

Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Facile Assembly of Nanocrystals by Optimizing Humidity

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Experimental

Materials: Tetraethoxysilane (TEOS, > 98 %, Merk), tetrapropylammonium hydroxide (TPAOH, 40 %, Sigma), tetramethylammonium hydroxide (TMAOH•5H₂O, > 97 %, Sigma), sodium hydroxide (Riedel-del Haen), aluminum isopropoxide (Al(O-*i*-Pr)₃, ≥ 99.99 %, Aldrich), hydrofluoric acid (38-40 %, Merck), iron (III) chloride hexahydrate (FeCl₃•6H₂O, 99 %, Sigma-Aldrich), sodium phosphate monobasic monohydrate (NaH₂PO₄•H₂O, ACS reagent, 98.0-102.0 %, Aldrich), urea (99.0-101.0 %, for analysis, Merck), hydroxypropyl cellulose (HPC, M.W. 100,000, Alfa Aesar) and poly(methyl methacrylate) (PMMA, M.W. 120,000, Aldrich) were used as chemicals.

Synthesis of nanocrystals: Pseudo-plate shaped MFI (denoted as MFI-OH) nanocrystals (40 nm) were synthesized according to a well-documented procedure,^[1] but with slight modifications. The suspension of nanosized MFI crystals was prepared from mixture with the molar composition: 1 TEOS: 0.36 TPAOH: 16.32 H₂O. After hydrolysis of the mixture on a shaker at room temperature for 24 h, the solution was subjected to hydrothermal treatment at 100 °C for 24 h. The solution of nanosized crystals resulting from hydrothermal treatment

was purified by separation from the mother liquor by three-steps of centrifugation (20,000 rpm, 30 min). After each step, the nanoparticles were redispersed in double distilled water using an ultrasonic bath for 30 min. The washed nanocrystals were freeze dried before use.

Flake-like MFI (denoted as MFI-F) crystals (200 nm × 100 nm × 20 nm) were synthesized in fluoride media at near neutral pH as described in detail elsewhere.^[2] In short, the synthesis mixture was prepared by mixing TEOS, TPAOH and distilled water. After stirring for 24 h, a fully hydrolyzed clear synthesis solution was obtained. Thereafter, some of the water and essentially all ethanol were removed from the solution using a rotary evaporator operated at 50 °C for 1 h. A certain amount of distilled water was added to the gel under stirring. Thereafter, HF was quickly added to the synthesis mixtures under stirring. The resulting molar ratio of the solid clear gel was 1 SiO₂: 0.36 TPAOH: 0.36 HF: 11.64 H₂O. Finally, the obtained gel was transferred into a polypropylene bottle, and kept at 60 °C for 2 months. After synthesis, the crystals were purified by repeated centrifugation and redispersion in distilled water, and freeze dried before use.

Sheet-like MFI crystals (340 nm × 170 nm × 60 nm) were synthesized from addition of urea in the starting solution.^[3] The crystals were hydrothermally synthesized from starting silicate mixture with molar ratios of 1 TEOS: 0.3 TPAOH: 40 H₂O: 0.36 urea. The synthesis mixture was prepared by mixing TEOS, TPAOH and distilled water. After shaking for 24 h, urea was introduced into the fully hydrolyzed clear solution. After shaking at room temperature overnight, the mixture was transferred to an autoclave, which was placed in an oil bath to crystallize at 180 °C for 8 h. After synthesis, the crystals were purified by repeated centrifugation and redispersion in distilled water, and freeze dried before use.

Cubic zeolite LTA crystals with an average size of 90 nm were prepared starting from a clear solution with a molar composition of 4.1 (TMA)₂O: 0.35 Na₂O: 1 Al₂O₃: 3.4 SiO₂: 239 H₂O. The solution was heated at 90 °C for 24 h under reflux.^[4] Cubic zeolite LTA crystals

with an average size of 200 nm were synthesized from a mixture having a molar composition of 13.4 (TMA)₂O: 0.6 Na₂O: 1.8 Al₂O₃: 11.25 SiO₂: 700 H₂O. The solution was heated at 100 °C for 24 h.^[5] All solutions were filtered with 200 nm Whatman® filters before synthesis. The synthesized crystals were purified by repeated centrifugation and redispersion in distilled water and freeze dried before use.

Octahedral FAU nanocrystals (80 nm) were synthesized according to a well-documented procedure,^[6] but with slight modification. The molar composition of the synthesis solution was 2.46 (TMA)₂O: 0.032 Na₂O: 1 Al₂O₃: 3.4 SiO₂: 400 H₂O. At first, TMAOH•5H₂O and NaOH were dissolved in distilled water. Then, Al(O-*i*-Pr)₃ was added under vigorous stirring until a clear solution formed. The solution was filtered through a 200 nm Whatman® filter. At last, TEOS was added to the mixture and hydrolyzed for 24 h, after which the solution turned clear again. Crystallization was performed at 100 °C for 120 h. The crystals were then purified by centrifugation and redispersion in distilled water under treatment by ultrasound. The purification procedure was repeated five times and then the crystals were freeze dried before use.

Hematite crystals with spindle morphology and a size of 500 × 100 nm were prepared by placing a solution of 0.02 M FeCl₃ also containing 4.0 × 10⁻⁴ M NaH₂PO₄ in a closed Pyrex bottle, which was then kept in a preheated oven at 100 °C for 3 days.^[7] The obtained spindle crystals were thoroughly washed by repeated centrifugation and dispersion in water and freeze dried before use.

Preparation of polymer coatings: HPC and PMMA were dissolved in ethanol and acetone, respectively, to obtain 2 wt. % solutions. Thin films of HPC and PMMA were deposited on glass plates using a spin-coater. The glass plates were sonication treated in acetone and ethanol, respectively, for 5 min and dried before coating. The dropwise added solution covered the whole area of the glass plate and then the film deposition was carried out for ca.

20 sec with a spinning rate of 2500 rpm for both HPC and PMMA. The polymer layers were thereafter cured at 105 °C for 1 h.

Preparation of monolayers by manual assembly: Monolayers of oriented nanocrystals were assembled on the polymer surfaces by rubbing the powders of freeze-dried crystals onto the surfaces using a Nitrile gloved finger in a humidity controlled chamber (at relative humidity RH = 10 % or 60 %) with proper contact pressure ($P \approx 0.03 \text{ kg/cm}^2$ or 0.3 kg/cm^2). After rubbing, the physisorbed multilayers were removed by gentle wiping with clean soft cotton or facial tissue.

Characterization: SEM images were recorded using a FEI Magellan TM 400 high resolution instrument without coating the samples prior to the investigation. XRD data were recorded using a PANalytical EMPYREAN X-ray diffractometer running in the Bragg–Brentano geometry employing Cu K α radiation in the 2θ range 5–50° for zeolite and 20–70° for hematite. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were recorded on a Bruker IFS 66v/S spectrometer equipped with a DTGS (Deuterated Triglycine Sulfate) detector. The samples were diluted with KBr in the ratio 1 part sample to 50 parts diluent. Spectra were recorded by co-adding 256 scans at a resolution of 4 cm^{-1} . Water contact angles were measured using a Fibro 1121/1122 DAT-Dynamic Absorption and Contact Angle Tester equipped with a CCD camera. For each surface investigated the contact angle was measured three times and the average value was reported.

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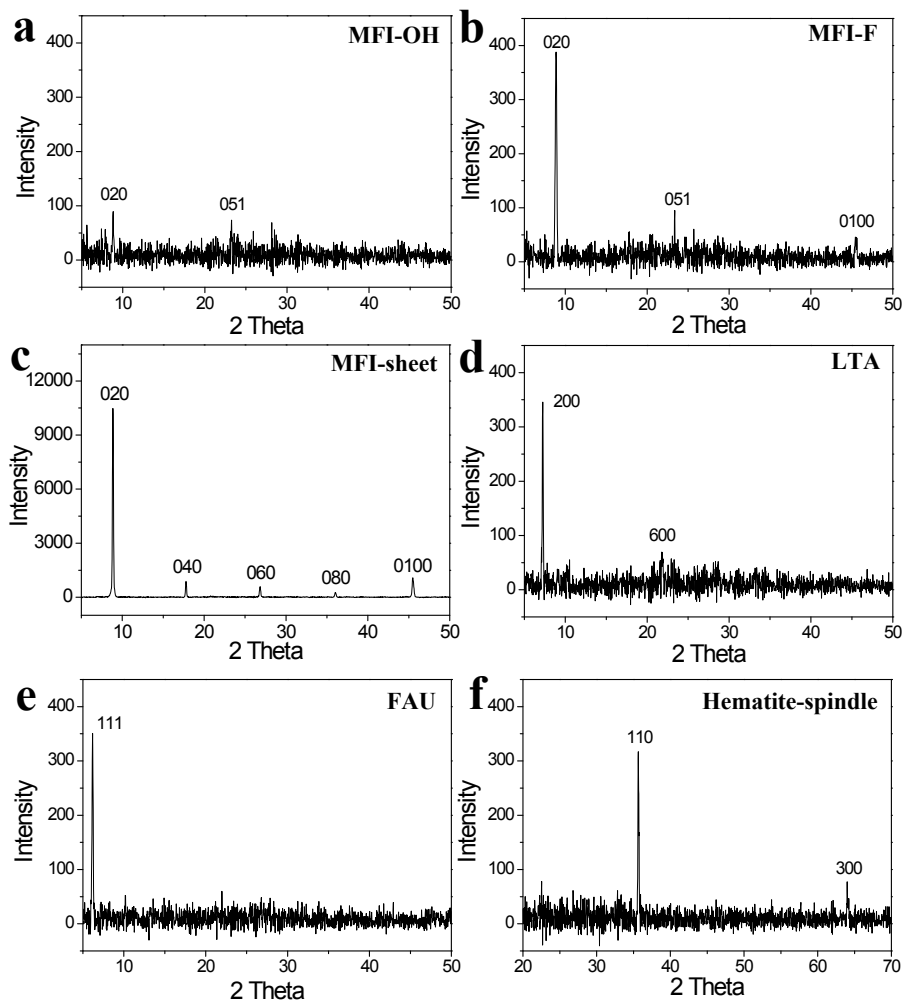


Fig. S1 XRD patterns of oriented MFI monolayers with crystal size of 40 nm a), $200 \times 100 \times 20$ nm b), and $340 \times 170 \times 60$ nm c); oriented cubic LTA and octahedral FAU monolayers with crystals sizes of 90 nm d) and 80 nm e), respectively; oriented spindle hematite monolayer with crystals sizes of 500×100 nm f).