Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Metallogels of Indium(III) with bile salts: soft materials for nanostructured In_2S_3 synthesis

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Materials and methods

Indium chloride, sodium deoxycholate (Na-DCh) were purchased from Sigma-Aldrich and sodium cholate (Na-Ch) was purchased from SRL and Sigma-Aldrich, thioacetamide (TAA) was purchased from S d Fine-Chem Limited, and were used without further purifications. FT-IR spectra were recorded on Bruker putting solid/ xerogel directly to the sample holder. HRMS was recorded in positive mode by using Q-TOF Mass Spectrometer. Small angle X-ray diffraction of the xerogels were recorded in PANalytical Empyrean (45 kV, 30 mA, Cu-K_α) in presence of beam knife. For SEM, the samples were gold coated before imaging and examined using SIRION and ESEM Quanta scanning electron microscope. AFM imaging was performed on Nanowizard II (JPK instrument). Dynamic rheological measurements were done of the gels on an AR 1000 rheometer (TA Instruments) using a parallel plate geometry (diameter 20 mm). The In-Ch gels were scooped, placed over the rheometer plate, and allowed to equilibrate under the experimental condition for 1 h. The In-DCh gels were kept at room temperature 24 h after sonication and allowed to equilibrate under the experimental condition for 30 min over the rheometer plate. The temperature of the plate was maintained at 25 °C using a Peltier system. All the rheology experiments were carried out 3 times. Powder XRD patterns of the prepared In_2S_3 powder was recorded in Philips XRD 'X' PERT PRO diffractometer using Cu-K_α radiation (λ = 1.5438 Å) as X-ray sources. The In_2S_3 powder sample was dispersed in MeOH using vortex mixer and the filtrate was used for TEM, absorbance and fluorescence measurement. Absorbance spectra were recorded on a Shimadzu spectrometer and fluorescence spectra were recorded on a Varian Cary Eclipse spectrophotometer. For TEM, JEOL machine was used. Thermogravimetric analysis (TGA) was carried out under O_2 using Mettler Toledo instrument from room temperature to 900 °C with a heating rate of 10 °C min^{-1}. Elemental analysis of the prepared In_2S_3 powder using In-Ch gel and In-Ch/DCh xerogels were recorded in Vario Micro cube (elementar) instrument.

Preparation of gel

Fresh stock solutions were prepared by dissolving appropriate amounts of the compounds in distilled water. Equal volumes of indium chloride (10 mM-30 mM) and sodium cholate or sodium deoxycholate (30 mM-60 mM) were mixed with different concentration ratios at room temperature (25 °C) followed by sonication for 15-30 sec in an ultrasonic bath. Whereas, In-Ch formed gel within 5-10 min after sonication, In-DCh took longer time (24 h after sonication) to from the gel. Mixing 5 mM of In(III) with 1 equivalent of Na-Ch (5 mM) was produced a translucent gel (Figure S1). The gel became less transparent and eventually turbid when cholate concentration was increased from 15 mM to 30 mM (with 5 mM of In^{3+}). No gel could be produced with 60 mM of cholate and 5 mM of In(III). On the other hand, keeping the cholate concentration at 15 mM the metal concentration was varied from 5 to 30 mM, which produced turbid (with 5 mM and 10 mM of In^{3+}) to translucent gels (with 15 mM and 30 mM of In^{3+}). No gel formation were observed by mixing equal volumes of gallium chloride (20 mM) or aluminium sulphate (20 mM) with sodium cholate (60 mM) or sodium deoxycholate (60 mM) at room temperature (25 °C) followed by sonication for 10-30 sec in an ultrasonic bath, white precipitate or suspension were formed.

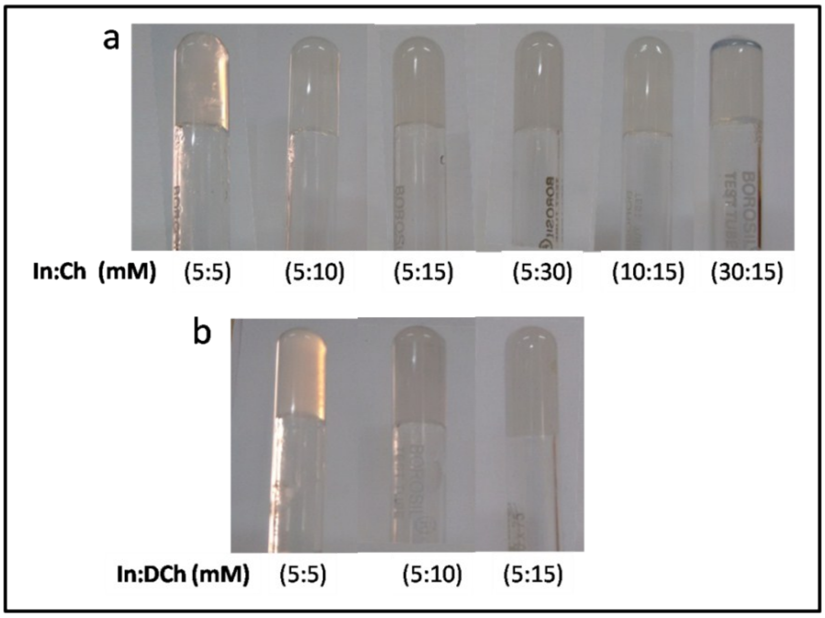

Figure S1. Photographs of In-Ch and In-DCh hydrogels at various ratios of In(III) to (a) Na-Ch and (b) Na-DCh

Preparation of xerogel

Gels were freeze dried to prepare xerogels. Xerogels were washed with water to remove inorganic salt NaCl, excess/unbound indium and then dried. Water washed xerogels were used for elemental analysis and XRD measurements.

FT-IR studies

FT-IR spectra of the ligands (Na-Ch and Na-DCh) and the xerogels (In-Ch and In-DCh = 5/15 mM) were recorded to get evidence of indium cholate/deoxycholate coordination. Carboxylate group showed anti-symmetric (ν_{as}) and symmetric (ν_s) stretching modes. The frequency separation $\Delta\nu = \nu_{as} - \nu_s$ can explicate the metal-carboxylate coordination modes. Generally, there are three coordination modes possible for metal-cholate, such as monodentate, bidentate chelating and bidentate bridging. Δν value of the unidentate complex is much higher than the corresponding ionic species. For bidentate chelating complex, Δν value is smaller than that of ionic species and bidentate bridging complexes have value close to the value of ionic state.[1,2]

In sodium cholate, the peak in 1552 and 1401 cm^{-1} corresponds to anti-symmetric and symmetric stretching modes of carboxylate, respectively, wherein the frequency separation Δν is 152 cm^{-1}. With the incorporation of indium ion, the peak of anti-symmetric and symmetric stretching modes shifted to 1545 and 1417 cm^{-1} respectively (Δν is 130 cm^{-1}, Figure S2). In sodium deoxycholate, the frequency separation Δν is 155 cm^{-1} and with the incorporation of indium ion, Δν value shifted to 131 cm^{-1} (Figure S2). The Δν value of indium-cholate and indium-deoxycholate were smaller than that of sodium cholate and deoxycholate. Therefore, it can be concluded that indium binds to carboxylate group of cholate and deoxycholate in a bidentate chelating mode. (The weak peak in 1706 cm^{-1} can be assigned to the presence of a small amount of cholic acid).

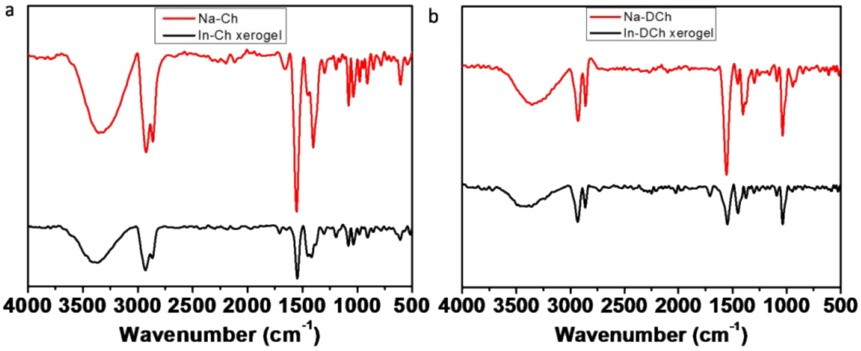

Figure S2. FT-IR spectra of (a) Na-Ch and In-Ch xerogel, and (b) Na-DCh and In-DCh xerogel

Electrospray ionization mass spectra (ESI-MS) of In-Ch xerogel

The formation of the coordination of indium(III) with cholate is obtained from electrospray ionization mass spectra (ESI-MS).2 In Figure S3, the peak at m/z 1337.7140, which can be identified into formula $[In(C_{24}H_{39}O_5)_3H]^+$ based upon their elemental composition (mass error = 27.6 ppm). This ion is corresponding to the 1:3 stiochiometry of indium ion and cholate (plus hydrogen). The other peaks at m/z 431.2824, 839.5659 and 1247.8263 corresponding to $[Na(C_{24}H_{39}O_5)H]^+$, $[Na(C_{24}H_{39}O_5)_2H_2]^+$ and $[Na(C_{24}H_{39}O_5)_3H_3]^+$ respectively.

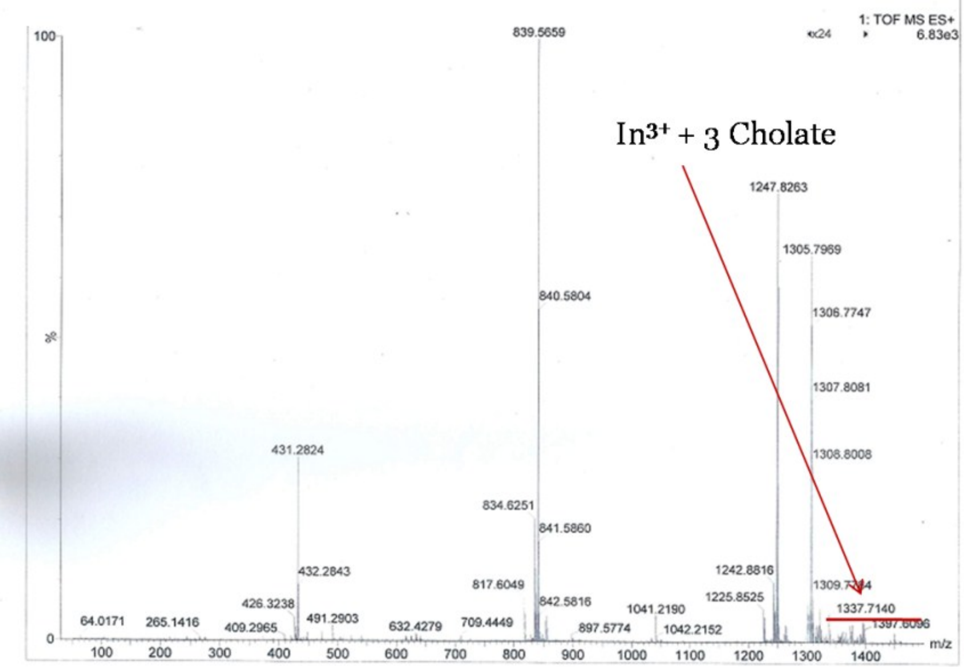

Figure S3. HRMS spectra of the In-Ch xerogel

Elemental analysis of In-Ch xerogel

The indium-cholate/indium-deoxycholate coordination can be also demonstrated by elemental analysis of the xerogels (Table S1). For elemental analysis, prepared xerogel was washed with water and then dried. Elemental analysis data of 5/15 mM, 5/10 mM and 5/5 mM of In-Ch xerogels showed the formation of 1:3 stoichiometry of Indium to cholate ($InCh_3$) although initial ratios were different. Similarly elemental analysis data of In-DCh xerogels with different ratio of In:DCh showed the formation of 1:3 stoichiometry of Indium to deoxycholate ($InDCh_3$).

Table S1. Elemental analysis data for In-Ch and In-DCh xerogels

Sample		C (%)	H (%)	N (%)
In-Ch (5/15 mM)	Found	59.34	8.809	0.00
	Calculated for $(C_{24}H_{39}O_5)_3$ In. $6H_2O$	59.82	8.99	0.00
In-Ch (5/10 mM)	Found	58.53	8.616	0.00
	Calculated for $(C_{24}H_{39}O_5)_3$ In. $8H_2O$	58.37	9.05	0.00
In-Ch (5/5 mM)	Found	60.33	9.085	0.00
	Calculated for $(C_{24}H_{39}O_5)_3$ In. $5H_2O$	60.58	8.97	0.00
In-DCh (5/15 mM)	Found	59.61	9.105	0.00
	Calculated for $(C_{24}H_{39}O_4)_3$ In. $9H_2O$	59.57	9.37	0.00
In-DCh (5/10 mM)	Found	59.65	9.065	0.00

Small angle X-ray diffraction of In-Ch xerogel

The XRD pattern of the In-Ch xerogel (prepared by mixing) showed the presence of Bragg refection peaks at 2θ = 3.47°, 6.39°, 6.87°, 8.01° and 9.31° (Figure S4). The corresponding d-spacing of these sets of peaks are 25.44, 13.82, 12.85, 11.03, 9.49 Å respectively.

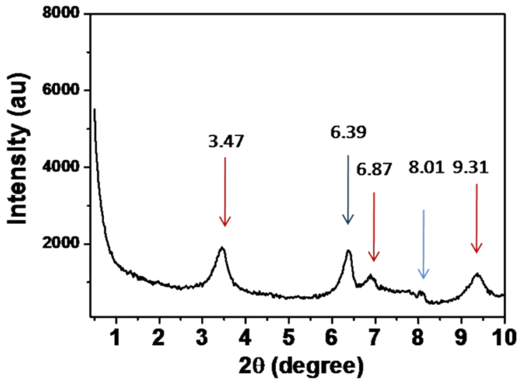

Figure S4. Small angle XRD of In-Ch xerogel: after mixing (no sonication)

NMR spectra of In-Ch and Na-Ch

NMR measurements of In-Ch xerogel and Na-Ch in MeOH-d_4 and DMSO-d_6 were carried out and no noticeable differences were observed (Figure S5 and S6).

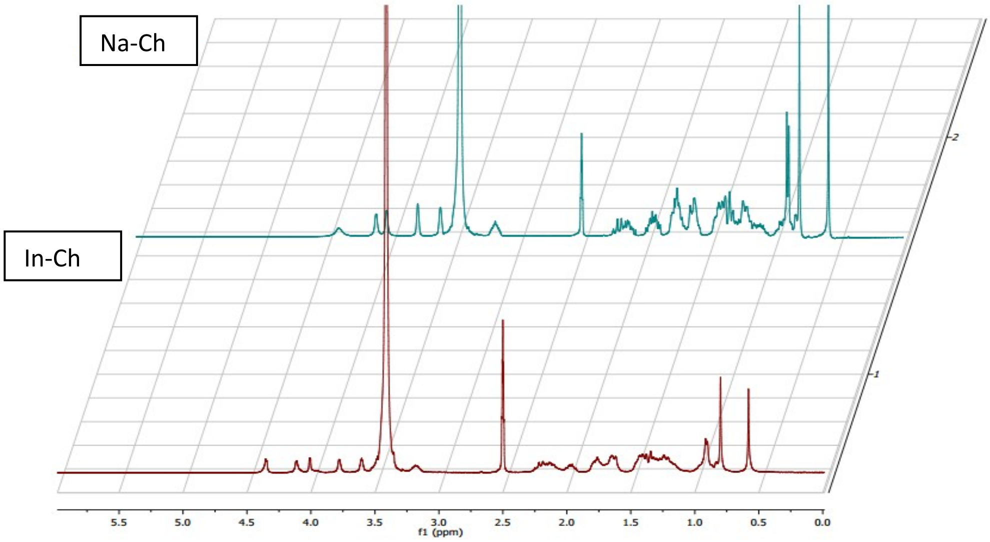

Figure S5. NMR spectra of In-Ch xerogel and Na-Ch in DMSO-d_6 (red: In-Ch and blue: Na-Ch)

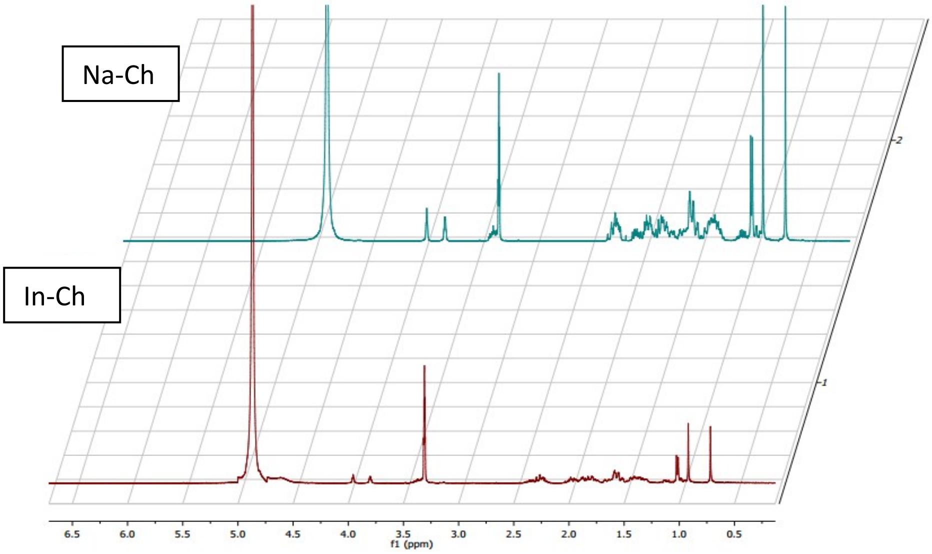

Figure S6. NMR spectra of In-Ch xerogel and Na-Ch in MeOH-d_4 (red: In-Ch and blue: Na-Ch)

SEM and AFM images of In-Ch and In-DCh

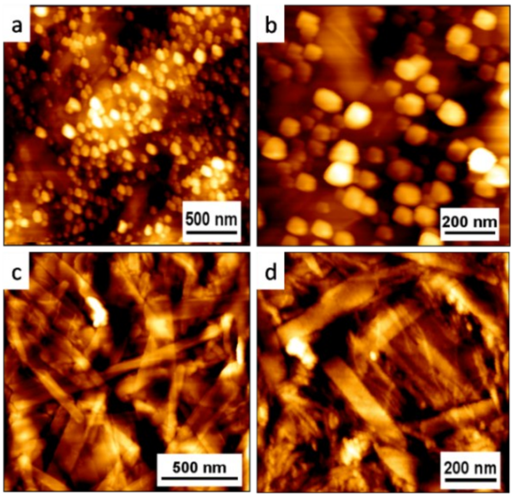

Figure S7. AFM images of In-Ch (5/15 mM): (a, b) just after sonication (before gel was formed) and (c, d) 1 h after sonication (after gel formed)

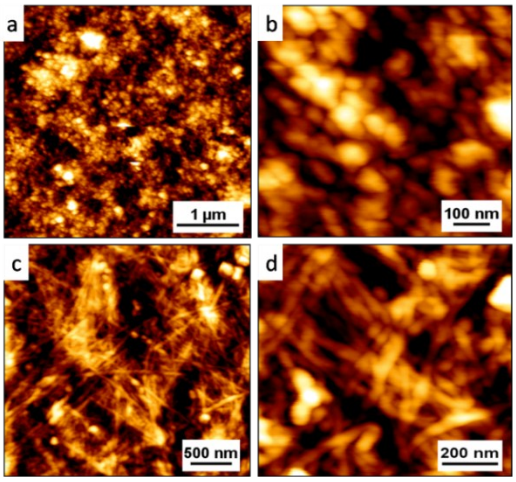

Figure S8. AFM images of In-DCh (5/15 mM): (a, b) just after sonication (before gel was formed) and (c, d) 24 h after sonication (after gel was formed)

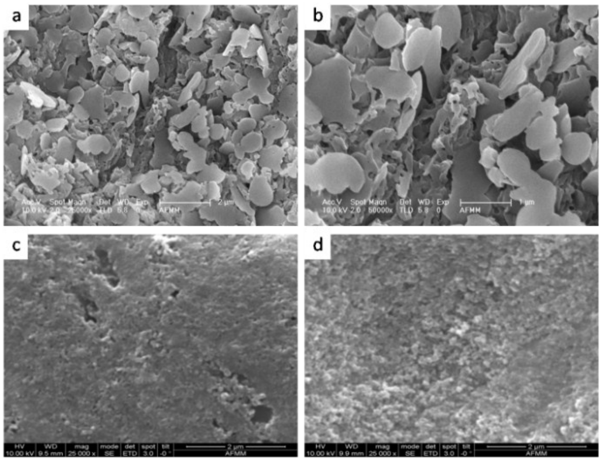

Figure S9. SEM images of (a) In-Ch (5/15 mM) and (b) In-DCh (5/15 mM) just after mixing (before gel was formed, scale bar a, c, d; 2 μm and b; 1 μm)

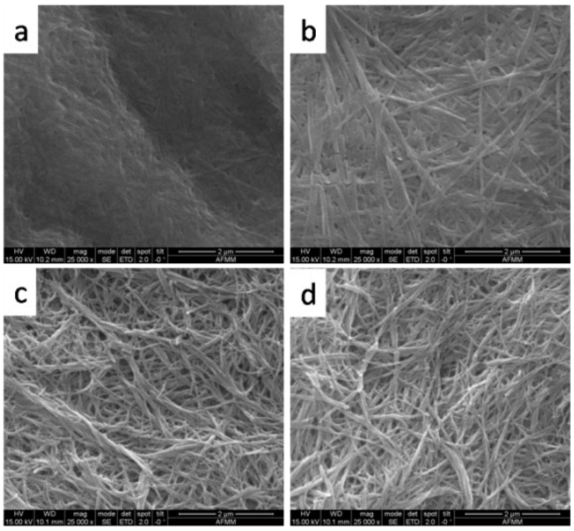

Figure S10. SEM images of (a) In-Ch gel (5/5 mM), (b) In-Ch gel (5/10 mM) and (c) In-DCh gel (5/5 mM), (d) In-DCh gel (5/10 mM) (scale bar a-d: 2 µm)

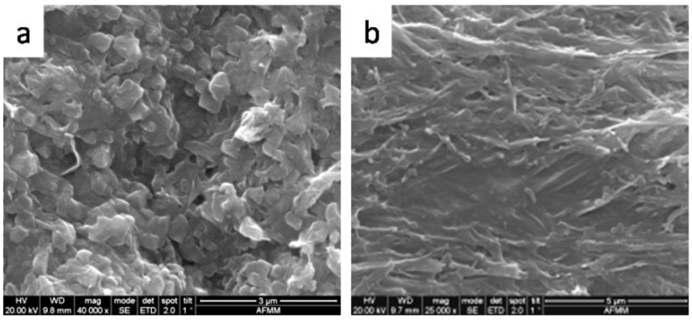

Figure S11. SEM images of In-Ch (5/15 mM, no sonication): (a) 1 h after mixing (scale bar 3 µm) and (b) 24 h after mixing (scale bar 5 µm)

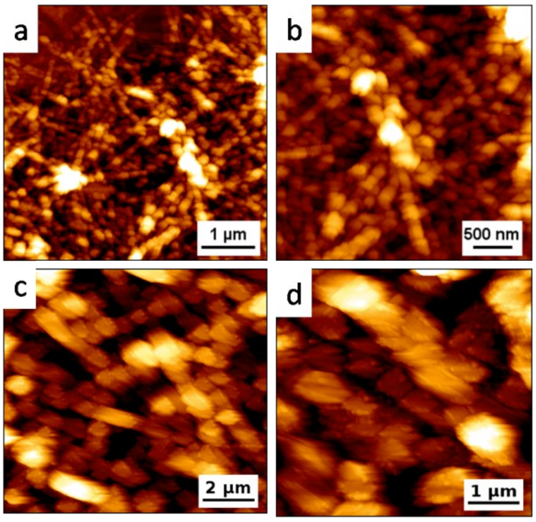

Figure S12. AFM images of In-Ch (5/15 mM, no sonication): (a) just after mixing and (b) 24 h after mixing

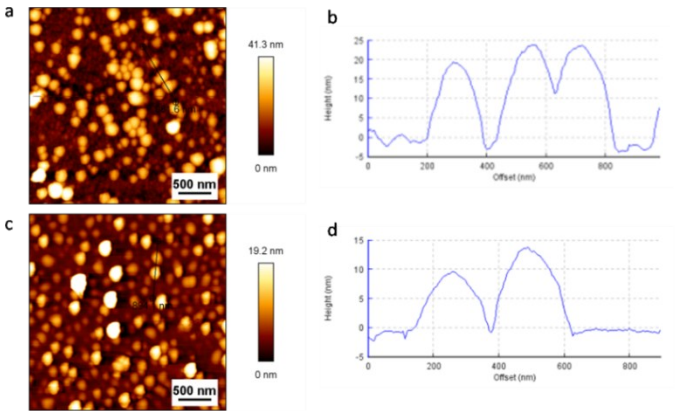

Figure S13. AFM images of In-Ch doped with TAA (6.6 mM/20 mM In-Ch with 13.2 mM TAA): (a, b) 1 h after sonication and (c, d) 24 h after sonication

In-Ch gel showed irregular spherical morphology and with time, it transferred to fibrous morphology. Whereas AFM images of In-Ch gel doped with thioacetamide (TAA) showed irregular spherical aggregates with average size of 100-200 nm (Figure S13). Hence, nanoflake morphology of indium sulphide probably originated from irregular spherical aggregates of TAA doped In-Ch gel.

Rheology

Frequency sweep and stress sweep experiment of In-Ch hydrogels (5/5 mM) and (5/10 mM) prepared by sonication, were shown in Figure S14 and Figure S15. The In-Ch gel with the composition of (5/15 mM) formed only by mixing (no sonication) was shown in Figure S16. These results are summarized in Table S2.

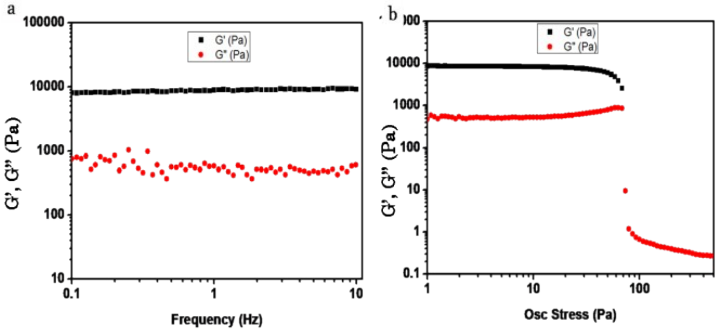

Figure S14. In-Ch hydrogel (5/5 mM): (a) frequency sweep at a constant oscillatory stress of 1 Pa and (b) stress sweep at fixed frequency of 1 Hz

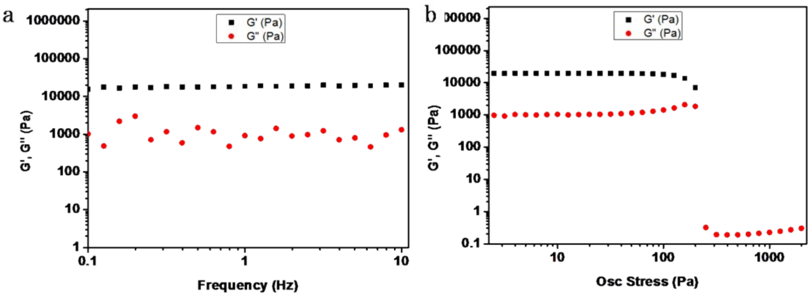

Figure S15. In-Ch hydrogel (5/10 mM): (a) frequency sweep at a constant oscillatory stress of 1 Pa and (b) stress sweep at fixed frequency of 1 Hz

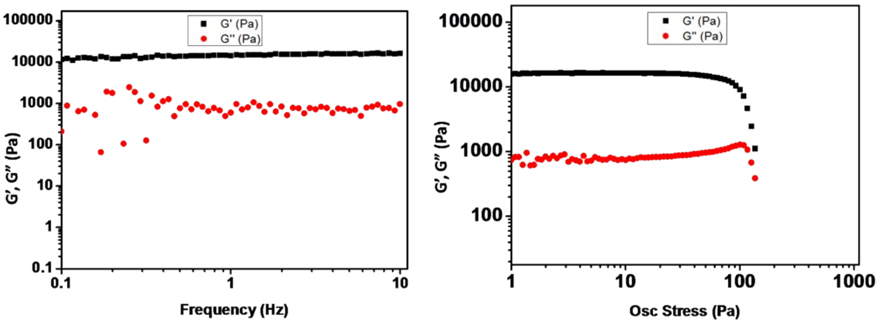

Figure S16. In-Ch hydrogel (5/15 mM) by mixing (no sonication): (a) frequency sweep at a constant oscillatory stress of 1 Pa and (b) stress sweep at fixed frequency of 1 Hz

Table S2. Rheological parameters of In-Ch and In-DCh gels prepared under different conditions

Gel systems	In(III):Na-Ch/Na-DCh	G′ (Pa)	G'' (Pa)	G′/G"	σ* (Pa)
In-Ch	5 mM: 5 mM	8005±1180	525±78	15.2±0.35	85±21
In-Ch	5 mM: 10 mM	16450±3139	845±106	19.3±0.98	195±0
In-Ch	5 mM: 15 mM	35373±1330	2720±433	13±1.96	440±96
In-Ch	5 mM: 15 mM (by mixing, no sonication)	16680±3082	821±313	21±4.2	150±14
In-DCh	5 mM: 15 mM	11135±134	533±47	20±1.9	530±0

Synthesis of In$_2$S$_3$ nanomaterials

In a typical procedure, 4 mL of 20 mM of indium chloride (InCl$_3$), 4 mL of 60 mM of sodium cholate (Na-Ch) and 4 mL of 40 mM of thioacetamide (TAA) were mixed and sonicated for 2-3 min. The resulting weak turbid gel was transferred into a 20 ml Teflon-lined autoclave. The autoclave was sealed and maintained at 150 °C for 7 h, then air-cooled to room temperature. The as-synthesized red-yellow product was washed several times with water and then with ethanol, and finally dried in vacuum. A yield of 26 mg was obtained. A control experiment was done through the same procedure as above except water was added instead of Na-Ch keeping other concentrations same.

Elemental analysis of In_2S_3 nanomaterials

Elemental analysis of the In_2S_3 prepared using In-Ch showed the presence of 80% of ligand (organic content Cholate, Table S3).

Table S3. Elemental analysis data for In_2S_3

Sample	C (%)	H (%)	N (%)	S (%)
Found	57.42	7.486	0.00	6.122
Calculated for $(C_{24}H_{39}O_5)_{10}$ $(In_2S_3)_3$	56.94	7.80	0.00	5.72
Calculated for Cholate $(C_{24}H_{39}O_5^-)$	70.73	9.65	0.00	0.00

Thermogravimetric analysis (TGA) of In_2S_3 nanomaterials

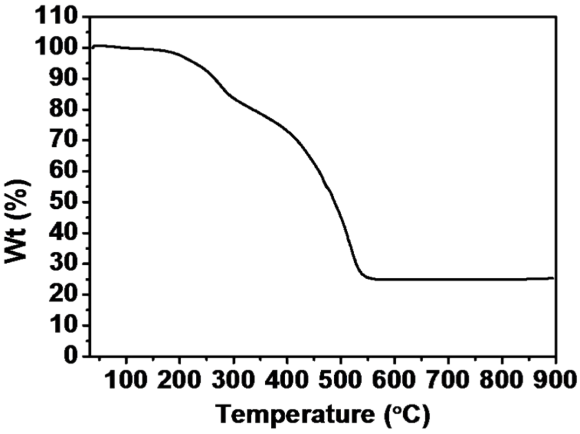

Figure S17. TGA plot of In_2S_3

References

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[1] Y. Qiao, Y. Lin, Y. Wang, Z. Yang, J. Liu, J. Zhou, Y. Yan and J. Huang, *Nano Lett.*, 2009, **9**, 4500.

[2] Y. Qiao, Y. Lin, Z. Yang, H. Chen, S. Zhang, Y. Yan and J. Huang, *J. Phys. Chem. B*, 2010, **114**, 11725.