Crystal-Facet Anisotropy Dictates the Alkali Dissolution Behavior of Struvite

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1.Method of calculation

The first principles calculations in the framework of density functional theory, including structural, electronic performances, were carried out based on the Cambridge Sequential Total Energy Package known as CASTEP. The exchange–correlation functional under the generalized gradient approximation (GGA) with norm-conserving pseudopotentials and Perdew–Burke–Ernzerhof functional was adopted to describe the electron–electron interaction. An energy cutoff of 500 eV was used and a k-point sampling set of 3 x 3 x 1 were tested to be converged. A force tolerance of 0.05 eV Å -1, energy tolerance of 2.0x10-5eV per atom and maximum displacement of 0.002 Å were considered. Each atom in the storage models is allowed to relax to the minimum in the enthalpy without any constraints. The Brillourin zone was sampled with Monkhorst mesh 3x3x1 through all the computational process. The self-consistent calculations applied a convergence energy threshold of 10-5 eV. A 15 Å vacuum space along the z direction was added to avoid the interaction between the two neighboring images.

To identify the most stable crystal surface structure, the surface energy for each configuration was calculated (Equation S1-1).

$$E_{surface} = (E_{slab} - nE_{bulk})/2A_0$$

where:

E_{slab} is the total energy of the surface slab (eV), E_{bulk} is the energy of the bulk unit cell (eV), n is the ratio of the number of atoms in the surface model to that in the bulk model (i.e., the number of bulk formula units equivalent to the slab), A is the cross-sectional area of the surface (Å²).

Table R2: Surface energy of all possible atomic exposure situations on different crystal faces of struvite.

crystal faces	E_{slab}(eV)	E_{bulk}(eV)	n	A(Å²)	$E_{surface}$(eV/ Å²)
$[002]_1$	-13695.86	-13700.2	1	42.71	0.050808
$[002]_2$	-13689.50	-13700.2	1	42.71	0.125263
$[002]_3$	-13697.60	-13700.2	1	42.71	0.030438

$[002]_4$	-13694.00	-13700.2	1	42.71	0.072583
$[002]_5$	-13688.95	-13700.2	1	42.71	0.131702
$[002]_6$	-13696.40	-13700.2	1	42.71	0.044486
$[002]_7$	-13695.28	-13700.2	1	42.71	0.057598
$[101]_1$	-27385.10	-13700.2	2	81.06	0.094375
$[101]_2$	-27384.10	-13700.2	2	81.06	0.100543
$[101]_3$	-27386.70	-13700.2	2	81.06	0.084505
$[101]_4$	-27385.81	-13700.2	2	81.06	0.089995
$[101]_5$	-27395.33	-13700.2	2	81.06	0.031273
$[101]_6$	-27389.65	-13700.2	2	81.06	0.066309
$[101]_7$	-27382.75	-13700.2	2	81.06	0.10887
$[012]_1$	-27382.31	-13700.2	2	115.70	0.078176
$[012]_2$	-27379.97	-13700.2	2	115.70	0.088289
$[012]_3$	-27385.42	-13700.2	2	115.70	0.064736
$[012]_4$	-27385.00	-13700.2	2	115.70	0.066551
$[012]_5$	-27388.33	-13700.2	2	115.70	0.052161
$[012]_6$	-27384.18	-13700.2	2	115.70	0.070095
$[012]_7$	-27387.29	-13700.2	2	115.70	0.056655
$[00\text{-}2]_1$	-13689.55	-13700.2	1	42.71	0.124678
$[00\text{-}2]_2$	-13692.13	-13700.2	1	42.71	0.094474
$[00\text{-}2]_3$	-13695.84	-13700.2	1	42.71	0.051042
$[00\text{-}2]_4$	-13697.60	-13700.2	1	42.71	0.030438
$[00\text{-}2]_5$	-13696.41	-13700.2	1	42.71	0.044369
$[00\text{-}2]_6$	-13695.29	-13700.2	1	42.71	0.057481
$[00\text{-}2]_7$	-13688.93	-13700.2	1	42.71	0.131936
$[10\text{-}1]_1$	-27395.34	-13700.2	2	81.06	0.031211
$[10\text{-}1]_2$	-27385.14	-13700.2	2	81.06	0.094128
$[10\text{-}1]_3$	-27384.21	-13700.2	2	81.06	0.099864
$[10\text{-}1]_4$	-27382.89	-13700.2	2	81.06	0.108006
$[10\text{-}1]_5$	-27389.61	-13700.2	2	81.06	0.066556
$[10\text{-}1]_6$	-27393.24	-13700.2	2	81.06	0.044165
$[10\text{-}1]_7$	-27395.36	-13700.2	2	81.06	0.031088
$[0\text{-}12]_1$	-27379.95	-13700.2	2	115.70	0.088375

$[0\text{-}12]_2$	-27382.28	-13700.2	2	115.70	0.078306
$[0\text{-}12]_3$	-27384.98	-13700.2	2	115.70	0.066638
$[0\text{-}12]_4$	-27388.33	-13700.2	2	115.70	0.052161
$[0\text{-}12]_5$	-27393.04	-13700.2	2	115.70	0.031806
$[0\text{-}12]_6$	-27387.29	-13700.2	2	115.70	0.056655
$[0\text{-}12]_7$	-27386.55	-13700.2	2	115.70	0.059853

$$E_{surface} = (E_{slab} - nE_{bulk})/2A_0$$

where:

E_{slab} is the total energy of the surface slab (eV), E_{bulk} is the energy of the bulk unit cell (eV), n is the ratio of the number of atoms in the surface model to that in the bulk model (i.e., the number of bulk formula units equivalent to the slab), A is the cross-sectional area of the surface (Å^2).

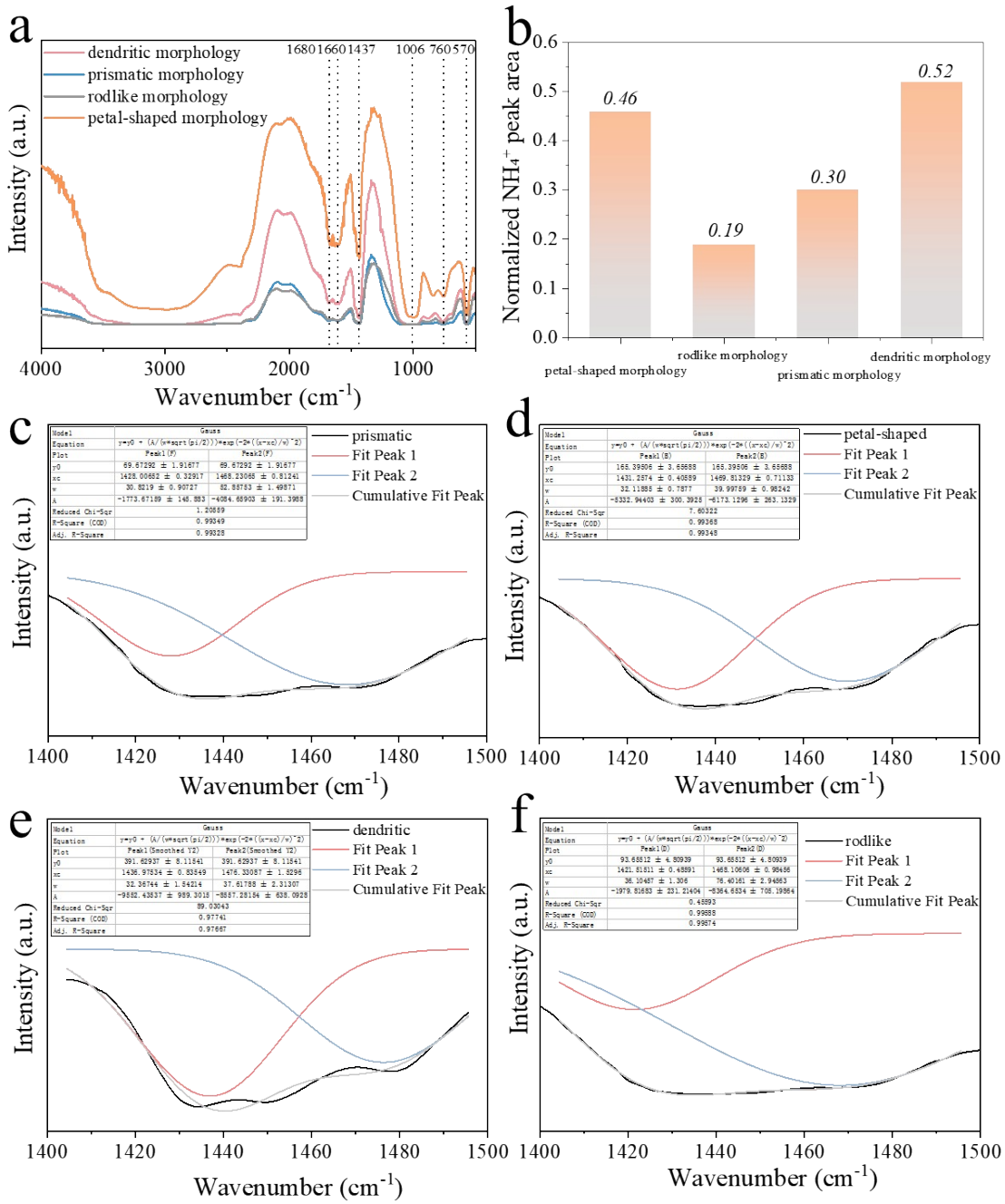

Fig. S1. (a) FT-IR patterns of different struvite morphologies after alkali dissolution (b) normalized peak areas of NH_4^+ for different struvite morphologies (c-f) gaussian fitting curves of the characteristic NH_4^+ peak in the FT-IR spectra of different struvite morphologies.

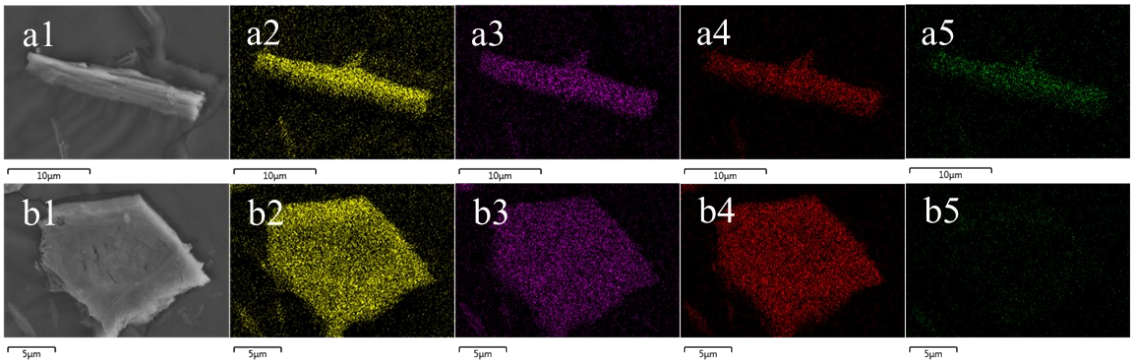

Fig. S2. EDS elemental mapping images of rodlike struvite: (a) before alkali dissolution; (b) after alkali dissolution.

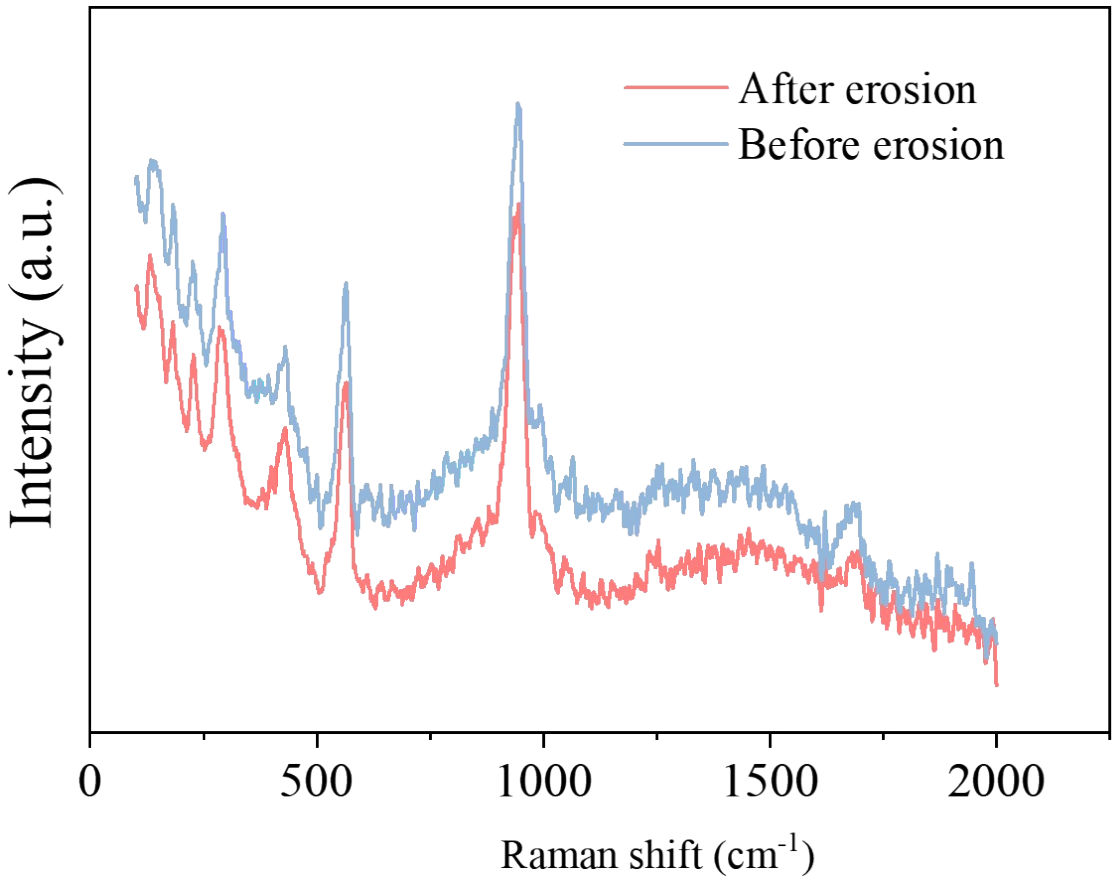

Fig.S3 Raman spectra of needle-like struvite before and after alkali dissolution.

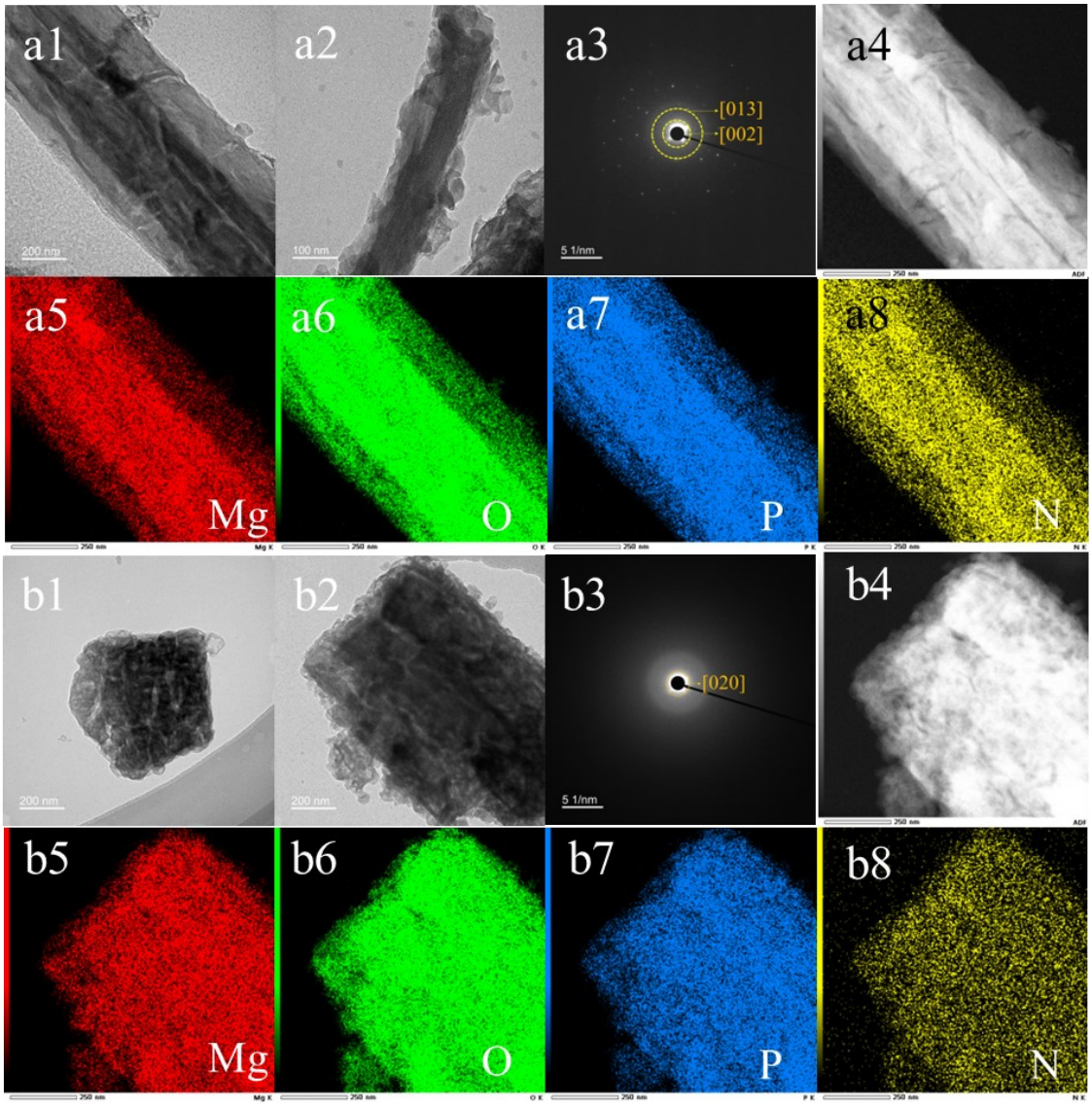

Fig. S4 TEM images (a1, a2), SAED pattern (a3), and corresponding EDS elemental mapping images (a4–a8) of rodlike struvite before dissolution; TEM images (b1, b2), SAED pattern (b3), and EDS elemental mapping images (b4–b8) of rodlike struvite after dissolution.