Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

The formation mechanism of fibrous metal oxalate prepared by ammonia coordination method

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Experiment

Synthesis of nickel oxalate dihydrate without ammonia: 50 mL of 0.2 mol/L nickel chloride solution and 50 mL of 0.2 mol/L sodium oxalate solution were simultaneously pumped into a three-neck flask containing 25 mL DI water with a speed of 1 mL/min at 80 ℃. After aging for 4 h, green nickel oxalate dihydrate powders were obtained.

Synthesis of fibrous nickel oxalate through nickel oxalate dihydrate suspension (Figure S5): 0.7 g of nickel oxalate dihydrate was dispersed in 25 mL DI water and then 50 mL of 1.2 mol/L ammonia solution was pumped into the suspension with a pump rate of 1 mL/min at 80 ℃. After aging for 1 h, fibrous nickel oxalate was obtained.

Figures

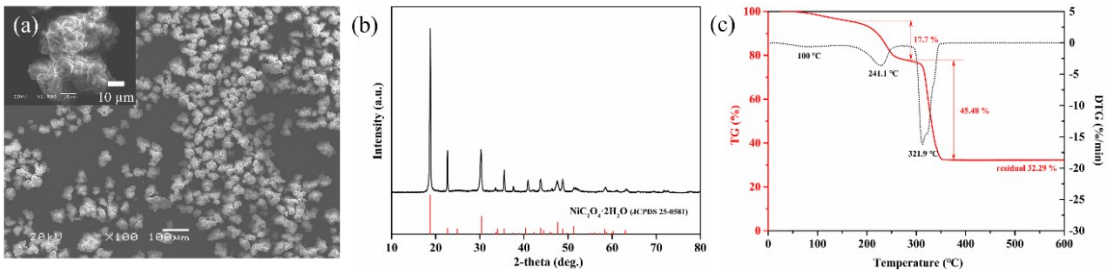

Figure S1. (a) SEM image of nickel oxalate prepared without ammonia (inset shows high magnification SEM image of one nickel oxalate particle). (b) XRD pattern of nickel oxalate prepared without ammonia. (c) thermogravimetric (TG, solid line) and thermogravimetric derivative (DTG, dotted line) curves for the nickel oxalate.

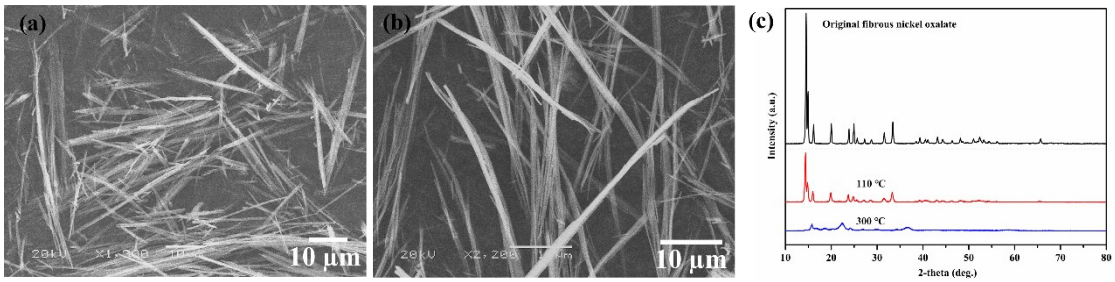

Figure S2. (a) SEM image of fibrous nickel oxalate after heating at 110 ℃ for 1 h under an argon atmosphere. (b) SEM image of fibrous nickel oxalate after heating at 300 ℃ for 1 h under an argon atmosphere. (c) XRD patterns of fibrous nickel oxalate after heating at 110 ℃ or 300 ℃ for 1 h under an argon atmosphere.

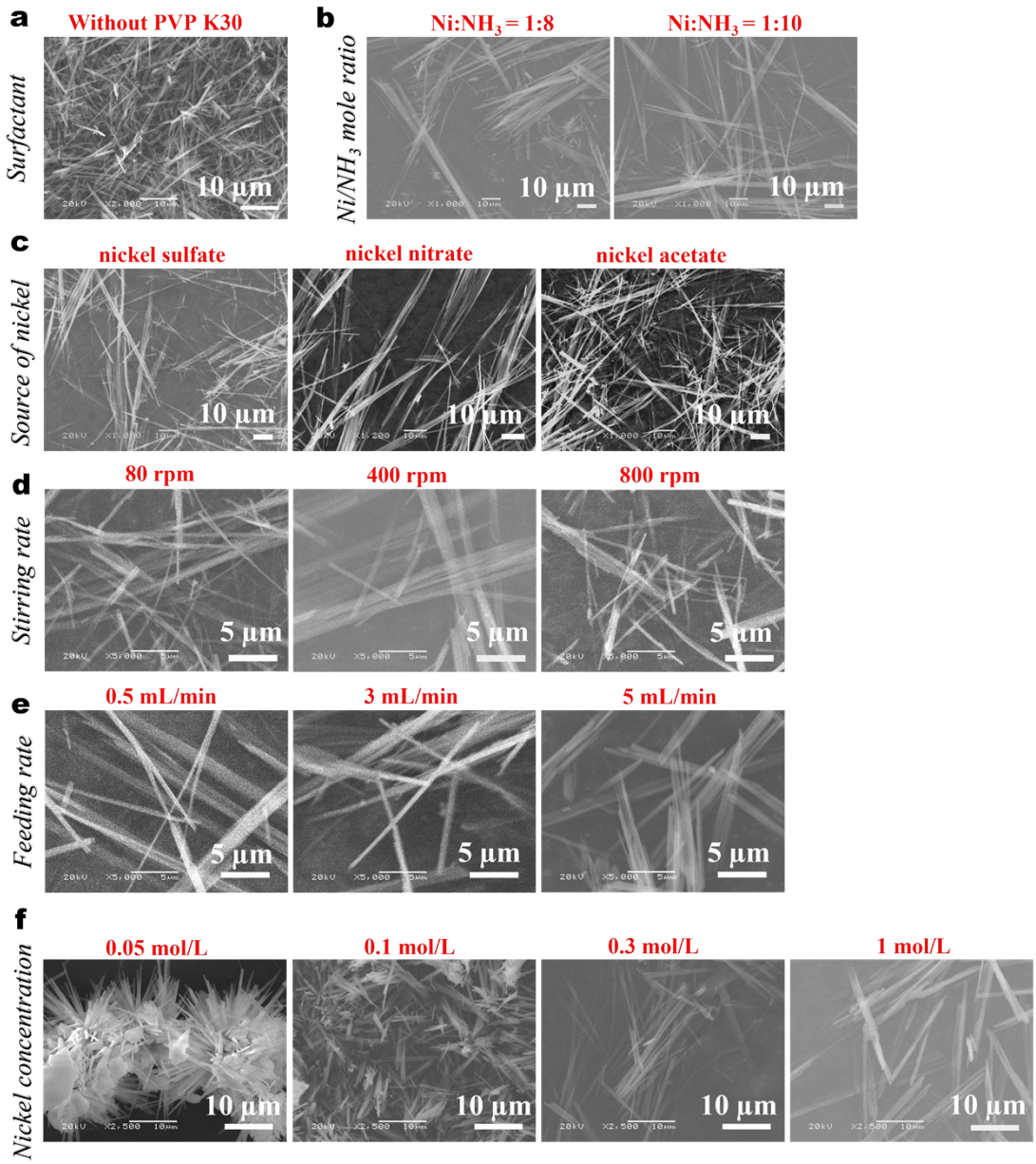

Figure S3. Influence of different factors on the morphology of nickel ammine oxalate. (a) surfactant of PVP K30. (b) nickel/ammonia mole ratio. (c) source of nickel ions. (d) stirring rate. (e) feeding rate. (f) nickel concentration.

Experiment:

(a) Sample was prepared without surfactant PVP K30 while other experiment conditions were kept consistent with the typical experiment.

(b-f) In these experiments, reaction temperature and solution pH were set at 90 ℃ and 9.0 respectively. Other experiment conditions were kept consistent with the typical experiment except the stduied factors.

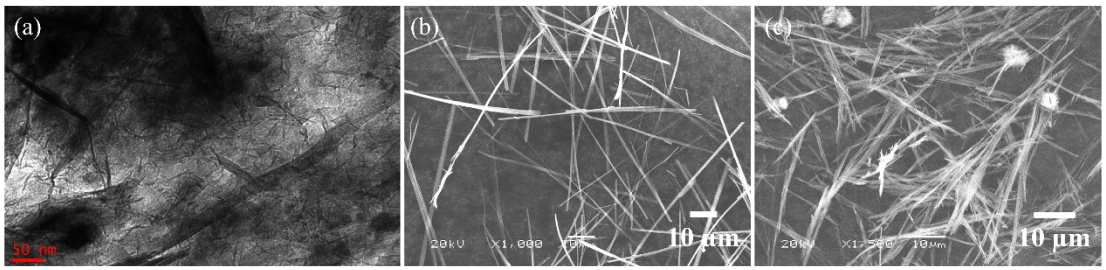

Figure S4. (a) High magnification TEM image of the bar-like nickel oxalate shows tiny fibrous particles existed on its surface. (b) SEM image of fibrous nickel oxalate formed from the reacted solutions collected in T = 25 °C experiment. (c) SEM images of fibrous nickel oxalate prepared at 50 ℃ with the aging time of 9 h.

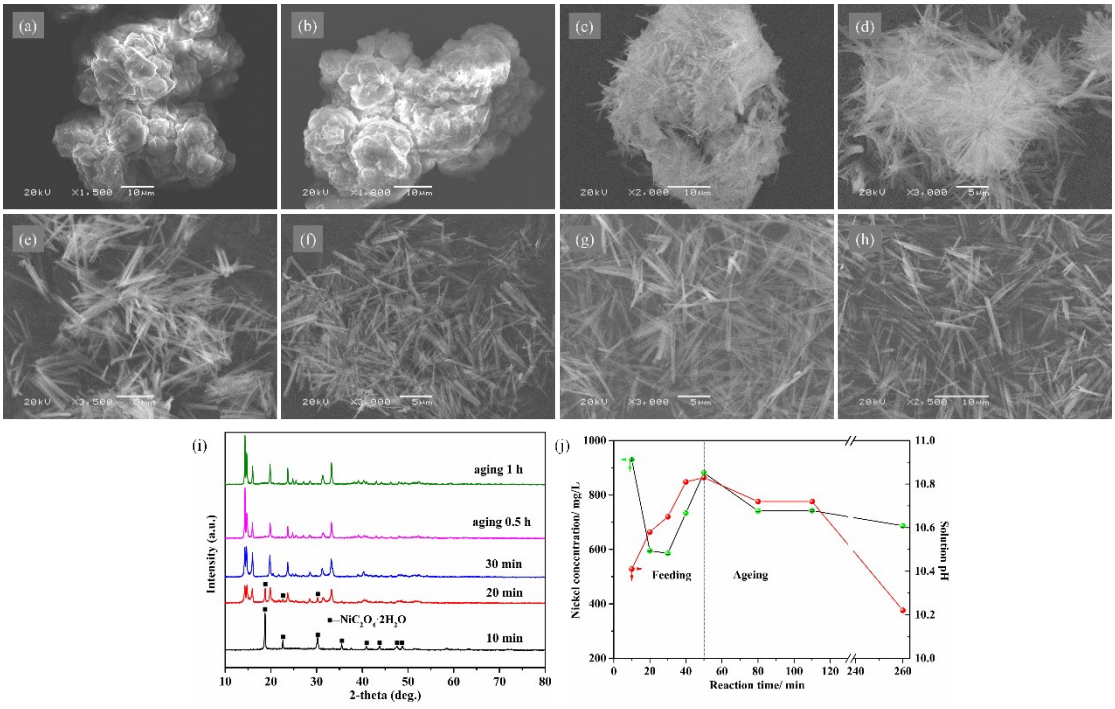

Figure S5. (a-h) SEM images of solid products at different time obtained by pumping ammonia solutions into a suspension of nickel dihydrate: (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) aging of 30 min and (h) aging of 1 h. (i) XRD patterns of solid products at different time obtained by pumping ammonia solutions into a suspension of nickel dihydrate. (j) plot shows the changes of nickel concentration and pH with time in the reaction solutions during the whole process.

Table

Table S1 Selected bond lengths [Å] and angles [°] for the synthesized blue crystal.

Atoms	Dist	Atoms	Dist	Atoms	Dist
Ni(1)-N(1)#1	2.0761(15)	Ni(1)-N(1)	2.0762(15)	Ni(1)-O(1)#1	2.0852(8)
Ni(1)-O(1)#2	2.0852(8)	Ni(1)-O(1)#3	2.0852(8)	Ni(1)-O(1)	2.0852(8)
O(1)-C(1)	1.2478(11)	N(1)-H(2A)	0.8900	N(1)-H(2B)	0.8900
N(1)-H(2C)	0.8900	N(1)-H(2A)#2	0.890(18)	N(1)-H(2B)#2	0.890(10)
N(1)-H(2C)#2	0.890(7)	C(1)-C(1)#4	1.567(3)		
Atoms	Angles	Atoms	Angles	Atoms	Angles
N(1)#1-Ni(1)-N(1)	180.0	N(1)#1-Ni(1)-O(1)#1	90.45(4)	N(1)-Ni(1)-O(1)#1	89.55(4)
O(1)#1-Ni(1)-O(1)#2	80.46(4)	O(1)#1-Ni(1)-O(1)#3	99.54(4)	O(1)#2-Ni(1)-O(1)#3	180.0
C(1)-O(1)-Ni(1)	112.94(7)	Ni(1)-N(1)-H(2A)	109.5	H(2A)-N(1)-H(2B)	109.5
H(2A)-N(1)-H(2A)#2	78.8	H(2B)-N(1)-H(2A)#2	134.2	H(2C)-N(1)-H(2A)#2	33.2
Ni(1)-N(1)-H(2C)#2	109.47(17)	O(1)#5-C(1)-O(1)	126.34(14)	O(1)-C(1)-C(1)#4	116.83(7)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z; #2 x,-y+2,z; #3 -x,y,-z; #4 -x,-y+1,-z; #5 x,-y+1,z.