Electronic Supplementary Information

Oriented Monolayers of Submicron Crystals by Dynamic Interfacial Assembly

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Experimental details

Synthesis of silicalite-1 and hematite submicron crystals

Zeolite silicalite-1 crystals (~800×600×300 nm) and iron (III) oxide hematite (~400×400×400 nm) crystals were synthesized according to procedures described in literature.[S1, S2] Typically, the silicalite-1 crystals were synthesized by hydrothermal growth at 130°C for 12 hours in a mixture with a molar composition of 1TEOS:0.2TPAOH:100H_2O. The crystals were purified by centrifugation and redispersion three times and then freeze-dried before use. For synthesis hematite crystals, a ferric chloride stock solution (2.9 *M*) was obtained by dissolving $FeCl_3$ salt at room temperature and filtered through a 0.2 μm Millipore membrane. Dilution was made by addition of ethanol to acidified (HCl) ferric chloride solution, resulting in system containing 50% ethanol by volume. The mixed solution (0.0190 *M* $FeCl_3$ and 0.0012 *M* HCl) was passed through 0.2 μm Millipore membrane and then aged at 100°C for 2 days. The crystals were purified by centrifugation and redispersion three times and then freeze-dried before use.

Substrates pretreatment

Porous α-alumina discs with a diameter of 25 mm and a top layer with a pore size of 100 nm were rinsed in acetone (p.a.), ethanol (absolute), and DDI water, in that order. Sheets of polytetrafluoroethylene (PTFE) with a thickness of 5 mm were cut into square plates (2×2 cm^2) and polished with silicon carbide grinding paper #4000 to achieve a smooth surface. Then the PTFEs substrates were cleaned in acetone and rinsed with distilled water. Gold substrates consisting of a gold film with a thickness of approximately 50 nm on the surface of silicon wafers (2×1 cm^2) were prepared by sputtering. The glass substrates (2×1 cm^2) were washed with DDI

water, immersed in piranha solution (H_2SO_4/H_2O_2=2/1 v/v) at room temperature for 1 day to remove organic impurities, and were then washed with DDI water. All these substrates were stored in DDI water before use.

Dynamic interfacial assembly

The suspensions of dispersed crystals were prepared using a method similar to that described in reference [14]. Typically, to prepare a silicalite-1 suspension, 0.02 g crystals were mixed with 5 ml of 2-butanol and 4 μL of linoleic acid; the alcohol-modified hematite suspension was prepared by mixing 0.058 g crystals with 5 ml of 2-butanol. The suspensions were vigorously stirred in a flask (10 mL) with flat base at room temperature for 1 week before use.

The self-assembly process was conducted at room temperature and room humidity. The substrates were first immersed horizontally in DDI water (45 mL) and suspended by a Teflon support in a polypropylene beaker (mouth diameter 44 mm), and a clean magnetic stirring bar (20 mm) was placed at the bottom of the beaker. The suspension of crystals was then slowly and continuously injected onto the air-water interface using a syringe pump (Kent Scientific Corp.) at a speed of 4 $\mu Lmin^{-1}$ while the stirring bar was rotated at a speed that was gradually increased from 200 to 1500 rpm. After formation of a complete monolayer, which took about 50 minutes, the substrate was either lifted up horizontally through the monolayer with tweezers, or the monolayer was lowered onto the substrate by decreasing the water level (drawing water with a pipet).

The details about determine the formation of silicalite-1 monolayer on the interface during preparation were given in figure S1. As shown in photograph (a), the porous alumina disc was supported by a teflon holder and placed beneath the air-water interface. With the continuous injection of silicalite-1 suspension onto the water surface, the density of floating islands of crytsal monolayer increased accordingly. After 50 minutes, the pieces of monolayer gradually merged together to form a full coverage over the entire interface, figure S1(b). The SEM images of the silicalite-1 monolayers formed by dynamic interfacial assembly for 20 minutes, 30 minutes, 50 minutes and then transferred to porous alumina surfaces were given in figure S1 (c), (d), (e) respectively.

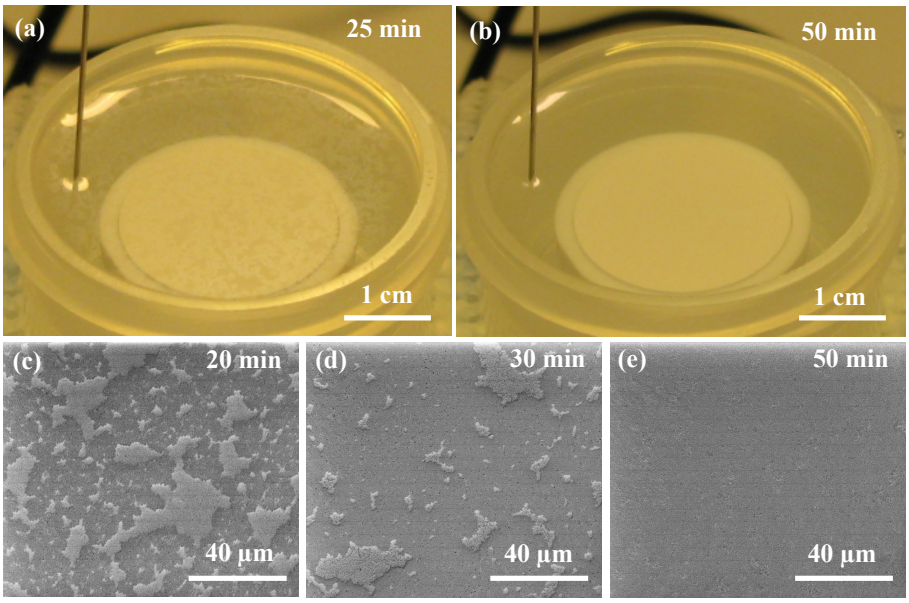

Figure S1. Photographs of (a) air-water interface floating with islands of silicalite-1 monolayer after the dynamic interfacial assembly proceeds 25 minutes, (b) the full air-water interface covered by *b*-oriented and close-packed silicalite-1 monolayer after 50 minutes; SEM images of the silicalite-1 monolayer formed by dynamic interfacial assembly for 20 minutes (c), 30 minutes (d), 50 minutes (e) and then transferred to porous alumina surfaces.

The details about determine the formation of hematite monolayer on the interface during preparation were given in figure S2. The glass plate was supported by a teflon holder and placed beneath the air-water interface. As the dynamic interfacial assembly proceed, the density of floating hematite crystals increase accordingly, figure S2 (a)-(c). The corresponding SEM images of hematite monolayer formed after 20 minutes, 30 minutes, 50 minutes and then transferred to glass plate surfaces were given in figure S2 (d), (e), (f) respectively.

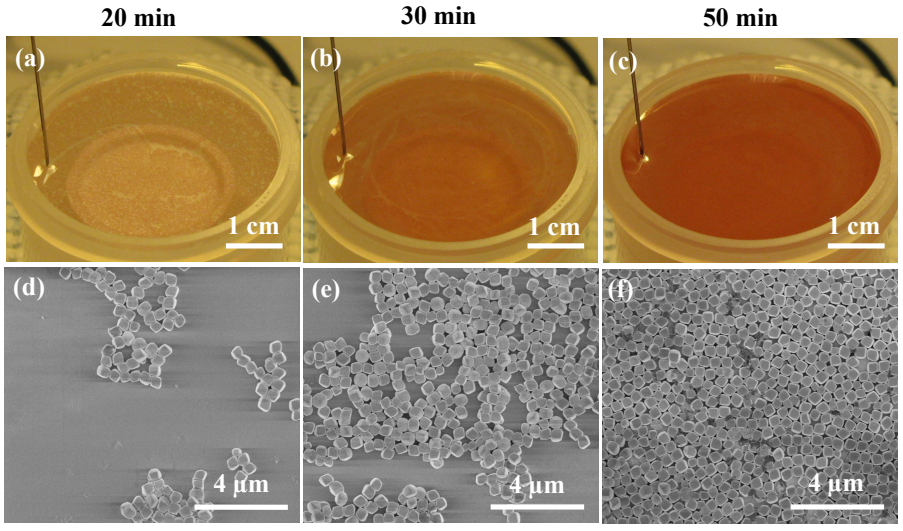

Figure S2. Photographs of air-water interface floating with islands of hematite monolayer after the dynamic interfacial assembly proceeds 20 minutes (a), 30 minutes (b), and the full air-water interface covered by (012) oriented and close-packed hematite monolayer after 50 minutes (c); SEM images of the hematite monolayer form by dynamic interfacial assembly for 20 minutes (d), 30 minutes (e), 50 minutes (f) and then transferred to glass plate surfaces.

Charaterization conditions

SEM images were recorded using a FEI Magellan™ 400 extreme high-resolution instrument, and samples for imaging were not coated prior to the investigation. XRD data was recorded using a Siemens D 5000 diffractometer running in Bragg-Brentano geometry employing Cu Kα radiation in the 2θ range 5°-50° for silicalite-1 and 20°-70° for hematite. The photographs were taken with a Canon PowerShot SX110 IS digital camera using a fluorescent tube for illumination.

References

S1 Z. P. Lai, G. Bonilla, I. Diaz, J. G. Nery, K. Sujaoti, M. A. Amat, E. Kokkoli, O. Terasaki, R. W. Thompson, M. Tsapatsis, and D. G. Vlachos, *Science*, 2003, **300**, 456-460.

S2 S. Hamada and E. Matijevic, *J. Colloid. Interface. Sci*., 1981, **84**, 274-277.