ESI for:

Formation of Hexagonal boron nitride nanoscrolls induced by Inclusion and Exclusion of Self-assembling molecules in solution process

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Experimental section

Chemicals and Materials

Boron nitride powder (<1µm, 98%), lithocholic acid (>97%), and dichlorobenzene (anhydrous) were purchased from Sigma-Aldrich. All reagents are used as received.

Preparation of the exfoliated boron nitride solution

Boron nitride (1.5g) was added to 300mL dichlorobenzene. The mixture was homogenized at 1000 rpm for 1 hour. Finally the slurry was centrifuged at 4400 rpm for 30 minutes.

Synthesis of starting material (*N-(2-aminoethyl)-3α-hydroxy-5β-cholan-24-amide (LCA))*

LCA was synthesized by the reaction of methyl lithocholate with excess of diaminoenthane according to the previous work[23]; The methyl lithocholate was dissolved in methanol and excess of diaminoethane (20-30 times) was added to methyl lithocholate solution. The solution was heated with an oil bath (80 – 90 °C) for 2 days. The resulting solution was poured into the water and the precipitate filtered. The product was recrystallized from acetonitrile and dried in a vacuum.

Synthesis of Methyl lithocholate

Methyl lithocholate was synthesized to the previous work[33]; To a stirred suspension of lithocholic acid (2.53 g, 6.27mmol) in methanol (25mL) was added Acetyl chloride (0.24mL, 3.38mmol) dropwise at room temperature for 3.3hrs. And then, di-water (25mL) was added to the mixture. The resulting precipitate was collected by filtration and dried at 50°C to give crude products (2.68g, quantitatively) as a colorless powder. Analytically pure methyl lithocholate was obtained by recrystallization from acetonitrile.

Synthesis of *N-(2-Hydroxyethyl)-3-hydroxy-5-cholan-24-amide*

N-(2-Hydroxyethyl)3-hydroxy-5-cholan-24-amide was synthesized by the reaction of methyl lithocholate with 2-aminoethanol according to the previous work[33]; 2-Aminoethanol (3.5 g, 57.6mmol) was dissolved in methanol (25mL) and methyl lithocholate (0.5g 1.28mmol) was added. The resulting mixture was stirred at room temperature for 5 days, then poured over ice-water (100mL). The white solid obtained was filtered off, washed with water, dried in a vacuum, and analyzed without further purification.

Preparation of Boron nitride scrolls (BNSs)

An amount of LCA was dissolved in dichlorobenzene (1ml) with heat treatment; a weight of LCA can be varied from 0.01 to 0.1mmol. And then immediately, the dissolved hot solution was poured into the exfoliated h-BN solution (5ml) in dichlorobenzene. The solution with precipitates was stored at room temperature for 24 hrs and the crude BNSs were observed. The resulting precipitate was obtained by filtering with a PTFE membrane, affording LCA induced Boron nitride nanoscrolls (BNS).

1. Synthesis of Smaller inner diameter size of boron nitride nanoscrolls (S-BNS)

To obtain S-BNSs, LCA of 0.02mmol was dissolved in ODCB (1mL) and heated to 60°C. Then, the dissolved LCA solution was immediately poured into the exfoliated boron nitride solution (5ml). The solution with the precipitates was stored at room temperature for 24 hrs. The resulting precipitate was obtained by filtering with a PTFE membrane washed with methanol followed by centrifugation at 4000 rpm for 20 minutes and by decantation. This procedure was at least repeated five times. The smaller solid core S-BNSs were obtained. To remove the included LCAs inside BNSs, S-BNSs were washed with methanol and followed by centrifugation at 4000 rpm for 20 minutes and by decantation. Additionally, the obtained

S-BNSs were stored in methanol for few days in order to have long time enough to dissolve LCAs. The hollow core S-BNSs were obtained.

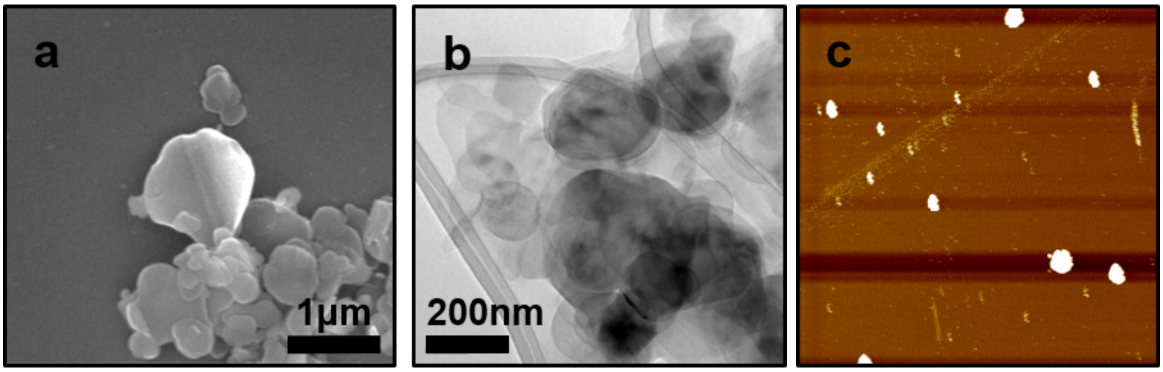
2. Synthesis of Larger inner diameter size of boron nitride nanoscrolls (L-BNS)

To obtain L-BNS, LCA of 0.003mmol was dissolved in ODCB (1mL) and heated to 60°C. Then, the dissolved hot solution was stored at room temperature for 24hrs. The dissolved hot solution was stored at room temperature for 24hrs. And then a LCA fiber solution was poured into the exfoliated boron nitride solution (5mL) at RT and the precipitates were obtained by filtering with a PTFE membrane, followed by centrifugation at 4000 rpm for 20 minutes and by decantation. Here, the LCA fiber as a template interacts with h-BN sheets and then larger solid core L-BNSs were obtained. To remove the LCA fiber inside BNSs, L-BNSs were sufficiently washed with methanol several times and followed by centrifugation at 4000 rpm for 20 minutes and by decantation. The hollow core L-BNSs were obtained.

Characterization

The purified solid sample was re-dissolved in methanol (2ml). A drop of sample by a micros yringe was placed on a holey carbon grid and then was allowed to evaporate methanol in a va cuum. TEM measurements were carried out on JEM-2100F with an accelerating voltage of 2 00 kV. Optical micrographs (OM) were taken with an OLYMPUS BX51 polarized optical mi croscope and AcquCAM II digital camera. TOMORO AcquPro 2005TM (Image partnership Co., Ltd.) was used for image capture. Atomic Force Microscopy (AFM) measurements were made with PSI AFM (XE-100). All the topography images were realized in a noncontact mod e using a PPP-NCHR (PointProbe® Plus Non-Contact High Resolution Frequency-Reflex Co ating) silicon probe with a tip radius of less than 10 nm (NanosensorsTM). System control an d data acquisition were performed by XEP software (Park Systems Corp.), and data analysis was done with XEI software (Park Systems Corp.). Scanning Electron Microscopy (SEM) measurements were carried out on Nova nano SEM 450 with an accelerating voltage of 15 kV. Micro-Raman spectrometer (JASCRO NRS-3100) analysis was carried out with excitation laser of 532nm wavelength using the 100 X objective. Samples were prepared by drop casting of the dispersion on SiO_2/Si and the solvent was evaporated at RT.

Figure S1. (a) SEM, (b) TEM and (c) AFM images of the exfoliatied boron nitride sheets.



The boron nitride in dichlorobenzene (ODCB) was homogenized at 1000 rpm for 1 hr followed by centrifugation at 4400 rpm for 30 minutes and collected from the supernatant dispersions. The concentration of the final exfoliated h-BN was calculated using the vacuum filter through a weighed membrane. The exfoliated h-BN solution had a concentration of 0.089mg/mL. SEM and TEM images of the exfoliated h-BN are shown in Figure S1a-b. The multi-layers boron nitride with the size of typically several hundred nanometers is observed. Additionally, an AFM image (Fig.S1c) shows the thickness of layers. The thickness of thinnest boron nitride is below few nm.

Figure S2. TEM images of the precipitates of (a) the bottom layer with the mixtures of the aggregated h-BN and multilayers of h-BN and (b) supernatant layers with BNSs.

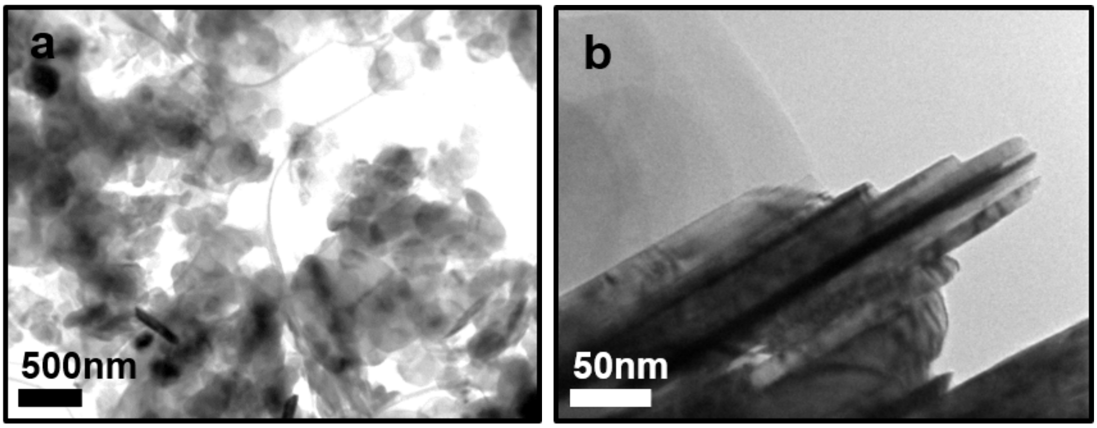
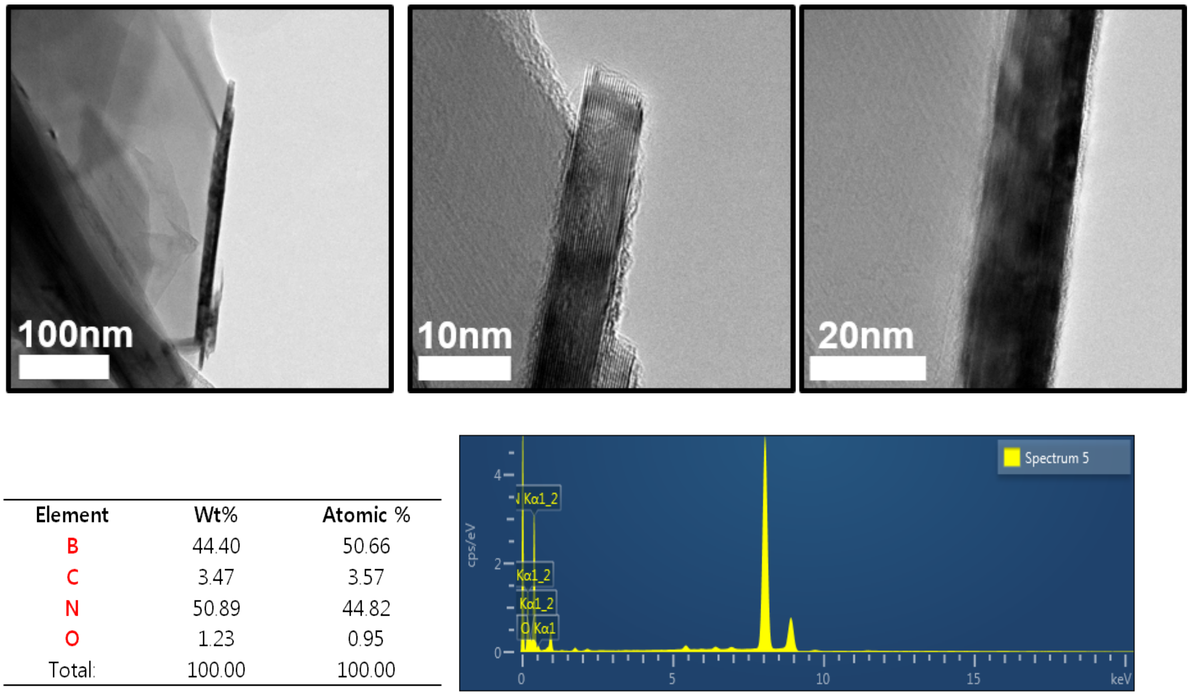


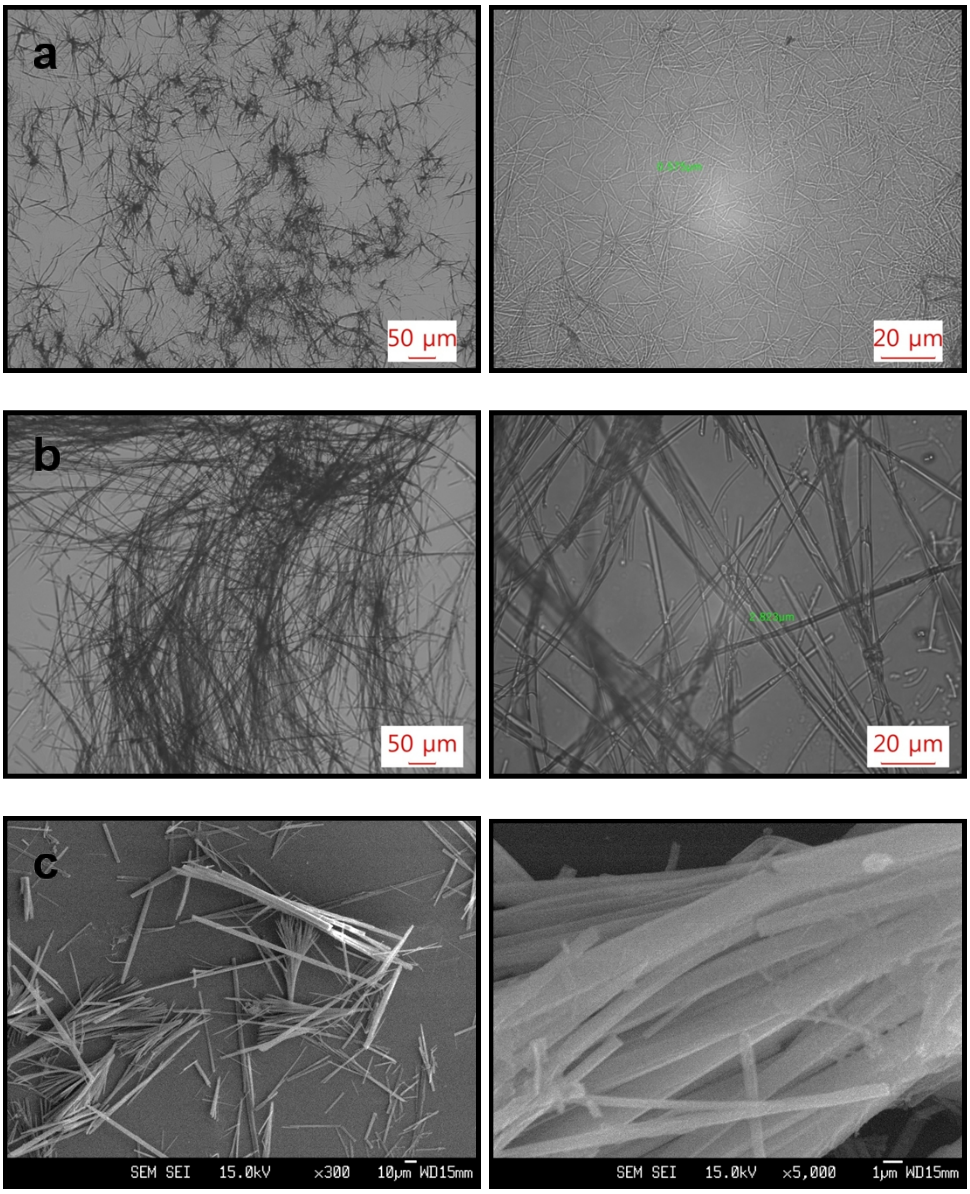
Figure S3. TEM images and Energy dispersive spectrometer (EDS) analysis of Hexagonal boron nitride nanoscrolls.



Element	Wt%	Atomic %
B	44.40	50.66
C	3.47	3.57
N	50.89	44.82
O	1.23	0.95
Total:	100.00	100.00

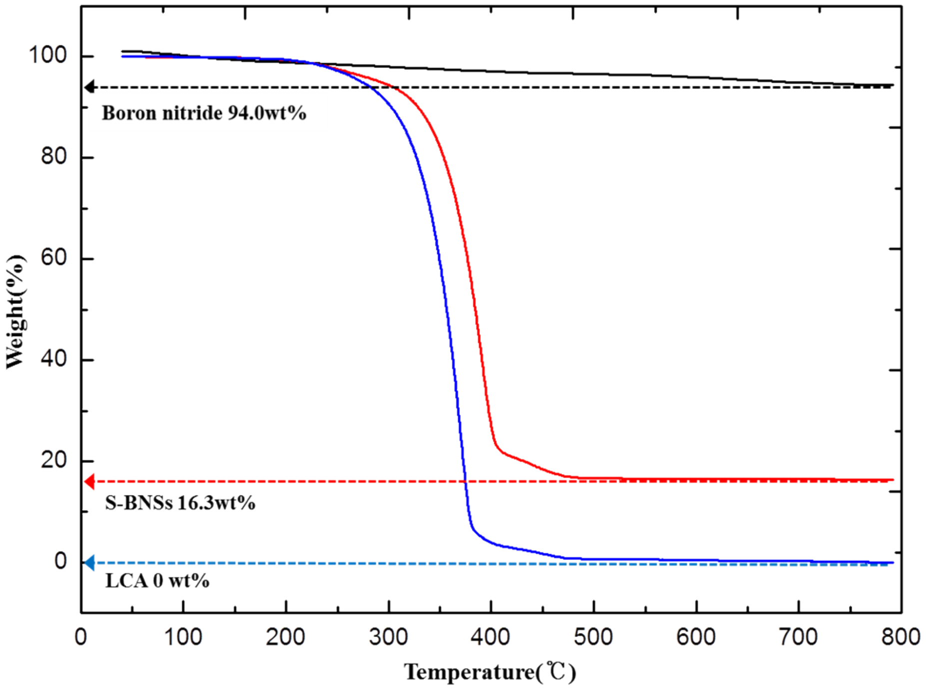
LCA induced BNSs at the center point were detected by the elementary analysis of Energy dispersive spectrometer (EDS) images. These data show BNSs with corresponding EDS mapping for B, C, N and O.

Figure S4. Optic microscopy images of LCA in two solvents, (A) ODCB and (B) Xylene and (C) SEM images of LCA in ODCB.



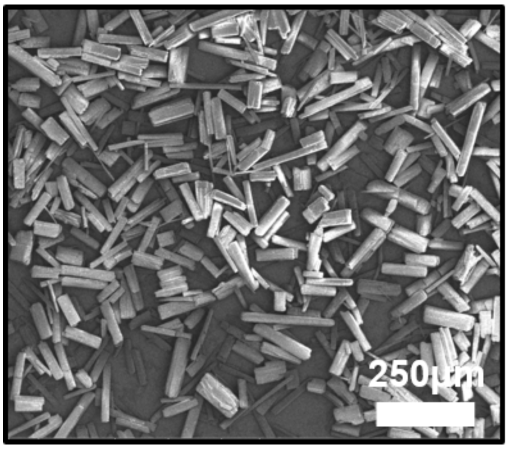
In general, it has been known that LCAs grow to be fibers in several solvents and SEM and OM images show LCAs grow to fibers in ODCB.

Figure S5. TGA curves and morphology of Hexagonal boron nitride nanoscrolls through the heat treatment. TGA curves of the exfoliated boron nitride (black), S-BNSs (red) and LCAs (blue).



Solid core S-BNSs were thermally treated under a N_2 atmosphere at a heating rate of 10°C/min to 800°C. The TGA curves show the thermal degradation of LCA, the exfoliated boron nitride and solid core S-BNSs. In case of LCA, the sharp degradation at 300°C and the slow degradation from 400°C to 800°C followed by zero wt% of LCA are observed in TGA curves. Boron nitride with slight reduction in the weight is stable up to 800°C. And the thermal degradation of LCAs in S-BNSs begins at 300°C maintaining the shape of solid core S-BNSs, which show the same shape of the TGA curve of LCAs. Likewise, the residual weight losses of S-BNSs are due to the boron nitride sheets and hollow core S-BNSs

Figure S6. SEM image of the supernatant precipitates before purification.



LCA fibers are dominantly observed. Thus it is necessary to wash excess LCA fibers with methanol in order to observe Hexagonal boron nitride nanoscrolls.

References

33. A. Valkonen, M. Lahtinen, E. Virtanen, S. Kaikkonen and E. Kolehmainen, Biosens. Bioelectron., 2004, 20, 1233–1241.