Electronic Supplementary Information

The aqueous colloidal suspension of ultrathin 2D MCM-22P crystallites

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In a typical procedure, MCM-22P (0.13 g) was treated with the solution of 20% TPAOH (3.3 mL) and deionized water (18.7 mL). The mixture (pH ~13.3) was magnetically stirred overnight at room temperature. After that, it was centrifuged at 4,000 rpm for 15 min, resulting in wet solid ‘4agg’ and the translucent suspension ‘4sus’. Occasionally, the suspension right after the reaction was employed for characterization prior to centrifugation. In some cases, the 4sus was subject to an additional centrifugation at 15,000 rpm for 15 min, resulting in the wet solid ‘+15agg’ and the suspension ‘+15sus’.

The repeated treatment with the TPAOH solution was performed as follows. Starting from the mixture of 4sus and 4agg in the previous paragraph, the 4sus was decanted, leaving 4agg in the tube. To this tube, 3.3 mL of 20% TPAOH and 18.7 mL of deionized water was added. The content in the tube was magnetically stirred overnight, followed by a 4,000-rpm centrifugation (15 min), which results in the suspension ‘4sus*’ and the wet solid ‘4agg*’.

All XRD measurements were performed with a Rigaku Rint 2200HF diffractometer with a Cu Kα radiation at 2-30° 2θ (scan speed 1°/min). The aggregates recovered by centrifugation in wet state (e.g., 4agg) were placed on a horizontal sample stage in a chamber where the relative humidity was controlled at 95%. The parent MCM-22P and the air-dried sample were analyzed under ambient.

SAXS measurements on wet aggregates were performed on a Rigaku NANO-Viewer with Cu Kα radiation, covering the range 0.08 < Q/ nm−1 < 2.3. Here, \( Q = \frac{4\pi \sin \theta}{\lambda} \) (λ =0.154056 nm) is the magnitude of the scattering vector. An adequate amount of wet aggregates from centrifugation was transferred to the holder, which was subsequently sealed with Scotch tape. The holder was allowed to rest for ~0.5 h after loading to remove the effect of injections. The exposure time per sample is 2 h. The interlayer spacing (d) can be calculated from the relation \( Q = \frac{2\pi}{d} \). The corresponding range of d detectable is 2.7 < d/ nm < 79.

Four types of the suspensions were employed to prepare the specimens for AFM analysis: the suspension prior to centrifugation, 4sus, +15sus, and 4sus*. An amount of 4 mL of each suspension was separately diluted with deionized water to a total volume of 200 mL. This approximates to a nominal concentration of 0.002% wt/vol. The final pH values of the diluted suspensions were all ~11.7. The ultrathin 2D crystallites were deposited onto a polyethylenimine (PEI)-coated Si substrate. AFM images were taken with an SPA-400 system (SPA400, Seiko Instruments Inc.) in noncontact mode using Si probes with a force constant of 20 N·m−1.

Dynamic light scattering of the suspensions was performed on four types of the suspensions mentioned above, but without any dilution, using an instrument of Photal Otsuka Electronics, model ELSZ-2. This instrument can measure the “particle size” in the range of 0.6 nm-7 μm. After the average value and the distribution of the particle size were well reproduced from one measurement to another, the readings (3 trials) were then collected.
Figure S1. (a) The suspension of MCM-22P (nominal concentration 0.6%wt/wt) treated with the TPAOH solution overnight prior to centrifugation; the photo was taken approximately an hour after the magnetic stirring was stopped. Sediments are visible at the bottom; (b) the suspension in (a) after the centrifugation at 4,000 rpm for 15 min which results in separation of the content into the aggregates 4agg and the suspension 4sus; (c) the Tyndall effect of the 4sus. The colloidal suspension 4sus is stable for at least 3 months.

Table S1. Peak positions of \(d_{001}\) and \(d_{002}\) for the pristine MCM-22P and several aggregates obtained from XRD measurements. The larger number of significant figures for pristine MCM-22P reflects its higher ordering nature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_{001}/\text{nm})</th>
<th>(d_{002}/\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wet</td>
<td>dry</td>
</tr>
<tr>
<td>MCM-22P</td>
<td>Not available</td>
<td>2.9</td>
</tr>
<tr>
<td>4agg</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>+15agg</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>4agg*</td>
<td>3.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Figure S2. Zoom-in XRD patterns from $2\theta = 2-10^\circ$ (top), $10-20^\circ$ (middle), and $20-30^\circ$ (bottom) of (a) pristine MCM-22P, and the wet aggregate: (b) 4agg, (c) +15agg, and (d) 4agg*. Patterns with primes (b’, c’, d’) are the aggregate air-dried for approximately a day.
Figure S3. AFM images of the deposited crystallites prepared from the diluted suspensions: (a) prior to centrifugation, (b) +4 sus, and (c) +15 sus. The right panel shows the normalized height distribution $h$, together with the total number $N$ of crystallites counted, the average thickness $<h>$ and the standard deviation.
Figure S4.  (a) The dependence of the hydrodynamic radius $R_H$ (in nm) on the centrifugation (speed in rpm) performed on the suspension treated with the TPAOH solution once; (b) The dependence of $R_H$ on the number of treatment with the TPAOH solution (once or twice) from the suspension centifuged at 4,000 rpm for 15 min. Different symbols in (b) indicate the values from the different trials of the treatment with the TPAOH solution.
Figure S5. SAXS profiles of wet aggregates: 4agg, +15agg, and 4agg*.
Figure S6. AFM images of the deposited crystallites from the diluted suspension ‘4sus*’, and selected profile analyses at different locations. The layered MCM-22P was treated with the TPAOH solution twice. A higher coverage of crystallites in these images can be observed compared to AFM images in the maintext where the crystallites were deposited from the suspension treated with TPAOH only once (4sus).