Supporting Information

Three-dimensional hierarchical 2,2,4,4,6,6-hexanitrostilbene crystalline cluster prepared by controllable supramolecular assembly and deaggregation process

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Expermental details:

1.1. Materials and Reagents

The HNS samples are provided by Institute of Chemical Materials, Chinese Academy of Engineering Physics. Dioxane (purity 99%) is supplied by Kermel Chemical Reagent Corporation (Tianjin, China). De-ionized water is supplied by the Institute of Electronic Engineering, China Academy of Engineering Physics. All reagents are analytical grade and used as received without further purification.

1.2 Preparation of micro/nano hierarchical HNS

HNS (5g) is dissolved in dioxane (1000mL) by heating up to 80-85 ^{o}C in a water bath with stirring and keeping in an ultrasonic bath and then the solution mixture is allowed to cool down to room temperature in procedure. The crystals formed are separated by suction filtration. Then the crystals are dried in vacuum oven at 100 ^{o}C and analyzed with power XRD，the course of deaggregation is lasting till the solvate has been reverted pure HNS phase. The forming microcrystalline clusters, desolvated HNS, is called HNS with 1st generation microstructure. Then this desolvated material is exposed to dioxane vapour resulting in supramolecular re-assembly to reform the HNS-dioxane solvate with the evidence of power XRD and FTIR. After drying in a vacuum oven the re-deaggregation crystalline is called HNS with 2nd generation microstructure. Similar procedure is followed for construction of micro/nano hierarchical HNS.

1.3 Characterization and measurement

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction patterns are recorded on a Bruker D8 Advance with a Cu–Kα radiation (λ=1.5406Å), the voltage and current applied were 40 KV and 40 mA, respectively. The data are collected from 5° to 50° in 2θ, with an increment of 0.02° and a scan speed of 0.1s per step.

Field emission scanning electron microscopy (FE-SEM). Scan electron microscopy (SEM) images are obtained with a ZEISS microscope operated at an acceleration voltage of 3 KV.

Fourier transform infrared spectroscopy (FTIR). The Infrared spectra are recorded on a Nicolet 6700 (Thermo Scientific) FTIR spectrometer with a resolution of 4cm^{-1}, in the scanning range of 500 cm^{-1}-4000 cm^{-1}. And the samples are ground and mixed thoroughly with KBr and disks are prepared by a hydrostatic press.

Particle size analyzer (PSA). The particle size distribution is measured with Malvern Mastersizer 2000, and the samples are dispersed by a ultrasonic dispersering system（Brasic 1510-MT） in the same treatment time of 0.5h.

N_2 adsorption/desorption measurement. The porous texture of the materials is investigated by nitrogen-desorption isotherm using JW-BK 300 (Beijing JWGB Sci& Tech Co.). The specific surface areas are determined by BET (Brunauer-Emmett-Teller) method and the pore size distribution of the samples are calculated by the BJH (Barrett-Joyner-Halenda) method from adsorption branch isotherms.

Figures:

Figure S1. SEM images of HNS in the process of 1st deaggregation

Figure S2 XRD patterns of HNS:dioxane solvate crystals in the process of deaggregation

Figure S3. FTIR spectra of HNS crystals

Figure S4. Pore size distribution of HNS crystals

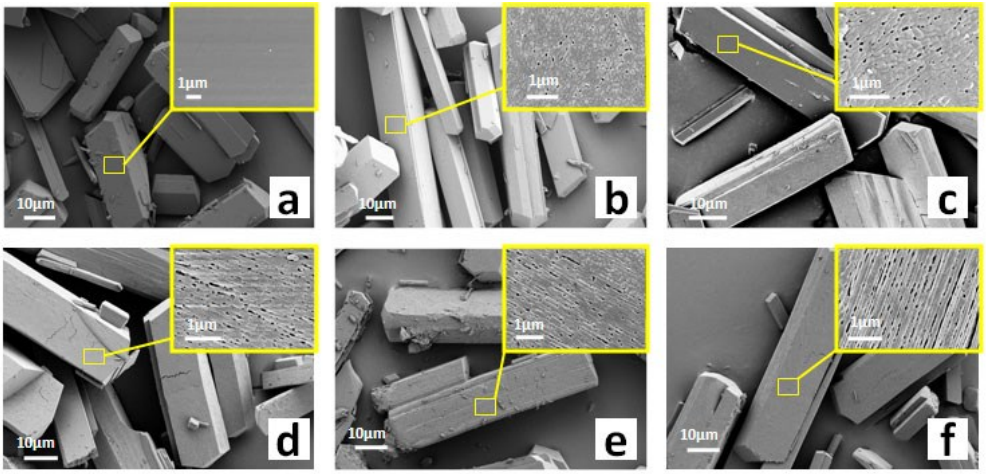

Figure S1. SEM images of HNS in the process of 1st deaggregation: (a) 0 min; (b)30 min; (c)60 min; (d)90 min; (e) 120 min; (f) 150min

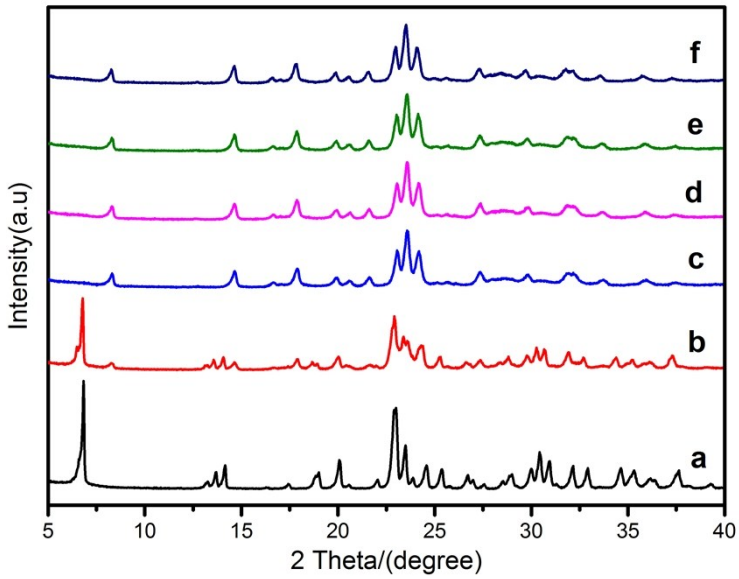

Figure S2. XRD patterns of HNS:dioxane solvate crystals in the process of deaggregation: (a) 0 min; (b)30 min; (c) 60 min; (d) 90 min; (e)120 min; (f)150 min.

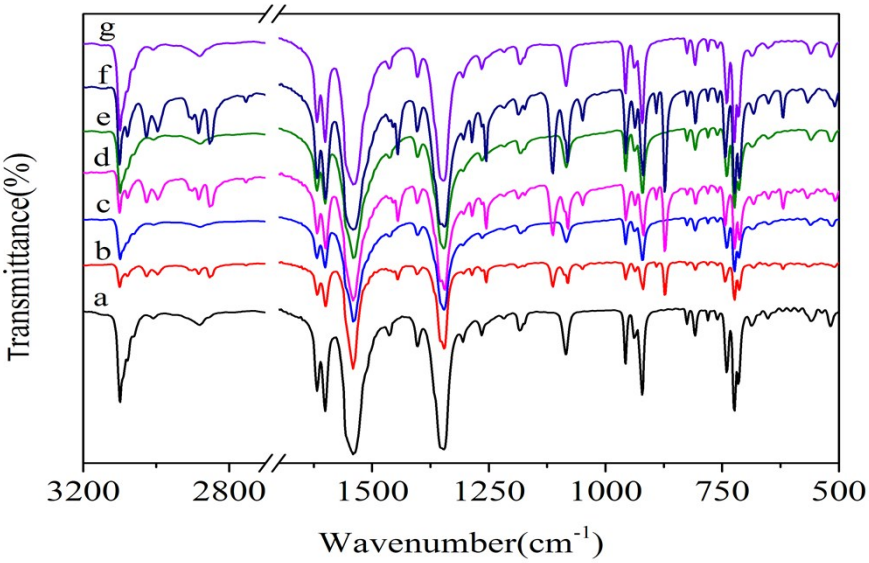

Figure S3. FTIR spectra of HNS crystals: (a) raw materials; (b)HNS:dioxane solvate; (c)1st generation HNS; (d) 2nd assembly HNS:dioxane; (e) 2nd generation HNS; (f) 3rd assembly HNS:dioxane; (g) 3rd generation HNS

FTIR spectra are performed for the HNS and its solvates with a detection range of 500-3200 cm^{-1} for the analysis of chemical information and major fuctional groups on the samples. The distinct peaks of HNS as follows, 3098cm^{-1} (aromatic C-H stretching), 2880 cm^{-1} (alkenic C-H str), 1618 cm^{-1} (aromatic C=C str), 1600 cm^{-1} (alkenic C=C str), 1539cm^{-1} (NO_2 asymmetric str), 1462, 1403, 1347 cm^{-1} (NO_2 symmetric str), 958 cm^{-1} (-CH= deformation in trans C=C), 920 cm^{-1} (-CH= out of plane deformation in the picryl group). It clearly indicates that

1st generation, 2nd generation and 3rd generation HNS have been completely transformed into the pure HNS. However, the other FTIR spectra (Fig. S3b, S3d, S3f) demonstrate that the difference of materials between the pure HNS owing to the new peaks occurred (1112, 1081, 1047 cm^{-1}), which are assigned to the characteristic peaks of HNS:dioxane. As a result, HNS and HNS:dioxane solvates crystals were effectively assembled and disassembled.

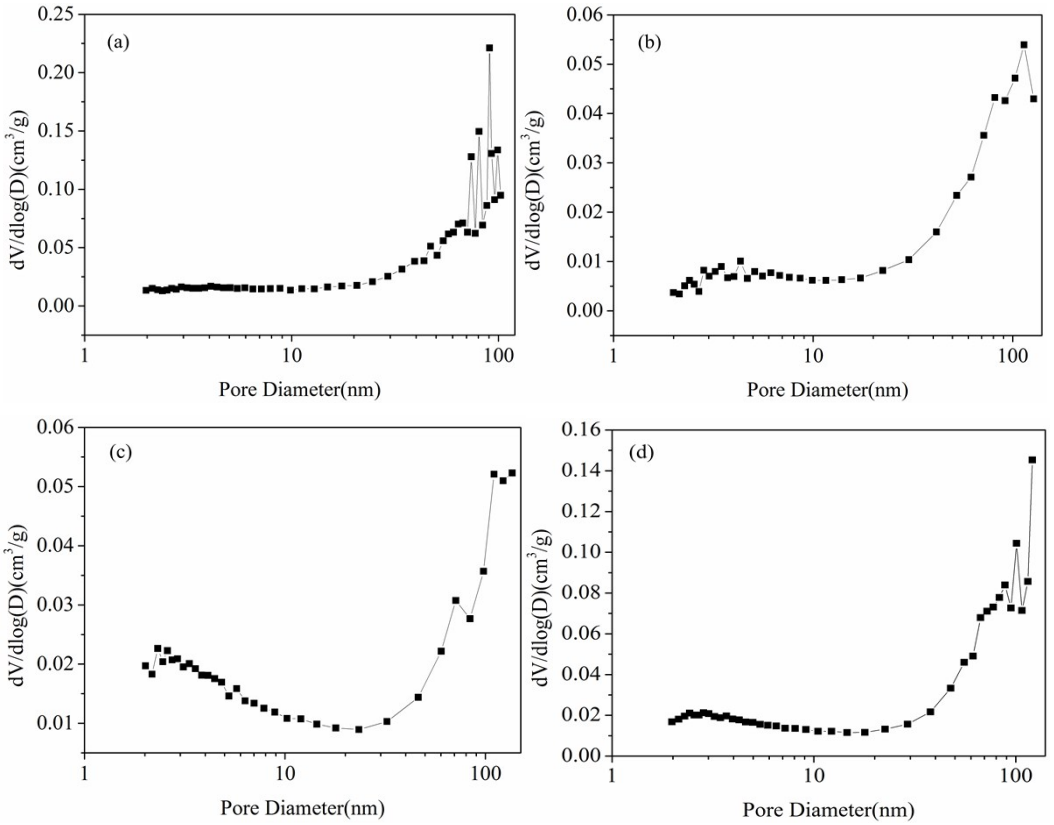

Figure S4. Pore size distribution of HNS: (a) raw materials; (b)1st generation HNS; (c) 2nd generation HNS; (d) 3rd generation HNS