Facile preparation of hydroxyapatite with novel morphology and hierarchical structures and potential application in water treatment

Feifei Wang, Yuming Guo, Huajie Wang, Lin Yang,* Kui Wang, Xiaoming Ma, Wenguang Yao, and Hua Zhang

College of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang 453007, P. R. China. Fax: +86-373-3328507; Tel: +86-373-3325058; E-mail:yanglin1819@163.com

1 Experimental Details

1.1. Preparation of aragonite precursor crystals

The hedgehog-like aragonite precursor crystals were prepared through gaseous diffusion method. Briefly, a number of glass beakers (25 ml) containing 0.01 mol/L of $CaCl_2$ and 0.01 mol/L of $MgSO_4$ were covered with Parafilm, punched with eight needle holes, and placed in a closed incubator. Another big glass beakers (100 ml) containing ammonium carbonate powder were also covered with Parafilm, punched with eight needle holes, and placed in the same incubator. After incubated at 30ºC for one week, the precipitate at the air/water interface was centrifuged, washed with double distilled water, and dried under vacuum at 30ºC for 24 hr.

1.2. Transformation from hedgehog-like aragonite to flower-like hydroxyapatite and real-time observation

The synthesis of flower-like hydroxyapatite (HAP) was performed by immersing the hedgehog-like aragonite precursor crystals into phosphate buffer solution (PBS, pH=7.2, 0.1M) at 30ºC. To investigate the transforming mechanism, the products immersed into buffer solution for 0.5, 12, 24, 48, 96 and 168 hr were

taken out and dried at 30 ℃ under vacuum for Scanning electron microscopy (SEM) observation, respectively.

1.3. Characterization of the hedgehog-like aragonite and flower-like HAP

The morphologies of the samples were observed by SEM (JSM-6390LV, JEOL). X-ray powder diffraction (XRD) measurements were performed on a Bruker D & Advance X-ray powder diffractometer with a graphite monochromatized Cu-Kα radiation source. (λ=0.15406 nm), and a scanning rate of 0.05 deg/s was applied to record the pattern in the 2θ range of 4-70°. The Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad FTS-40 FTIR spectraphotometer in the wavenumber range of 4000-400 cm^{-1}. And the spectra were collected at 2 cm^{-1} resolution with 64 scans by preparing KBr pellets with a 3:100 "sample- to -KBr" ratio.

1.4. Adsorption of heavy metal ions onto the flower-like HAP

1.4.1. Selective adsorption of the flower-like HAP for heavy metal ions

In order to study the selective adsorption activity of the flower-like HAP for different heavy metal ions, the as-prepared flower-like HAP was mixed with the aqueous solution containing different heavy metal ions, including Pb^{2+}, Cd^{2+}, and Hg^{2+}. After 60 min, the adsorption contents of different heavy metal ions on the flower-like HAP were analyzed by using the atomic absorption spectrophotometry (HITACHI Z-5000).

In addition, for comparison, the bulk HAP was prepared as the control through the direct reaction between Na_2HPO_4 and $CaCl_2$ at 70ºC with pH 9.2 according to the literature.

1.4.2. Effect of pH on the adsorption activity of the flower-like HAP

The effect of pH on the adsorption activity of the flower-like HAP was carried out and the pH varied from 1 to 6. The pH value of the solution was adjusted with HCl and/or NaOH and recorded with a pH

meter. After mixed with the as-prepared flower-like HAP for 60 min, the adsorption contents of different heavy metal ions on the flower-like HAP were analyzed by the atomic absorption spectrophotometry.

1.4.3. Effect of contact time on the adsorption activity of the flower-like HAP

25 mg of the as-prepared flower-like HAP was added into the aqueous solution containing 50 mg/L of Pb^{2+}, Cd^{2+} and Hg^{2+}, respectively. The adsorption study was conducted in a 37 ℃ incubator for the given time intervals. The supernatant of the suspension was collected by centrifugation at 4000 rpm for 10 min, and then the concentration of heavy metal ions in the supernatant was analyzed by the atomic absorption spectrophotometry.

2 Results and Discussion

2.1 Syntheses and Characterization of the hedgehog-like aragonite and flower-like HAP

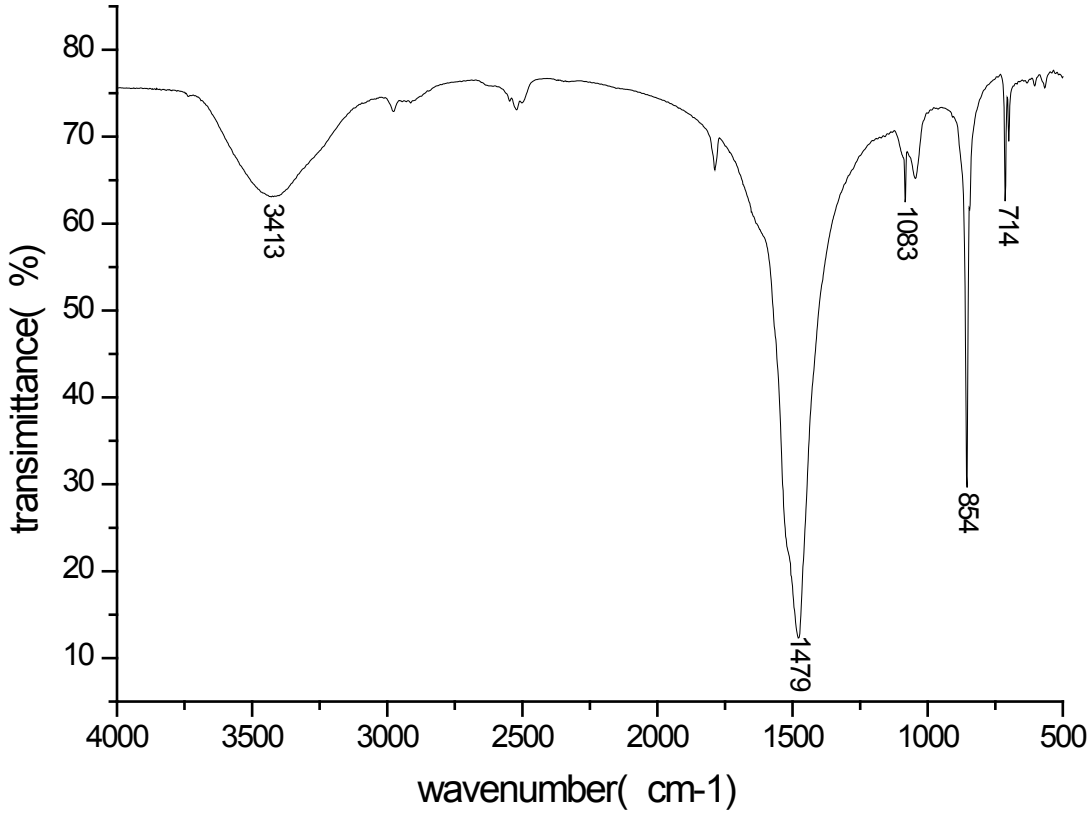

Fig. S1 FTIR spectrum of hedgehog-like aragonite $CaCO_3$.

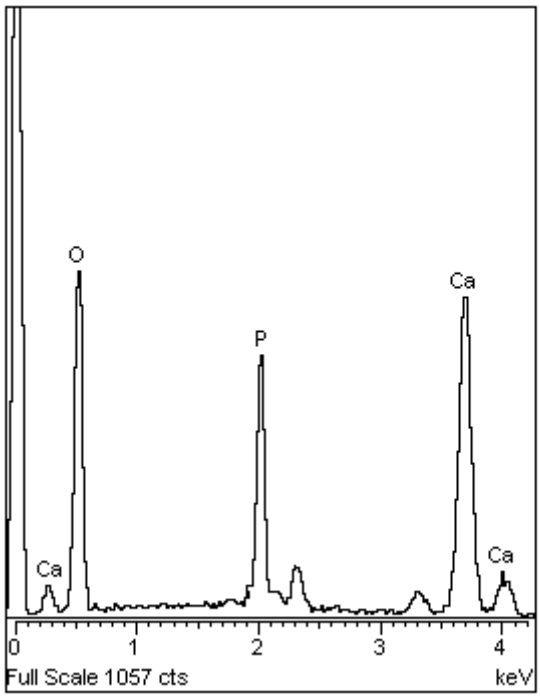

Fig. S2 EDS spectrum of the as-prepared flower-like HAP.

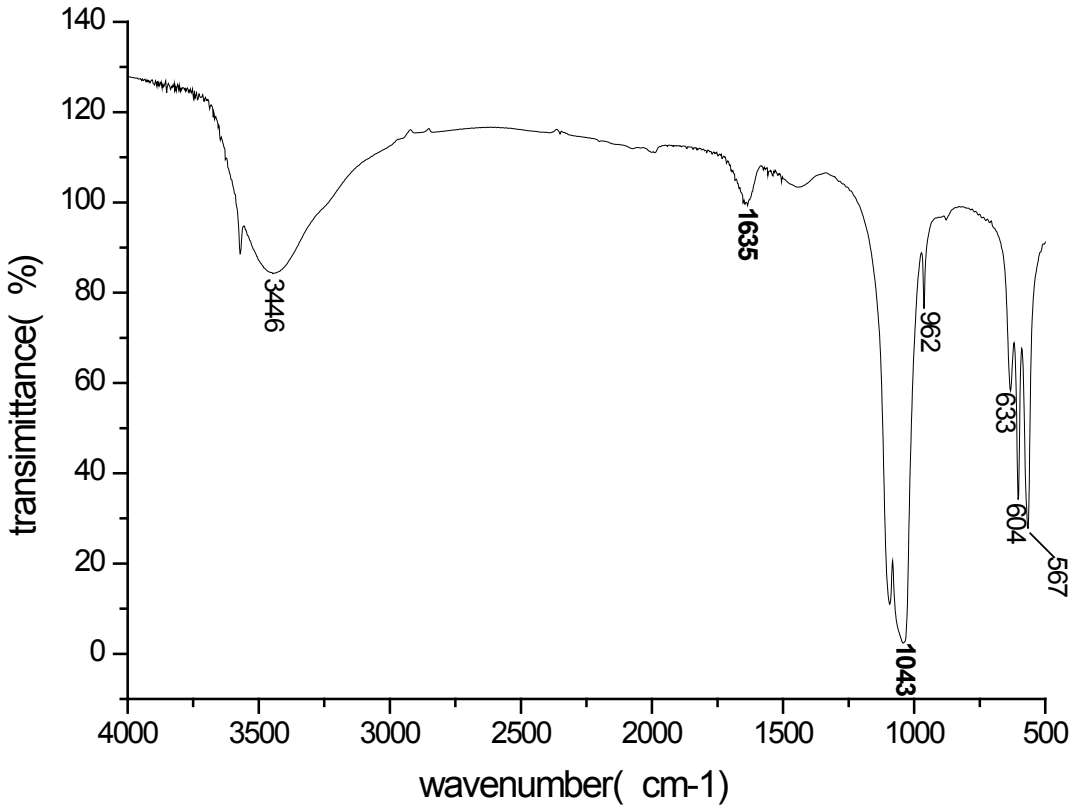

Fig. S3 FTIR spectrum of the as-prepared flower-like HAP.

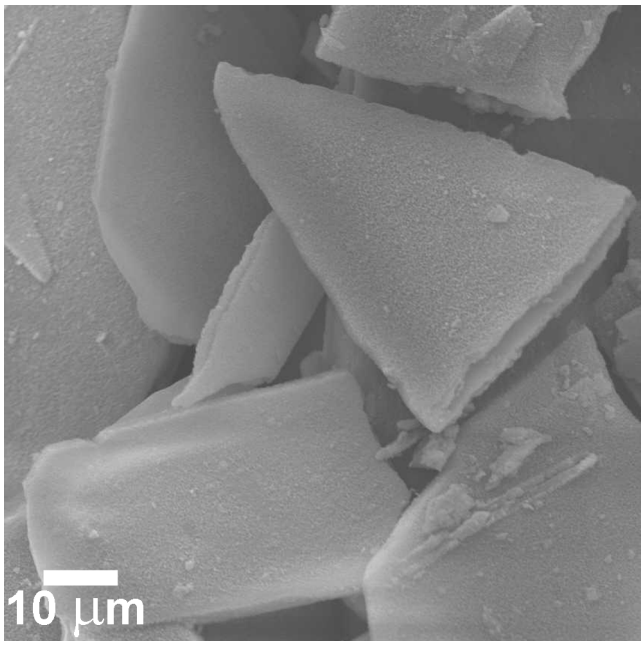

Fig. S4 SEM images of the control commercial HAP