

Electronic Supplementary Information

A general method to prepare transition-metal ammonium phosphate nanoflake constructed microspheres

Changfeng Zeng,^a Wei Wei^b and Lixiong Zhang^b

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a College of Mechanic and Power Engineering, Nanjing University of Technology, No 5 Xin Mofan Rd., Nanjing 210009, China.

b State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing, China. Fax: 86 25 8317 2263; Tel: 86 25 8317 2265; E-mail: lixiongzhang@yahoo.com

10 Experimental section

Synthesis of copper ammonium phosphate nanoflake constructed microspheres. First, 3 g urea was dissolved into 50 mL distilled water. To this solution, 0.25 g SDS was added. The solution was stirred until a clear solution was obtained. Afterwards, 0.0624 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.026 g H_3PO_4 (85%) were successively added. Finally, 0.1 g 5 wt.% NaOH solution was dropwisely added under vigorously stirring to get a light blue
15 clear synthesis solution. The molar composition of the synthesis solution was 0.25Cu^{2+} : 0.87SDS : $0.23\text{H}_3\text{PO}_4$: 0.375NaOH : 50urea : $2780\text{H}_2\text{O}$. The synthesis solution was hydrothermally treated in a Teflon-lined autoclave at 80°C for 12 h. The microspheres were obtained after separation by centrifuging, washing and drying at 80°C overnight.

20 **Synthesis of cobalt or magnesium ammonium phosphate nanoflake constructed microspheres.** Same procedure and receipt as those for preparation of copper ammonium phosphate nanoflake constructed microspheres were used except that 0.0703 g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ or 0.0616 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was added instead of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

25 **Synthesis of binary or ternary transition metal ammonium phosphate nanoflake constructed microspheres.** Same procedure and receipt as those for preparation of copper ammonium phosphate nanoflake constructed microspheres were used except that calculated amounts of the transition metal precursor were added instead of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was used as Zn precursor.

30 **Characterization.** The structure of the microspheres was determined on a powder X-ray diffractometer (XRD, Bruker D8-Advance) with Ni-filtered $\text{Cu K}\alpha$ radiation source at 40 kV and 40 mA and a Braun position sensitive detector at a scan rate of $5^\circ/\text{min}$ and step size of 0.05° . The Fourier transform infrared (FTIR) spectra were obtained on a Nexus 870 FTIR spectrometer. The size and morphology of the microspheres were observed with scanning electron microscopy (SEM, LEO-1530 and Hitachi-S4800) as well as transmission electron
35 microscopy (TEM, JEOL-200CX). Element composition in the microspheres was analyzed by Energy-dispersive X-ray spectroscopy (EDX, Sigma) attached to the SEM. Simultaneous differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TG) were carried out on the microspheres in air up to 700°C using a NETZSCH STA 409 instrument with a heating rate of $10^\circ\text{C}/\text{min}$.

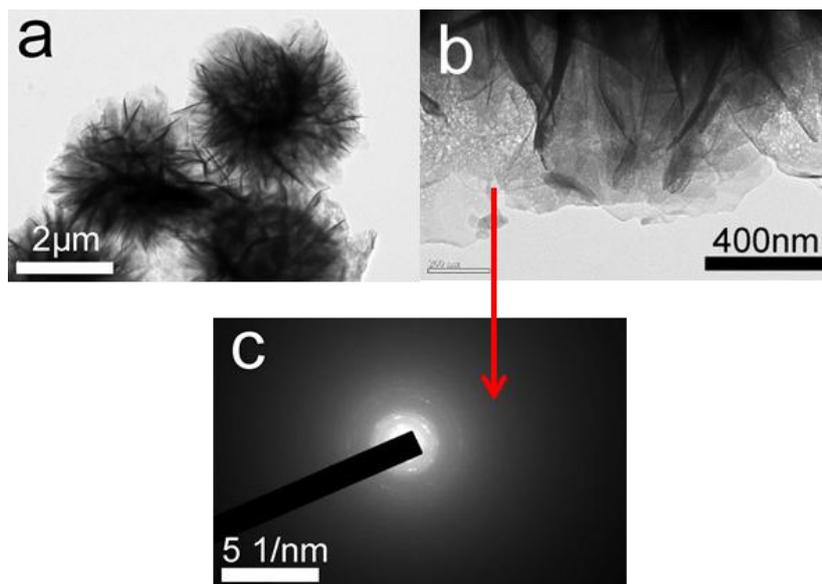


Fig. S1 TEM pictures (a and b) and electron diffraction (c) of the sample prepared from the synthesis solution with a molar composition of 0.25Cu^{2+} : 0.87SDS : $0.23\text{H}_3\text{PO}_4$: 0.375NaOH : 50urea : $2780\text{H}_2\text{O}$ at 80°C for 12 h.

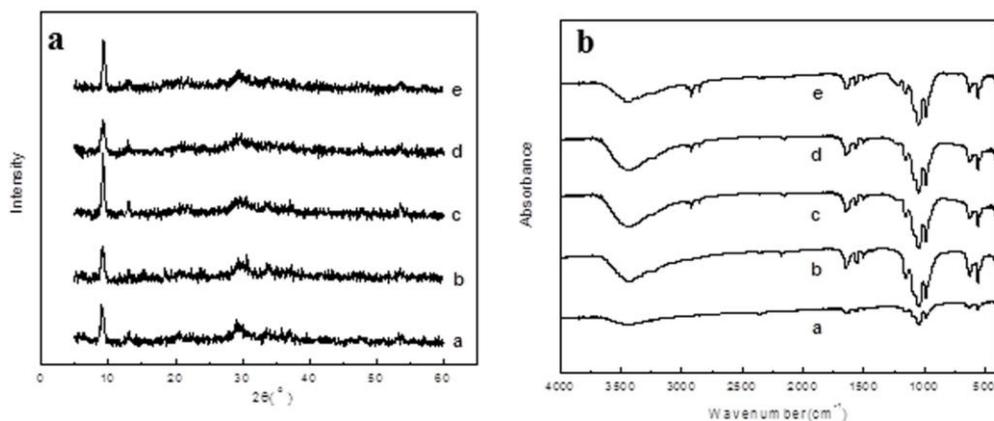


Fig. S2 XRD patterns (A) and FT-IR spectra (B) of the samples prepared from the synthesis solution with a molar composition of 0.25Cu^{2+} : 0.87SDS : $0.23\text{H}_3\text{PO}_4$: $x\text{NaOH}$: 50urea : $2780\text{H}_2\text{O}$ at 80°C for 12 h. $x=0.125$ (a), 0.25 (b), 0.375 (c), 0.5 (d), and 0.625 (e).

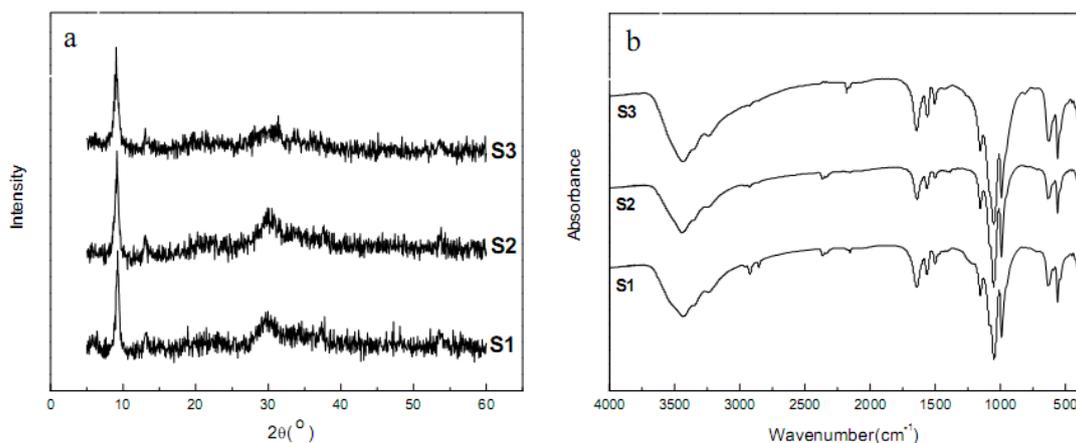


Fig. S3 XRD patterns (a) and FT-IR spectra (b) of the samples prepared from the synthesis solutions by doubling the contents of urea (S1), SDS (S2) and H_3PO_4 (S3) in the basic molar composition of 0.25Cu^{2+} : 0.87SDS : $0.23\text{H}_3\text{PO}_4$: 0.375NaOH : 50urea : $2780\text{H}_2\text{O}$.

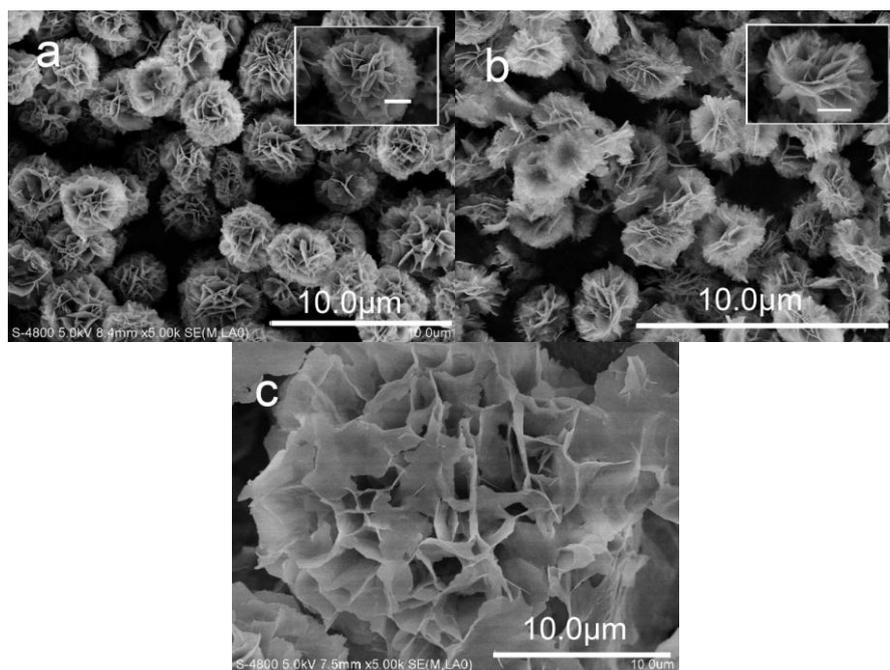


Fig. S4 SEM pictures of the samples prepared from the synthesis solutions by doubling the contents of urea (a), SDS (b) and H_3PO_4 (c) in the basic molar composition of 0.25Cu^{2+} : 0.87SDS : $0.23\text{H}_3\text{PO}_4$: 0.375NaOH : 50urea : $2780\text{H}_2\text{O}$. The scale bar in the insets was $2\ \mu\text{m}$. The scale bar in the insets stands for $1\ \mu\text{m}$.

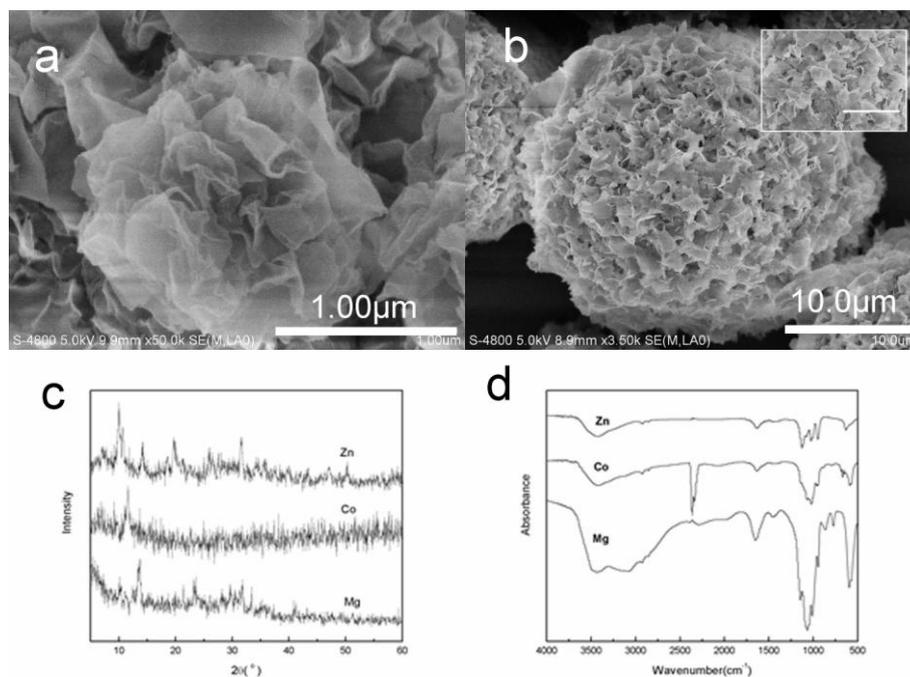


Fig. S5 SEM images of CoNH_4PO_4 (a) and MgNH_4PO_4 (b), XRD patterns (c), and FTIR spectra (d) of the samples prepared from the synthesis solutions with a molar composition of 0.25metal ion : 0.87SDS : $0.23\text{H}_3\text{PO}_4$: 0.375NaOH : 50urea : $2780\text{H}_2\text{O}$ at $80\ ^\circ\text{C}$ for 12 h. The scale bar in the inset stands for $500\ \mu\text{m}$.

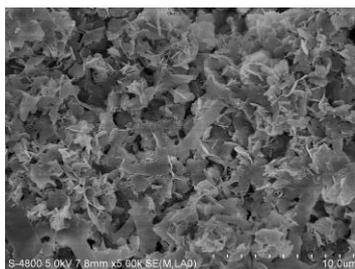
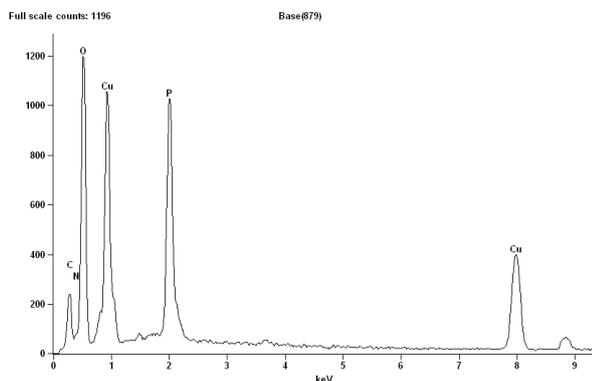
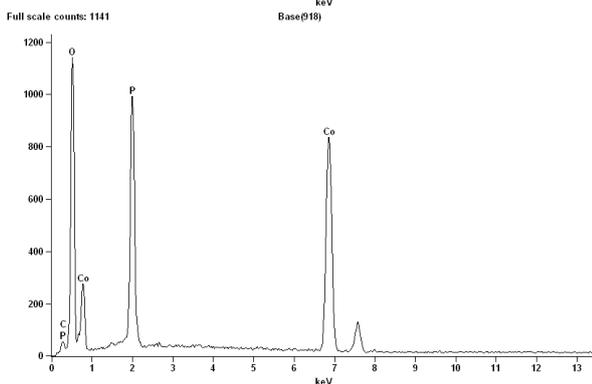


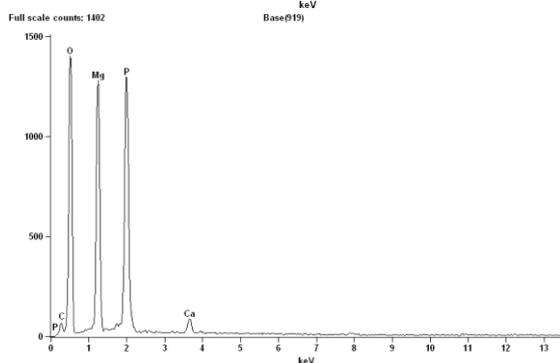
Fig. S6 SEM picture of a sample prepared from the synthesis solutions with a molar composition of 0.25 Mn²⁺: 0.87SDS: 0.23H₃PO₄: 0.375NaOH: 50urea: 2780H₂O at 80 °C for 12 h. MnSO₄ was used as the Mn²⁺ precursor.



Element Line	Weight %	Atom %
C K	28.26	39.39
N K	5.47	6.53
O K	44.75	46.82
P K	5.76	3.11
Cu K	15.76	4.15
Total	100.00	100.00



Element Line	Weight %	Atom %
O K	44.01	70.35
P K	13.65	11.27
Co K	42.33	18.37
Total	100.00	100.00



Element Line	Weight %	Atom %
O K	64.34	75.73
Mg K	16.49	12.78
P K	18.01	10.95
Ca K	1.16	0.55
Total	100.00	100.00

Fig. S7 EDS spectra of the copper, cobalt, and magnesium ammonium phosphates (up, middle and bottom, respectively).

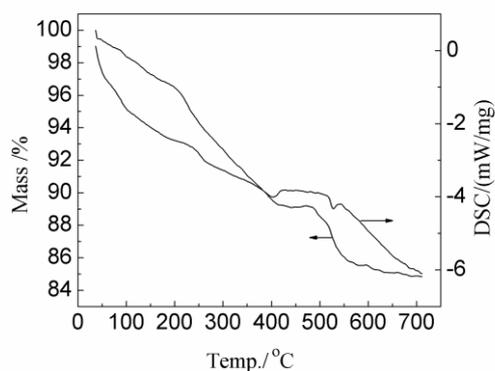


Fig. S8 Thermal analysis curves of copper ammonium phosphate hydration obtained in air, heating rate 10 K min⁻¹.

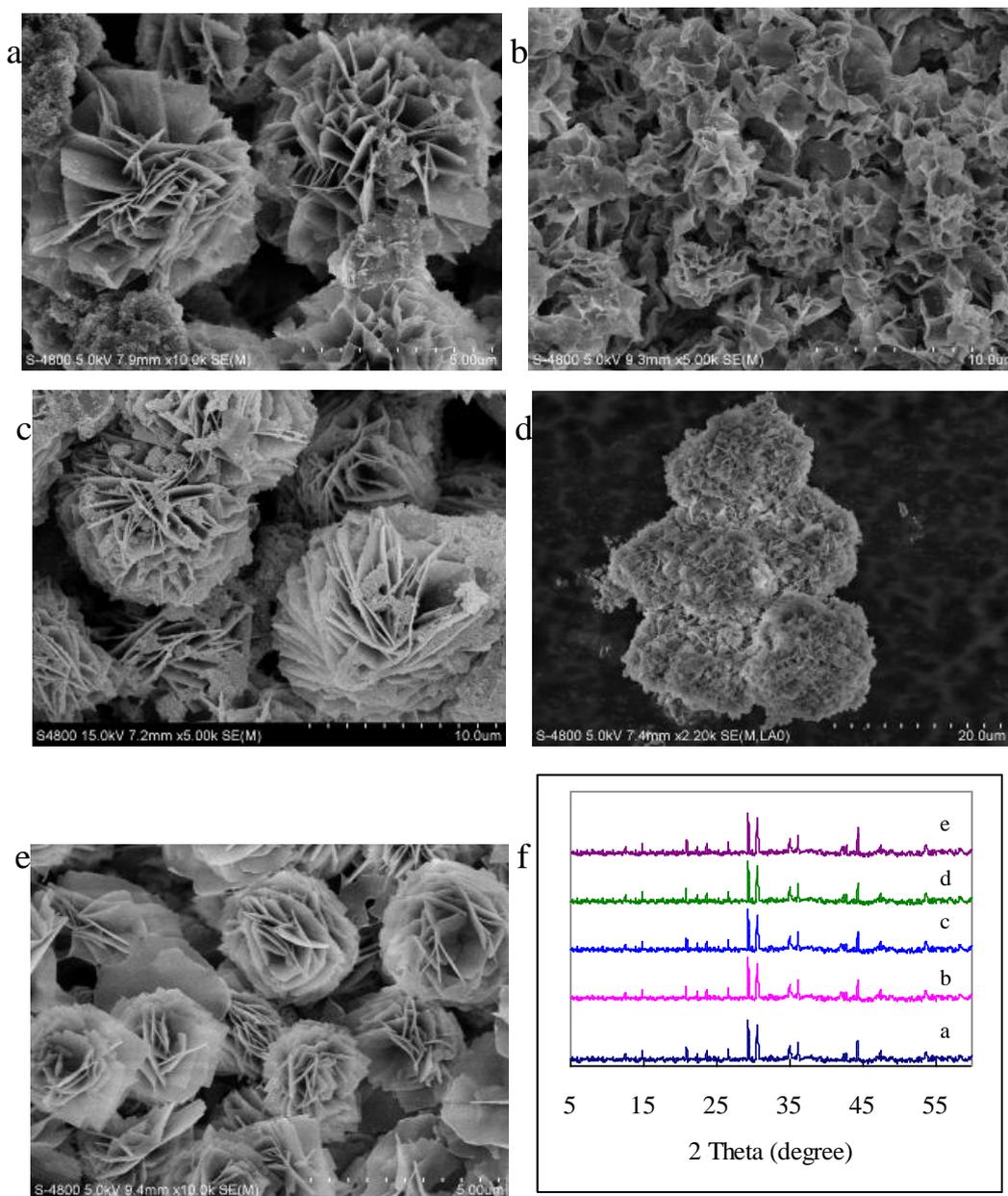


Fig. S9 SEM photos (a-e) and XRD patterns (f) of the calcined MAPNCM samples. (a) Cu ammonium phosphate; (b) Co ammonium phosphate; (c) Cu-Zn ammonium phosphate; (d) Co-Zn ammonium phosphate; (e) Cu-Mg-Zn ammonium phosphate.

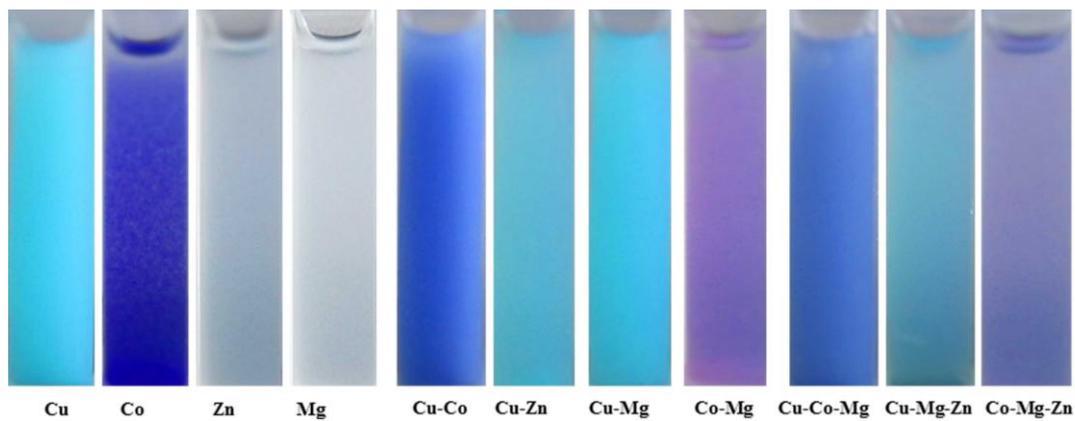


Fig. S10 Color contrast photos of unitary (Cu, Co, Zn and Mg) and multinary (Cu-Co, Cu-Zn, Cu-Mg, Co-Mg, Cu-Co-Mg, Cu-Mg-Zn, and Co-Mg-Zn) metal ammonium phosphate microspheres dispersed in water.