Highly crystalline iron/iron oxide nanosheets via lyotropic liquid crystal templating

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Electronic Supplementary Information (ESI)

Experimental:

Materials and methods: Iron(III)chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%), sodium borohydride ($NaBH_4$, 98%), 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethyleneglycol (Triton X-100, laboratory grade) were purchased from Sigma-Aldrich and used as such for synthesis. Nickel foil (0.006") was purchased from McMaster Carr and pre-treated for the electrode fabrication. Poly(vinylidene fluoride) (PVDF, MW 180,000) pellets and 1-methyl-2-pyrrolidinone (99%) were purchased from Sigma-Aldrich. Carbon black (Black Pearls 2000) was purchased from Cabot. Millipore deionized (DI) water (R = 18 MΩ) was used in the reaction and purification steps.

Powder X-ray diffraction (XRD) measurements were carried out using a PANalytical X'Pert Pro Bragg-Brentano powder X-ray diffractometer equipped with a diffracted beam Ni-filter and an X'Celerator detector. Cu $K\alpha_{1,2}$ radiation (λ = 1.540598, 1.544426 Å) were used as the X-ray sources. Transmission electron microscopy (TEM) was carried out on Jeol ultra-high resolution FEG-T/STEM instrument operating at an accelerating voltage of 200 kV. The nanosheets were dispersed in methanol and a droplet was placed onto a carbon coated copper grid (400 mesh) and air-dried prior to analysis. Small-angle X-ray scattering (SAXS) was measured in a Rigaku SAXS instrument system with Ni-filter and a multi-wire detector. Polarized Optical Microscopy (POM) studies were carried out in an Olympus BX51-P polarizing microscope coupled with a Linkam LS350 heating and cooling stage. Electrochemical studies were performed using CH Instrument electrochemical workstation (CHI 760C) in a three-electrode cell containing 1 M

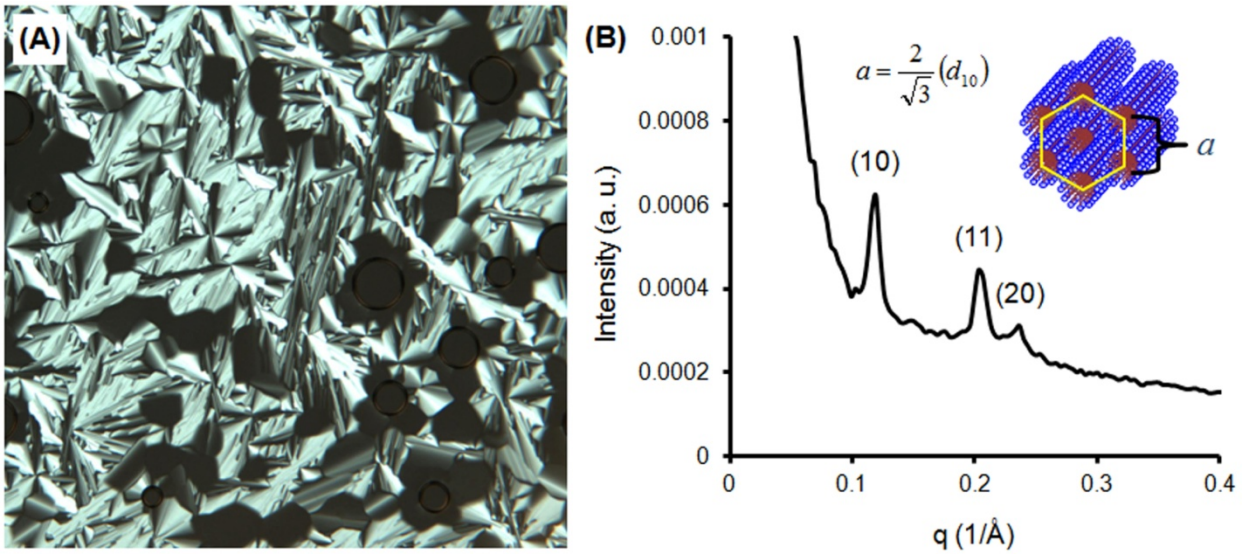
KOH as an electrolyte. I-IONS$_{TX100}$, Ag/AgCl and a platinum wire were used as working, reference and counter electrodes respectively. The working electrode was electrochemically cycled between -1.15 and 0.1 V for several times before recording the cyclic voltammogram.

Synthesis of I-IONS$_{TX100}$: Triton X-100 (48 g) in the reaction flask was degassed under high vacuum for two hours. Separately, $FeCl_3 \cdot 6H_2O$ (2 mmol) in 52 g of DI water was purged with nitrogen for one hour. $FeCl_3$ solution was added to Triton X-100 in the reaction flask under steady flow of nitrogen and was maintained till the completion of the reaction. The contents were mixed using a mechanical stirrer at 100 RPM, until the mixture turned to a taffy-like consistency. At this stage, the contents were slowly warmed to 45 ˚C (until all solids disappeared) and cooled back to ambient temperature to form a clear yellow LC phase. $NaBH_4$ (20 mmol) in 10 ml deoxygenated DI water was added rapidly to the reaction vessel with occasional mechanical stirring. The yellow gel turned almost immediately to black color along with formation of excess froth that filled the reaction vessel. Although the reaction is complete after approximately two minutes, after an additional 30 minutes from adding $NaBH_4$, the black colored froth was collected by adding 200 ml DI water in portions leaving the gel part behind. The crude product from the froth was collected using a rare earth magnet and washed several times with DI water and followed by ethanol. The final product after washing was dried under air at room temperature to yield a black powder. The product isolated from the gel portion (I-IONS$_{TC100gel}$) after washing with copious amount of water followed by ethanol was a dark red powder.

Electrode fabrication: The working electrode with I-IONS$_{TX100}$ was fabricated on a nickel foil that was used as a current collector. Nickel foil were cut into 1 cm wide strips of a desired length

and washed thoroughly with soap and water. The dried strips were dipped in dilute *aqua regia* (50%) for 1 minute and washed under copious amount of distilled water; dried and weighed. The active material was prepared by mixing I-IONS$_{TX00}$ or I-IONS$_{water}$ (70 wt.%), Carbon black (15 wt.%), PVDF (15 wt.%) in 1-methyl-2-pyrrolidinone (2 mg/ml) and sonicating the above mixture for a minute and resting it for 12 hours in a tightly sealed vial. A thin coating of the active material was uniformly applied on both sides of the pre-treated half of the nickel strips (2 cm^2) and dried at room temperature for 2 hours and under high vacuum for at least 12 hours before weighing. Later, a wire was attached to the nickel strip using copper tape and the exposed nickel strip was wrapped in Parafilm.

Supplementary Figures:



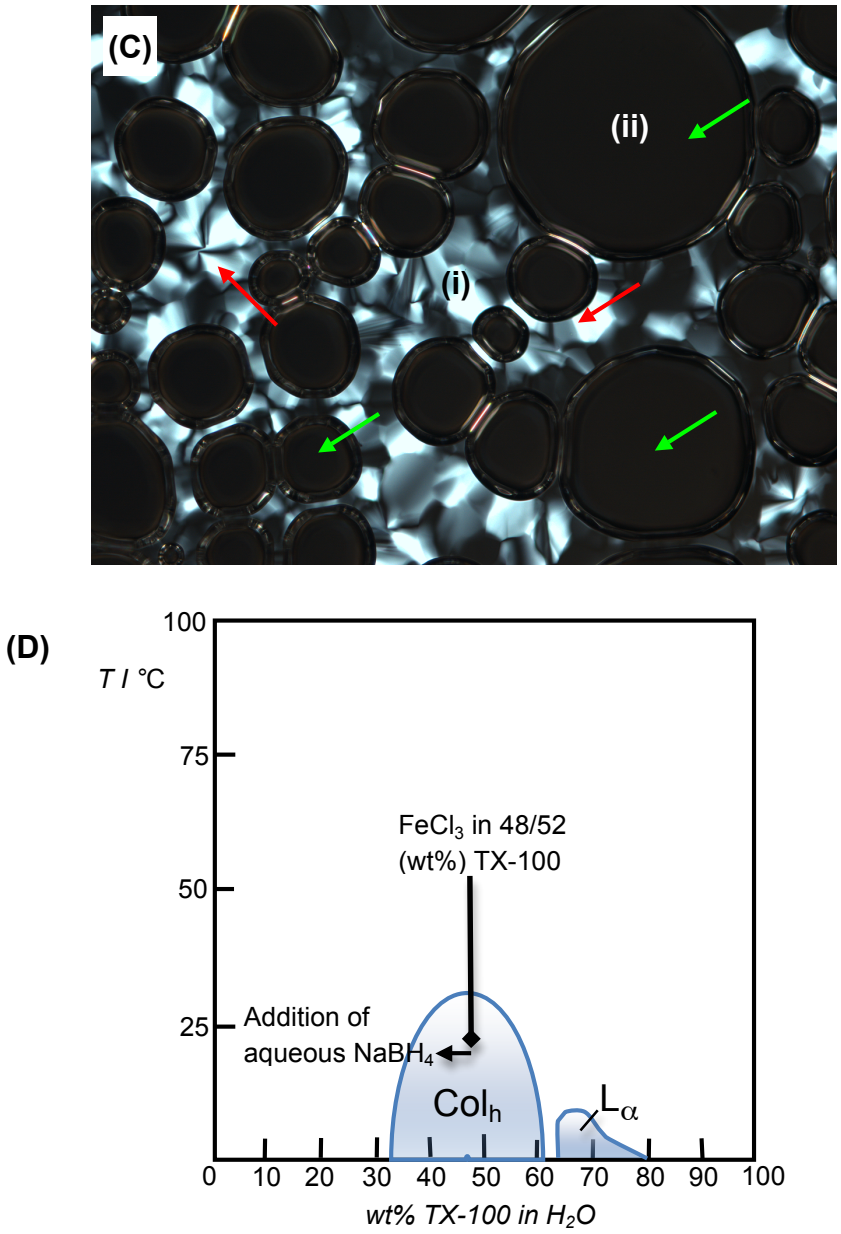


Fig. S1 (A) Polarized optical micrograph (crossed polarizers), (B) small angle X-ray scattering (azimuthally averaged intensity of the scattering vector q in $Å^{-1}$ vs. intensity from 2D SAXS pattern) of $FeCl_3$-H_2O/ TX-100 ($FeCl_3$: 2 mmol, H_2O/TX-100 52/48 wt.%) both at 20 °C. (C) Polarized optical micrograph (crossed polarizers) of the $FeCl_3$-H_2O/ TX-100 mixture after addition of aqueous $NaBH_4$ showing: (i) spherulitic texture (red arrows indicate some typical

textural defects) indicative of Col_h phase and (ii) the formation of H_2 gas bubbles (indicating the ongoing reaction as in Fig. S2B, green arrows). (D) Schematic phase diagram of Triton-X 100 in water. The Lα phase is only formed at higher concentrations of the non-ionic surfactant TX-100 and at temperatures below 10 °C.[1] Addition of aqueous $NaBH_4$ positions the reaction further left (lower TX-100 concentration) in the phase diagram. POM images confirm the existence of the normal Col_h phase in the nanosheet formation step (formation of froth in which the nanosheets form via coalescence of nanocrystallites).

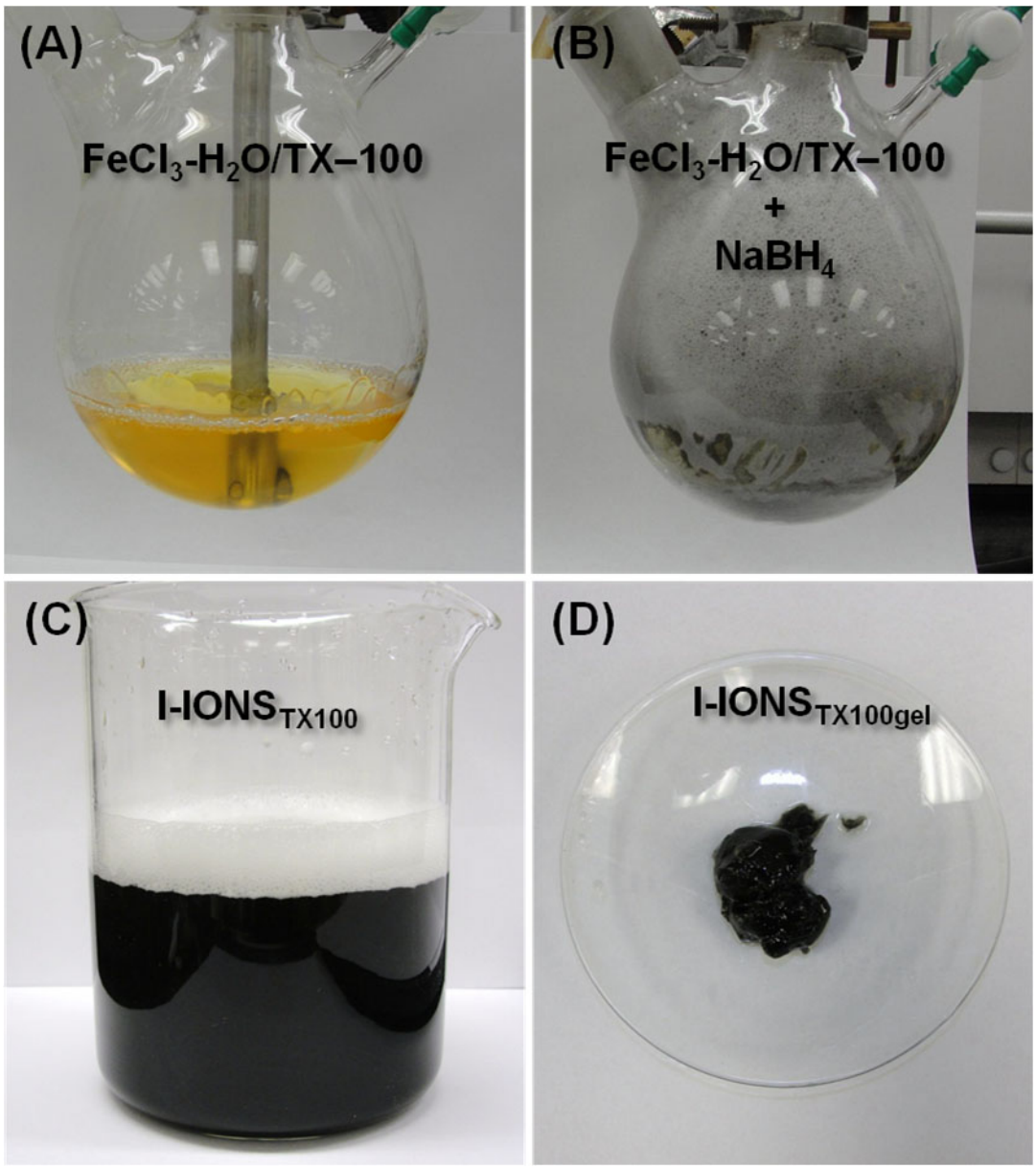


Fig. S2 (A) $FeCl_3$ in the lyotropic Col_h liquid crystal phase of water/TX-100 (52/48 w/w); (B) after addition of aqueous $NaBH_4$, hydrogen evolved forming froth; (C) I-$IONS_{TX100}$ dispersion in water from the froth; after being washed off the gel. (D) The gel part of H_2O/TX-100 after the reaction was black, but turned reddish brown on exposure to air (see powder XRD data in Fig. S5 conforming the existence of other Fe(III) species).

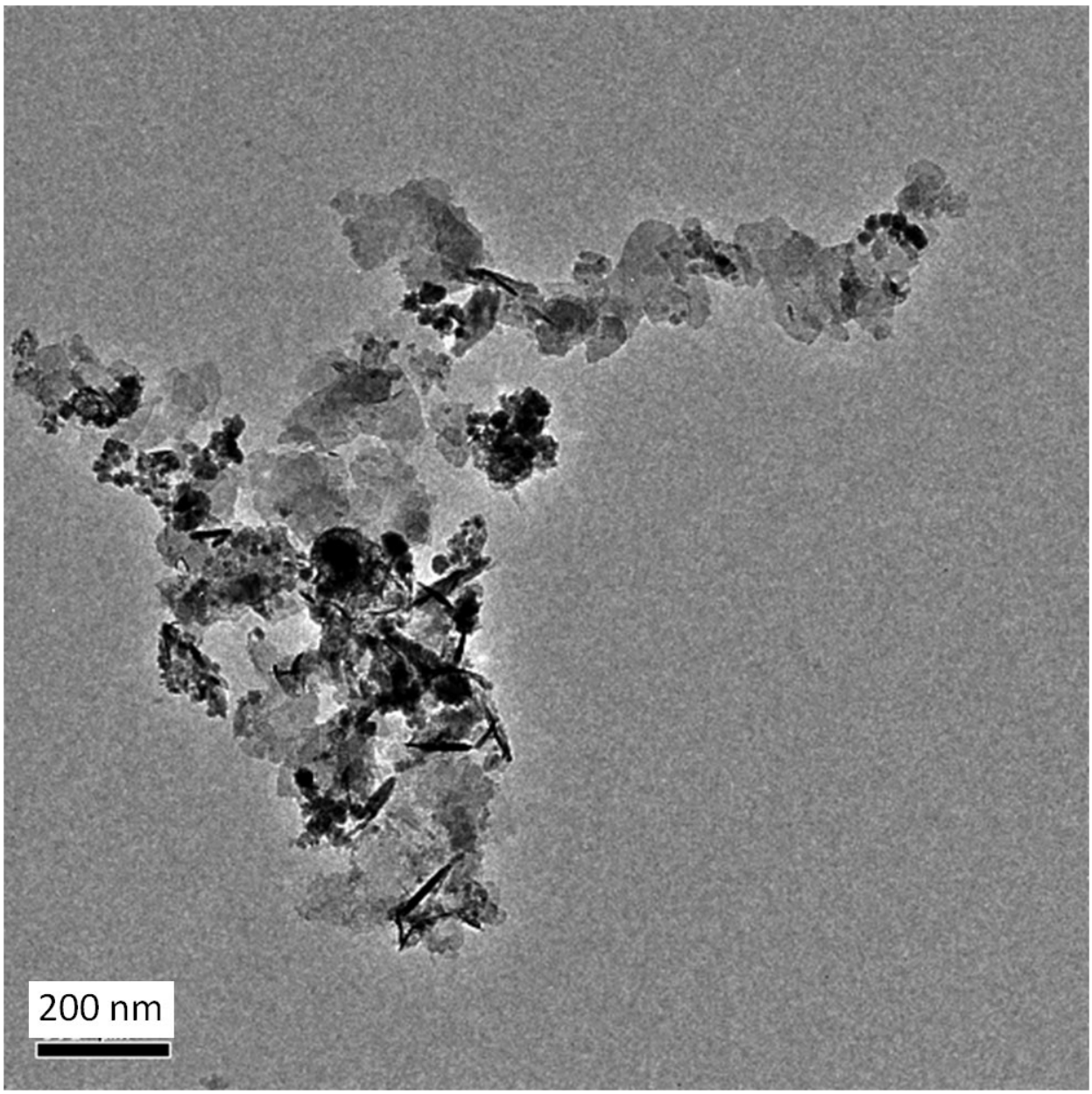


Fig. S3 TEM image of I-IONS$_{TX100}$.

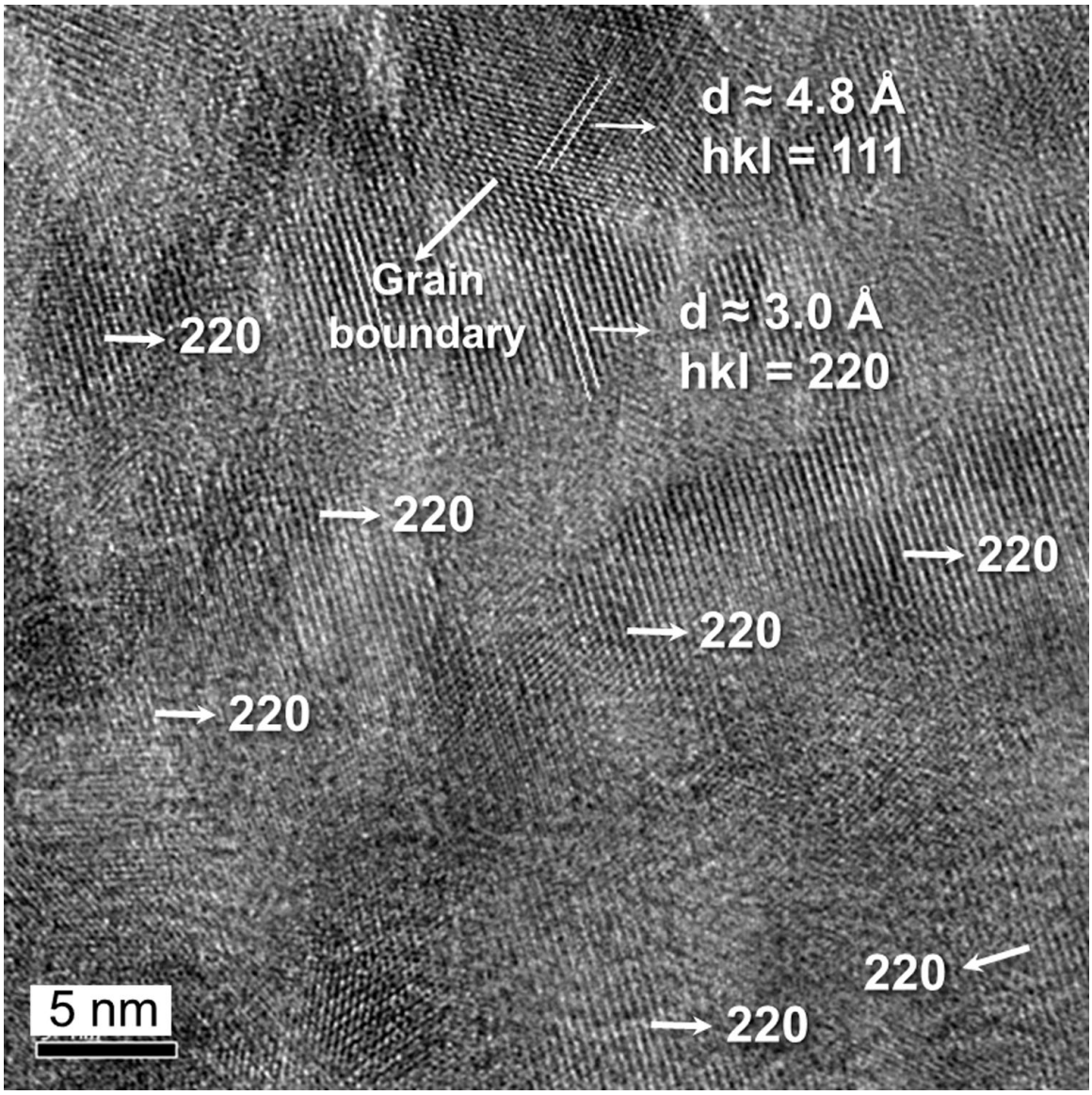


Fig. S4 HR-TEM image of I-IONS$_{TX100}$ showing long-range order of 220-plane with few out of focus protrusions (enlarged view of Fig. 2C)

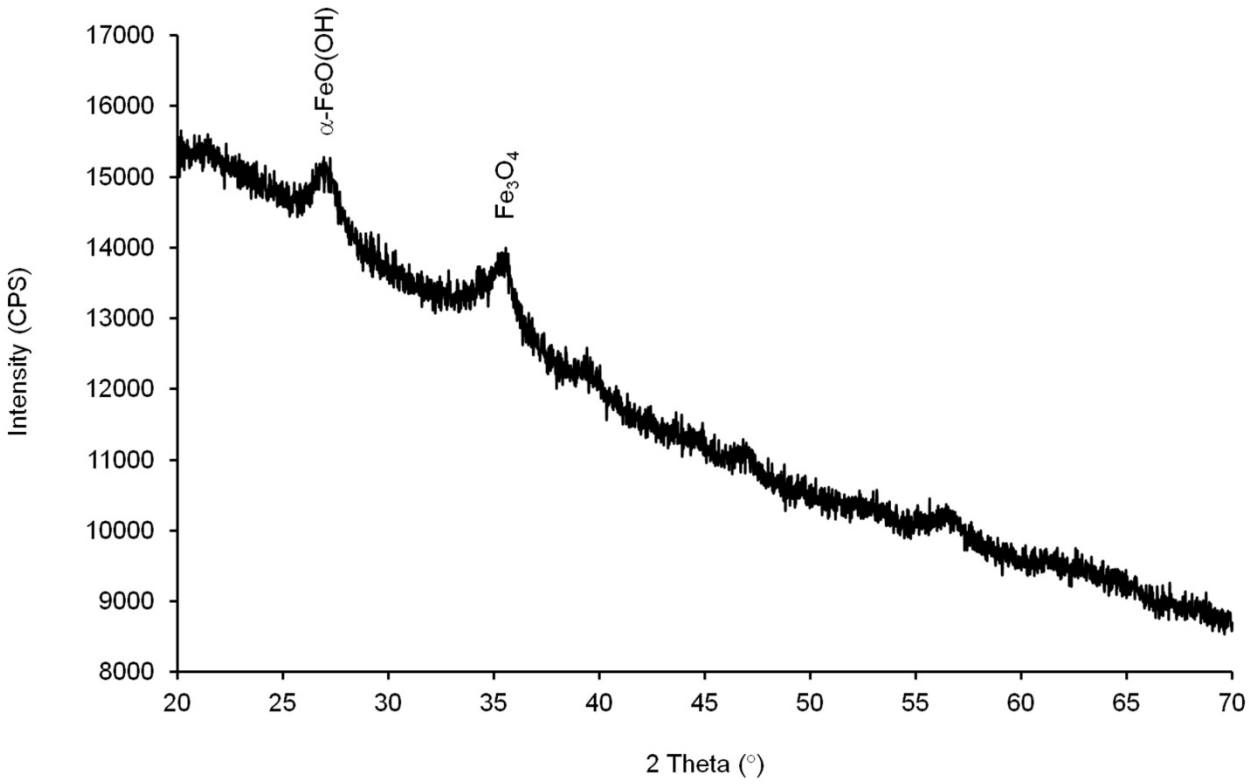


Fig. S5 Powder XRD pattern of $IONS_{TX100gel}$.

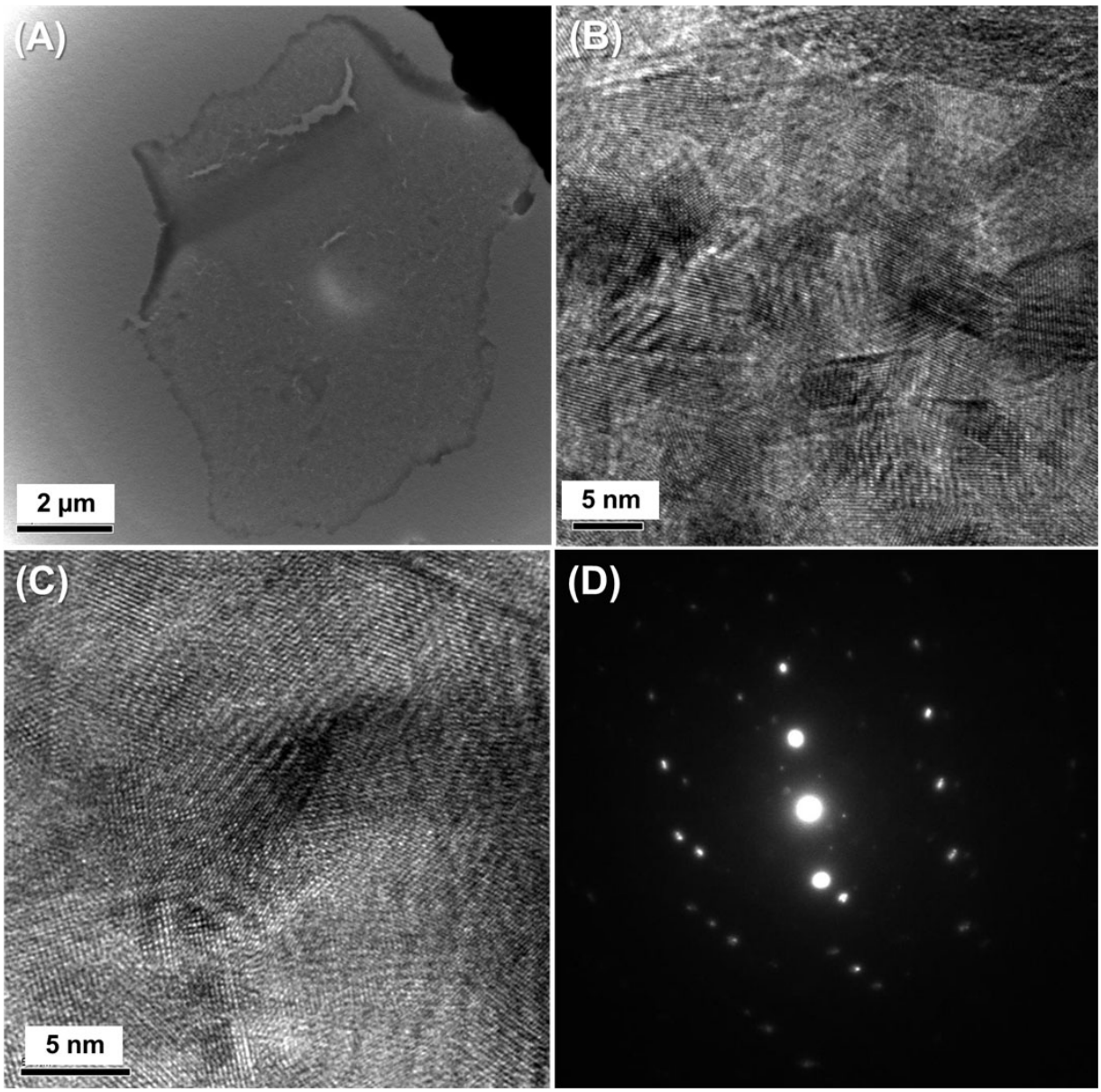


Fig. S6 (A) Representative TEM image of $IONS_{TX100gel}$ measuring microns across with visible tear in the sheet. (B and C) HR-TEM images of crystalline $IONS_{TX100gel}$ with visible lattice fringes and grain boundaries. (D) SAED pattern (from C) of $IONS_{TX100gel}$ with defined spots indicating its single-crystalline nature.

References:

1 Phase diagram reconstructed after: K. J. Beyer, *Coll. Interf. Sci.*, 1982, **86**, 73.