SUPPLEMENTARY INFORMATION

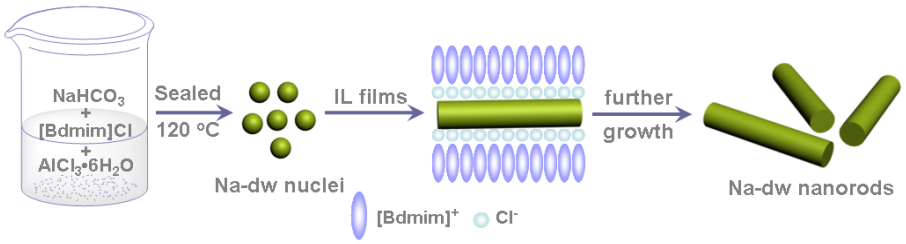
Formation of Alumina Nanocapsules by High-Energy-Electron Irradiation of Na-dawsonite Nanorods

Xiaochuan Duan,[a] Tongil Kim,[a] Lili Han,[b] Jianmin Ma,[a] Xiwen Du,*[b] and Wenjun Zheng.*[a]

[a] Department of Materials Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (MOE), and TKL of Metal and Molecule-Based Material Chemistry, College of Chemistry, Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, People's Republic of China.

[b] School of Materials Science and Engineering, Tianjin University, Tianjin, 300072, People's Republic of China.

Results and Discussion



Scheme S1. Schematic illustration of the formation of Na-dawsonite nanorods *via* an ionic liquid-assisted hydrothermal route.

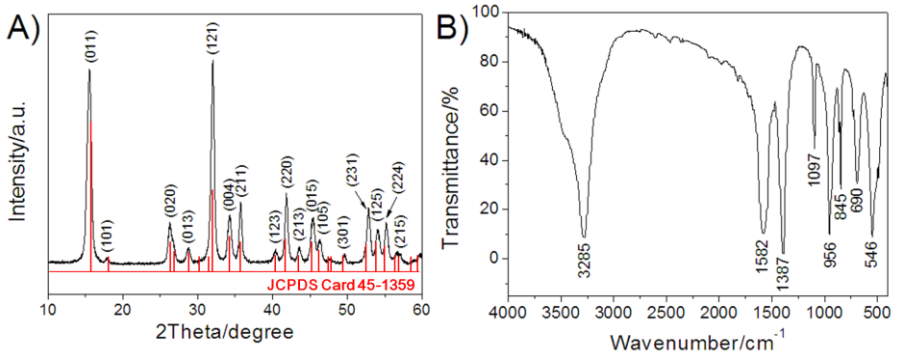


Figure S1. (A) XRD pattern of as-prepared Na-dawsonite using an ionic liquid-assisted hydrothermal route. All of the diffraction peaks in can be indexed to the orthorhombic structure of $NaAl(OH)_2CO_3$ (JCPDS Card 45-1359). (B) FT-IR spectra of as-prepared Na-dawsonite. The bond at around 3285 cm^{-1} is assigned to the stretching vibration of the O-H group. The presence of CO_3^{2-} in the as-prepared sample is evidenced by its fingerprint peaks of D_{3h} symmetry at 1547, 1097, and 845 cm^{-1}, which are assigned to vibrational modes of v_3(E'), v_2(A1") and v_4(E") respectively, according to normal modes of vibration of planar CO_3^{2-}. The peak located at 690 and 546 cm^{-1} should be ascribed to Al-O lattice vibrations.

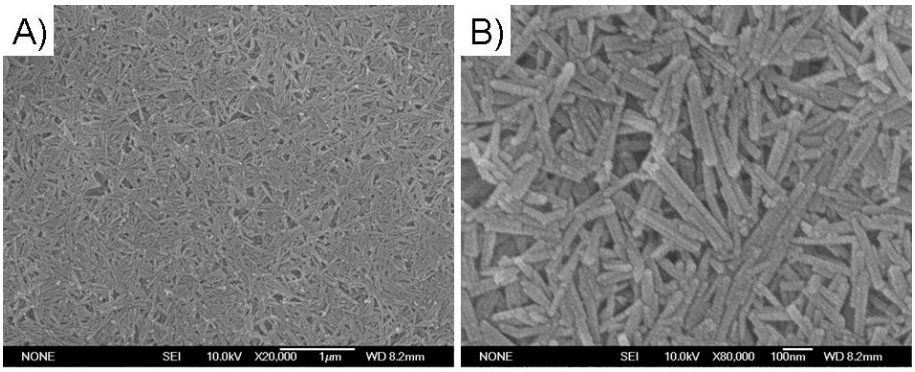


Figure S2. (A) Low- and (B) high-magnification SEM images of as-prepared Na-dawsonite nanorods.

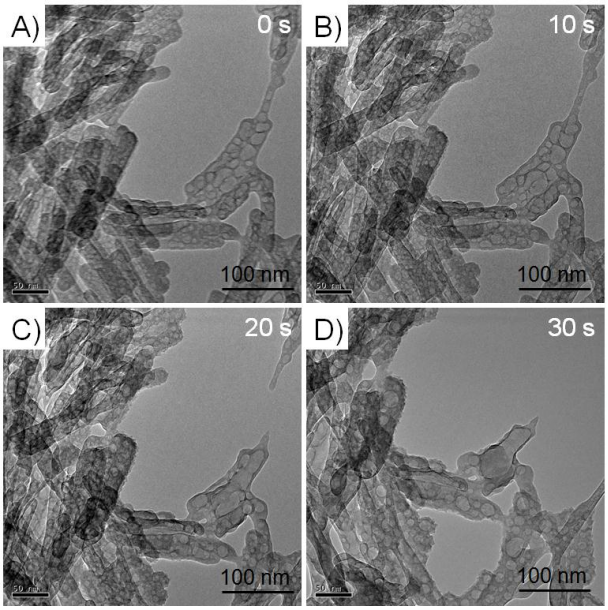


Figure S3. TEM images of Na-dawsonite nanorods exposed at approximately (A) 5, (B) 18, (C) 60, and (D) 180 sec under 200 kV electron beam.

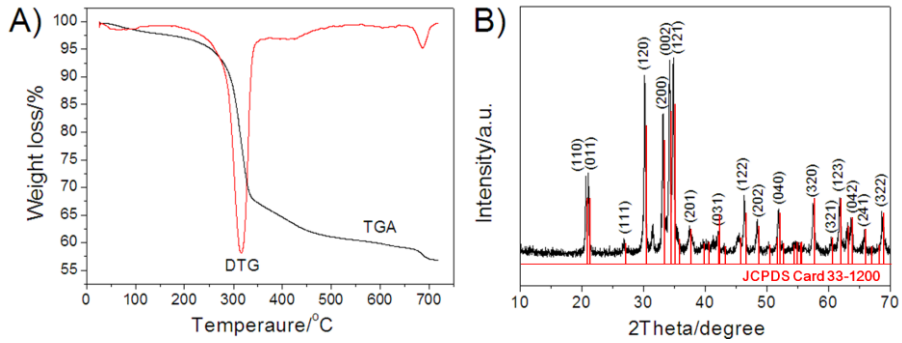


Figure S4. (A) TGA and DTG curves of the as-prepared Na-dawsonite; (B) XRD patterns of the samples prepared through annealing at 600 °C for 2 h from Na-dawsonite at atmosphere. From the TGA curve, it can be seen that the decomposition of Na-Dawsonite appears to occur in three steps with in a total weight loss of

approximately 41.1 % up to 720 °C, which is close to the theoretical value (43.1 %). The first step from room temperature to 150 °C can be attributed to the presence of a minute amount of weakly held water molecules (weight loss of about 2.3 %), the second step from 150 t0 430 °C should involve the decomposition of Na-dawsonite into the $Na_3Al_3O_5CO_3$ (weight loss of about 34.3 %) and the third step from 430 to 720 °C should be attributed to the conversion of the $Na_3Al_3O_5CO_3$ into the $NaAlO_2$ (weight loss of about 6.8 %), respectively. Correspondingly, there is an aculeated exothermic peak at 310 °C on the DTA curve which is associated with the decomposition of Na-dawsonite. When the temperature is above 720 °C, the weight loss of precursor no longer changes, indicating that the complete transformation to the $NaAlO_2$ phase. Those results can also be confirmed by the XRD results. All of the diffraction peaks in the XRD patterns of the product calcinated at 700 °C for 2 h can be indexed to the cubic structure of $NaAlO_2$ with lattice constants a = 5.387 Å, b = 7.033 Å, c = 5.218 Å (JCPDS Card 33-1200).

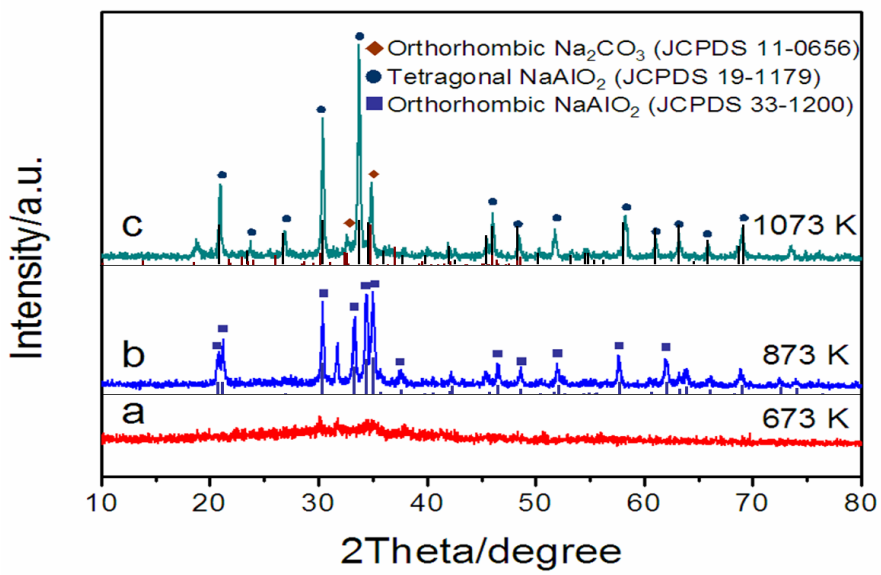


Figure S5. XRD patterns of the samples prepared through vacuum annealing at different temperature for 2 h: (a) 400 °C, (b) 600 °C, (c) 800 °C, respectively.

Table S1. Bond Dissociation Energies for the Na-dawsonite structure.

Bond	ΔHf_{298} (kJ/mol)	Bond	ΔHf_{298} (kJ/mol)
Na-O	257	C-H	337
Na-H	201	O-H	428
C-O	1076	Al-O	512

The data are taken from *Lange's Handbook of Chemistry (the 15th edition), Section 4: Properties of Atoms, Radicals, and Bonds.*

Calculation on the temperature rise due to beam heating

The highest temperature rise due to beam heating for uniform film sample can be expressed as the following equation:

$$T = \frac{W_0[1 + 2\ln(R/r_0)]}{4\pi l_0 k} (W_0 = \varepsilon V \rho_0 \pi r_0^2)$$

Where, W_0 is the total absorbed power, R is the radius of the film within a hole of copper grid, r_0 is the radius of the irradiated region, l_0 is the specimen thickness, which is 20 nm for Na-dawsonite nanorods, k is the thermal conductivity, which is 0.0634 W/m•K for Na-dawsonite at 300 K, ε is the fraction of energy absorbed, usually 0.01, V is the accelerating voltage, and ρ_0 is the current intensity.

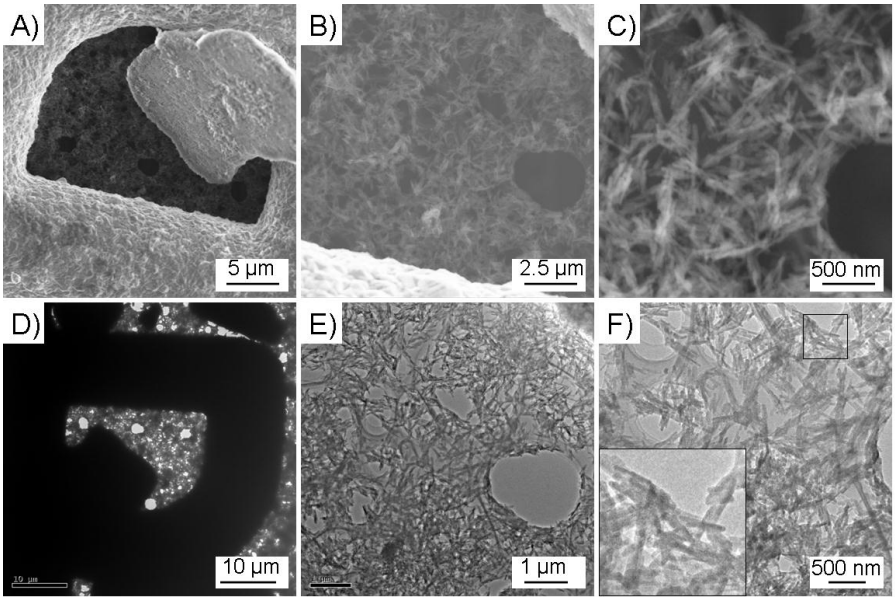


Figure S6. (A, B and C) SEM images of Na-dawsonite nanorods at 10 min exposure in the 10 kV electron beam; (D, E and F) TEM images of the above Na-dawsonite nanorods after 10 min irradiation under 10 kV electron beam. It can be clearly seen that the nanorods do not transform into nanocapsules after 10 min irradiation, indicating that the decomposition induced by electron-beam irradiation could not occur when a lower beam voltage was employed.