkaline Batteries and Electrocatalysis. *ACS Applied Materials & Interfaces* **2017,** *9* (6), 5244-5253; (b) Meng, X.; Deng, D., Trash to Treasure: Waste Eggshells Used as Reactor and Template for Synthesis of Co_9S_8 Nanorod Arrays on Carbon Fibers for Energy Storage. *Chemistry of Materials* **2016,** *28* (11), 3897-3904.
2. Tan, Y.; Gao, Q.; Li, Z.; Tian, W.; Qian, W.; Yang, C.; Zhang, H., Unique 1D Co_3O_4 crystallized nanofibers with (220) oriented facets as high-performance lithium ion battery anode material. *Scientific reports* **2016,** *6*.
3. Huang, G.; Xu, S.; Lu, S.; Li, L.; Sun, H., Micro-/nanostructured Co_3O_4 anode with enhanced rate capability for lithium-ion batteries. *ACS applied materials & interfaces* **2014,** *6* (10), 7236-7243.
4. Mujtaba, J.; Sun, H.; Huang, G.; Mølhave, K.; Liu, Y.; Zhao, Y.; Wang, X.; Xu, S.; Zhu, J., Nanoparticle decorated ultrathin porous nanosheets as hierarchical Co_3O_4 nanostructures for lithium ion battery anode materials. *Scientific reports* **2016,** *6*, 20592.
5. Chen, S.; Zhao, Y.; Sun, B.; Ao, Z.; Xie, X.; Wei, Y.; Wang, G., Microwave-assisted synthesis of mesoporous Co_3O_4 nanoflakes for applications in lithium ion batteries and oxygen evolution reactions. *ACS applied materials & interfaces* **2015,** *7* (5), 3306-3313.
6. Su, D.; Xie, X.; Munroe, P.; Dou, S.; Wang, G., Mesoporous hexagonal Co_3O_4 for high performance lithium ion batteries. *Scientific reports* **2014,** *4*, 6519.
7. Li, C.; Chen, T.; Xu, W.; Lou, X.; Pan, L.; Chen, Q.; Hu, B., Mesoporous nanostructured Co_3O_4 derived from MOF template: a high-performance anode material for lithium-ion batteries. *Journal of Materials Chemistry A* **2015,** *3* (10), 5585-5591.
8. Zhan, L.; Wang, S.; Ding, L.-X.; Li, Z.; Wang, H., Grass-like Co_3O_4 nanowire arrays anode with high rate capability and excellent cycling stability for lithium-ion batteries. *Electrochimica Acta* **2014,** *135*, 35-41.
9. Li, L.; Seng, K. H.; Chen, Z.; Guo, Z.; Liu, H. K., Self-assembly of hierarchical star-like Co_3O_4 micro/nanostructures and their application in lithium ion batteries. *Nanoscale* **2013,** *5* (5), 1922-1928.