Support information

Construction of coral-like architectures of boron-containing compounds: coral-like boric acid and its application performances

Shengnan Bi[a] , Peihan Zhu[b] , Peng Tian[a,b] , Jianchu Zhong[a,b] , Junwei Ye[a,b] , Guiling Ning[a,b] *

[a] *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian, Liaoning, 116024, P. R. China.*

[b] *Engineering Laboratory of Boric and Magnesic Functional Material Preparative and Applied Technology, 2 Linggong Road, Dalian, Liaoning, 116024,* P. R. China

***Corresponding author.**

E-mail address: ninggl@dlut.edu.cn .

Tel./Fax: +86 411 84986065.

1. Experimental Section

1.1. Bunch-like boric acid prepared in methanol

Boric acid (0.24 mol, ≥ 99%) was added into a beaker containing 50 ml of methanol. The beaker was vigorously stirred and heated to 64°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 0.5 h to obtain bunch-like boric acid.

1.2. Coral-like boric acid prepared in ethanol

Boric acid (0.16 mol, ≥ 99%) was added into a beaker containing 50 ml of ethanol. The beaker was vigorously stirred and heated to 78°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 1 hour, then raised to 20℃ at a temperature increase rate of 3～5℃/min, and placed for 3 h, (**The process of increasing the temperature**). Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain coral-like boric acid.

1.3. Coral-like boric acid prepared in isopropanol

Boric acid (0.08 mol, ≥ 99%) was added into a beaker containing 50 ml of isopropanol. The beaker was vigorously stirred and heated to 82°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 1 hour, then raised to 20℃ at a temperature increase rate of 3～5℃/min, and placed for 3 h (**The process of increasing the temperature**). Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain coral-like boric acid.

1.4. Flower-like boric acid prepared in sec-butyl alcohol

Boric acid (0.08 mol, ≥ 99%) was added into a beaker containing 75 ml of sec-butyl alcohol. The beaker was vigorously stirred and heated to 99°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min. and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain coral-like boric acid.

1.5. Preparation boric acid with hollow-box gathered on the surface of the aggregation

Boric acid (0.16 mol, ≥ 99%) was added into a beaker containing 30 ml of ethanol and 20 ml methanol. The beaker was vigorously stirred and heated to 78°C to obtain a clear solution. The

temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 1 hour, then raised to 20℃ at a temperature increase rate of 3～5℃/min, and placed for 3 h (**The process of increasing the temperature**). Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain boric acid with hollow-box gathered on the surface of the aggregation.

1.6. Preparation of coral-like boric acid with tube gathered on the surface of the aggregation

Boric acid (0.16 mol, ≥ 99%) was added into a beaker containing 30 ml of ethanol and 20 ml methanol. The beaker was vigorously stirred and heated to 78°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain coral-like boric acid.

1.7 Small hollow particles of boric acid in ethanol

Boric acid (0.16 mol, ≥ 99%) was added into a beaker containing 50 ml of ethanol. The beaker was vigorously stirred and heated to 78°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 2 h, Then suction filter and filtrate was left. The filtrate was placed for 1h, and then filtered again to obtain small particles.

1.8 Preparation of crystalline boric acid with different concentrations in ethanol

(a) Boric acid (0.16 mol, ≥ 99%) was added into a beaker containing 50 ml of ethanol. The beaker was vigorously stirred and heated to 78°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain spherical boric acid.
(b) Boric acid (0.12 mol, ≥ 99%) was added into a beaker containing 50 ml of ethanol. The beaker was vigorously stirred and heated to 78°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain spherical boric acid.
(c) Boric acid (0.08 mol, ≥ 99%) was added into a beaker containing 50 ml of ethanol. The beaker was vigorously stirred and heated to 78°C to obtain a clear solution. The temperature of the solution was lowered to 5℃ at a cooling rate of 3～5℃/min, and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60℃ for 3 h to obtain spherical boric acid.

1.9 Preparation of crystalline boric acid with different concentrations in sec-butyl alcohol

(a) Boric acid (0.08 mol, ≥ 99%) was added into a beaker containing 75 ml of sec-butyl alcohol. The beaker was vigorously stirred and heated to 99°C to obtain a clear solution. The temperature of the solution was lowered to 5°C at a cooling rate of 3～5°C/min. and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60°C for 3 h to obtain coral-like boric acid.

(b) Boric acid (0.06 mol, ≥ 99%) was added into a beaker containing 75 ml of sec-butyl alcohol. The beaker was vigorously stirred and heated to 99°C to obtain a clear solution. The temperature of the solution was lowered to 5°C at a cooling rate of 3～5°C/min. and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60°C for 3 h to obtain coral-like boric acid.

(c) Boric acid (0.04 mol, ≥ 99%) was added into a beaker containing 75 ml of sec-butyl alcohol. The beaker was vigorously stirred and heated to 99°C to obtain a clear solution. The temperature of the solution was lowered to 5°C at a cooling rate of 3～5°C/min. and placed for 3 h. Then a large amount of white precipitate was obtained in the solution. The solution was suction filtered and dried at 60°C for 3 h to obtain coral-like boric acid.

2. Comparison of crystal morphologies of boric acid with different concentrations in ethanol.

As shown in Figure S1, in the same volume of ethanol, with the decrease of the concentration of boric acid added, the crystal shape of boric acid hardly changes, but the surface morphology is slightly different. For specific preparation methods, see Supporting Information 1.8.

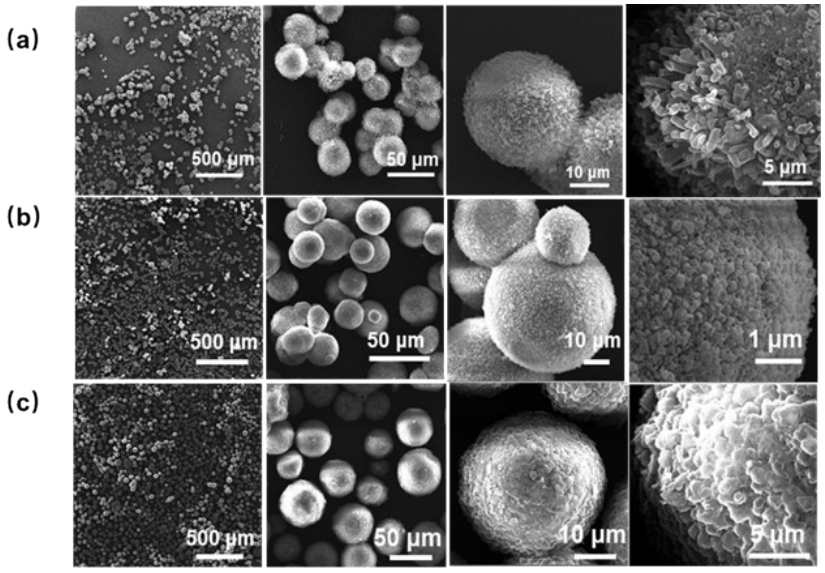

Fig. S1. Crystal morphologies of boric acid at different concentrations in ethanol. High: 3.2 mol/L (a); Medium: 2.4 mol/L (b); Low: 1.6 mol/L (c)

3. Comparison of crystal morphologies of boric acid with different concentrations in sec-butanol.

As shown in Figure S2, similar to ethanol, in the same volume of sec-butanol, the crystal shape of boric acid hardly changes with the decrease of the concentration of boric acid added, but the surface morphology is slightly different. For specific preparation methods, see Supporting Information 1.9.

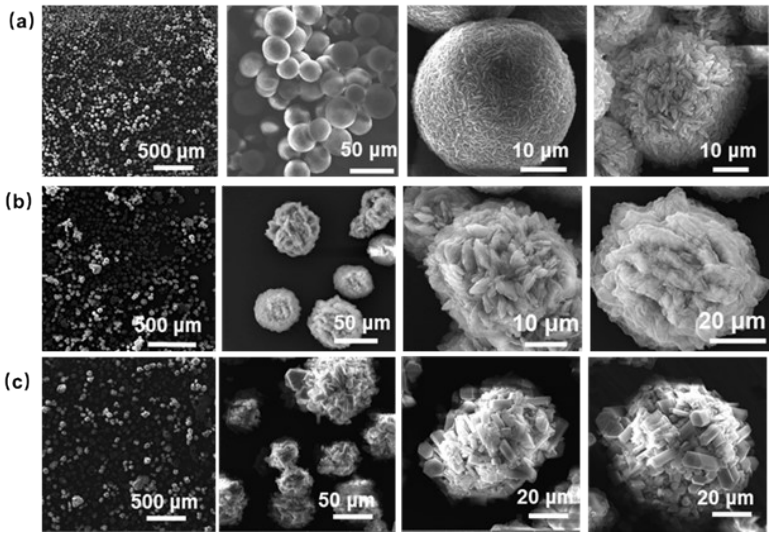

Fig. S2. Crystal morphologies of boric acid at different concentrations in sec-butanol. High: 1.1 mol/L (a); Medium: 0.8 mol/L (b); Low: 0.5 mol/L (c)

4. TEM image of crystalline boric acid in water.

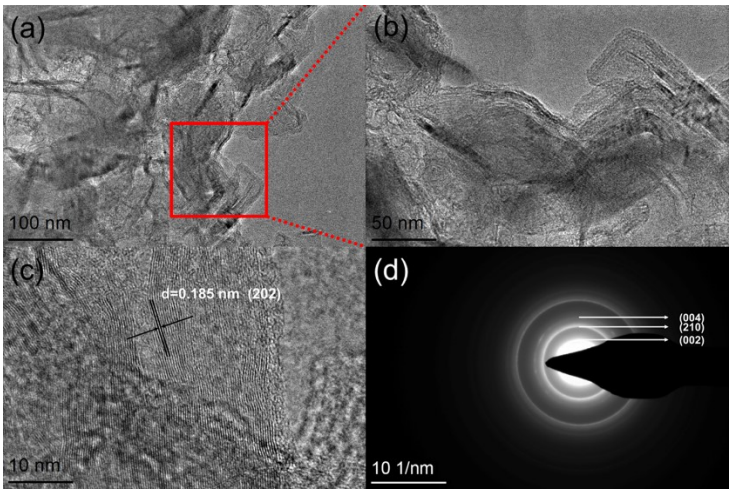

Fig. S3. TEM image of crystalline boric acid in water

5. TEM image of crystalline boric acid in ethanol.

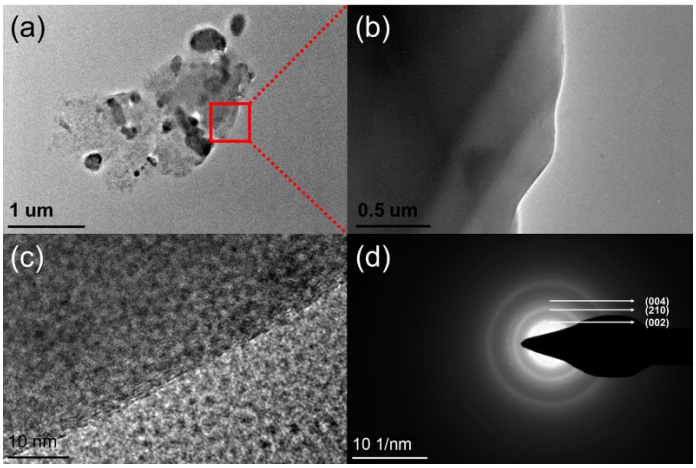

Fig. S4. TEM image of crystalline boric acid in ethanol

6. Test method for solubility of boric acid

Boric acid is a weak acid and cannot be completely dissociated, so the concentration cannot be obtained directly by titration with NaOH solution. Here we use a general method to add a small amount of mannitol to completely dissociate the boric acid, and then use NaOH solution to monitor the concentration change after dissolution(J. Chem. Educ. 2012, 89, 767−770).

First, 15 g of boric acid was added to 200mL of deionized water, 1mL was sampled at regular intervals, 0.5 mL of 0.2 mol/L mannitol ethanol solution was added, then 2 g of phenolphthalein was added, and finally 0.2 mol/L NaOH solution was titrated to test the concentration change.

7. Schematic diagram of sheet-like boric acid structure

Fig. S1 is a structure diagram of boric acid. It can be clearly seen that the hydrogen bonds of boric acid appear on the 010 crystal plane, while the 002 crystal plane does not have hydrogen bonds that are easy to combine with water.

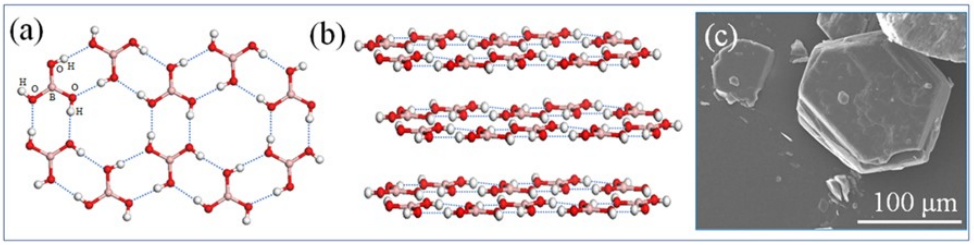

Fig. S5. Schematic diagram of sheet-like boric acid structure.

8. Coral-like boric acid and sheet-like boric acid physical map

Fig. S2 is a physical comparison between coral boric acid and flake boric acid. It can be clearly seen that they are different in appearance

Fig. S6. Coral-like boric acid and sheet-like boric acid physical map

9. Thermogravimetric Analysis

Boric acid will continue to lose water molecules during the heating process. It can be seen from the TGA curve that the two types of boric acid combine with water in different ways.

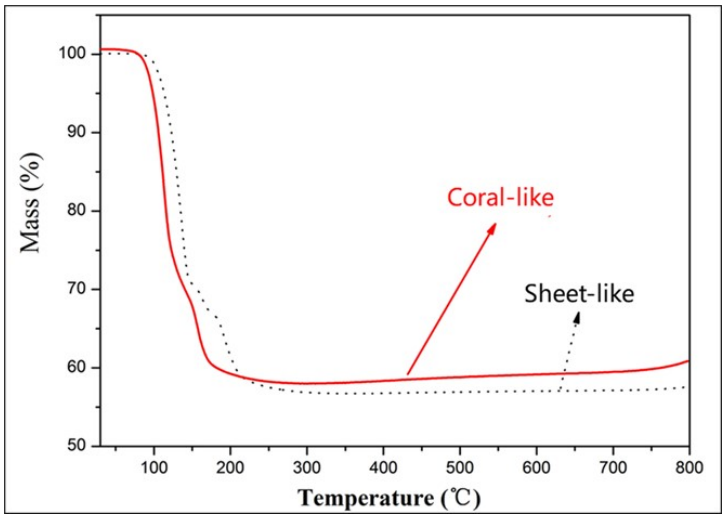

Fig. S7. TGA trace of coral-like boric acid and sheet-like boric acid.

10. Nitrogen adsorption test

In the higher P/P_0 zone, capillary condensation of adsorbate occurs, and the isotherm rises rapidly. When all pores are aggregated, adsorption only occurs on the outer surface, which is much smaller than the inner surface area, and the curve is flat. When the relative pressure 1 approaches, it adsorbs on the macropores and the curve rises.

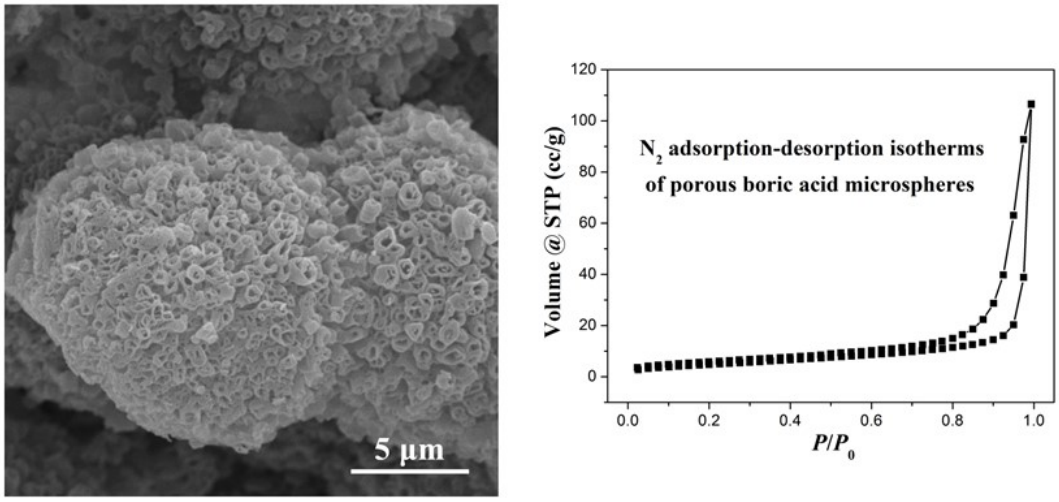

Fig. S8. Nitrogen adsorption-desorption isotherms of coral-like boric acid.