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Supporting Information

Metal cholate hydrogels: versatile supramolecular systems for nanoparticle embedded soft hybrid materials

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1. Experimental details

POM/ SEM imaging of CdS/ CaCh hybrid gel

The $CdCl_2$ doped calcium cholate hydrogel was prepared in the following fashion: 10 μL of aqueous (aq.) $CdCl_2$ (120 mM) was mixed with 0.19 mL of aq. $Ca(NO_3)_2.4H_2O$ (120 mM) and it was added to 0.20 mL of aq. sodium cholate (60 mM) at room temperature (28 ^oC) and the mixture immediately formed a translucent gel. After 45 min, 0.1 mL of aq. $Na_2S.9H_2O$ (30 mM) was added at the top of the gel layer and it was allowed to diffuse slowly through the gel network. After 12 h, a yellow semi-transparent gel was obtained which was further investigated with optical and electron microscopic techniques.

TEM imaging of CdS/CaCh hybrid gel

The hybrid gel was made by diffusing H_2S gas through the $CdCl_2$ (0.47 mM) doped calcium cholate (14/14 mM) hydrogel for 45 min (3% of doping). For TEM investigation of CdS/ calcium cholate hybrid gel, a thin film of the sample was made on a Cu grid and excess fluid was wiped out. The sample was dried under vacuum.

Synthesis of ZnS, HgS, CoS, NiS and CuS nanomaterials in CaCh hydrogel

Ten microliters of the aq. transition metal salt (120 mM) was mixed with 0.19 mL of aq. $Ca(NO_3)_2.4H_2O$ (120 mM) and the resulting mixture was added to 0.2 mL aq. sodium cholate (60 mM) at room temperature. $Zn(ClO_4)_2$, $HgCl_2$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ were used as the metal precursors (dopant). In case of Zn^{2+} and Cu^{2+}, the hydrogel formed immediately upon mixing two solutions; for Co^{2+}, Hg^{2+} and Ni^{2+}, the hydrogels formed after 3 min, 1.5 min and 25 min, respectively. It was interesting to note that the calcium cholate gel in water formed *after 30 min from mixing* the two solutions at room temperature at identical concentration of Ca^{2+} and sodium cholate as above. After 45 min, 0.1 mL of aq. $Na_2S.9H_2O$ (30 mM) was added at the top of the gel layer and it was allowed to diffuse slowly through the gel network. After 12 h, formation of semi-transparent gels with different colours indicated the presence of metal sulphides inside the hydrogel networks.

Synthesis of gold nanoparticles in calcium cholate hydrogel

The gold precursor used as “dopant” in calcium cholate gel was either $HAuCl_4.3H_2O$ or $AuCl_3$. Two millilitres of aq. $Ca(NO_3)_2.4H_2O$ (120 mM) was heated to 50 °C for 5 min. 0.4 mL of aq. $HAuCl_4.3H_2O$ (4 mM) or 0.020 mL of aq. $AuCl_3$ (40 mM) was mixed with 1.6 mL (or 1.98 mL) of aq. sodium cholate (60 mM) and heated to 50 °C for 5 min. The calcium nitrate solution was added to the gold doped sodium cholate solution. The gel formed within 5 min. The final concentrations of the components were as follows: Ca^{2+}: 60 mM, Au^{3+}: 0.4 mM and NaCh: 24 mM. The addition of higher concentration of Au^{3+} resulted in weaker gel; whereas increasing the concentration of Ca^{2+} was needed to make a better gel with Au^{3+} doping (Ca^{2+}: NaCh = 2:1). The reduction of Au(III) to Au(0) was done using 0.4 mL of 100 mM $Na(CN)BH_3$ which was added at the top of the gel layer and allowed to diffuse through the gel network. After 30 h, a magenta coloured gel was obtained to indicate the formation of gold nanoparticles in the hydrogel. To show the blue shift of SPR band in the gel, AuNPs were synthesized in NaCh solution (without calcium nitrate).

Synthesis of silver nanoparticles in calcium cholate hydrogel

To synthesize silver nanoparticles in the calcium cholate hydrogel, 0.04 mL of aq. $AgNO_3$ (4 mM) was mixed with 0.2 mL of aq. $Ca(NO_3)_2.4H_2O$ (120 mM) and 1.76 mL of distilled water, heated to 50 °C for 5 min. The resulting mixture was added to 2 mL of aq. sodium cholate (60 mM, also heated to 50 °C for 5 min). The resulting solution formed a gel within 1-2 min. Final concentrations of the components were as follows: Ca^{2+}: 6 mM, Ag^{+}: 0.04 mM and NaCh: 30 mM. After 20 min, 0.4 mL of aq. sodium cyanoborohydride (1 mM) solution was added at the top of the gel layer and allowed to diffuse slowly through the gel network. However, it was found that increasing the concentration of dopant (> 1%), led to the agglomeration of small AgNPs to bigger clusters. Therefore, diminutive doping (0.6%) of Ag^+ precursor in the calcium cholate hydrogel template was necessary for the smooth formation of silver nanoparticles inside the gel fibres. Since Ag^+ induced gelation of aqueous sodium cholate solutions, $AgNO_3$ was mixed with $Ca(NO_3)_2.4H_2O$ first and then added to sodium cholate solution to make the gel.

2. pH-metric studies of copper choalte, zinc cholate, silver cholate hydrogels

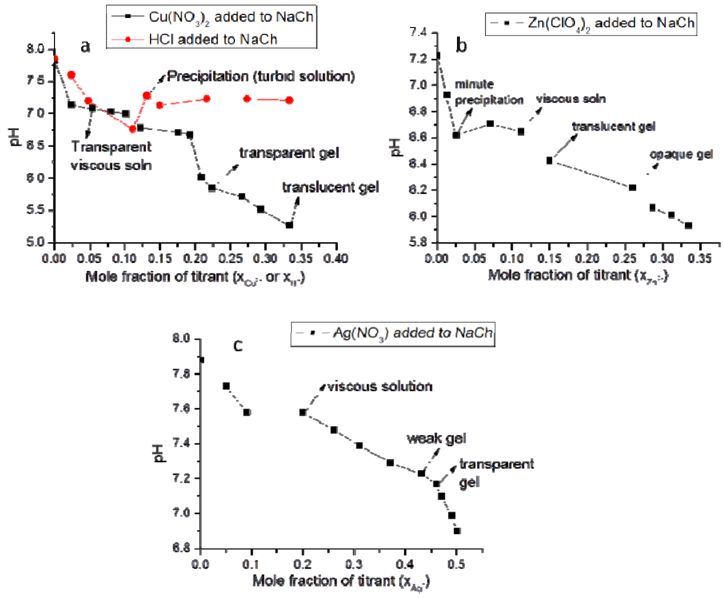

Fig. S1 (a), (b) & (c) pH-metric titration of sodium cholate vs (a) $Cu(NO_3)_2$, (b) $Zn(ClO_4)_2$ and (c) $AgNO_3$ (the metal salt solution was added to sodium cholate). Concentrations of sodium cholate were 40 mM, 20 mM and 60 mM respectively; concentrations of metals: 20 mM (Cu^{2+}), 10 mM (Zn^{2+}) and 60 mM (Ag^+). In the first plot (Fig. S1a), the red curve is the titration of sodium cholate vs HCl (HCl was added to NaCh) for comaprison. In all the cases, characteristic pH drops were observed during gel formation.

3. Rheological Studies with copper choalte hydrogel

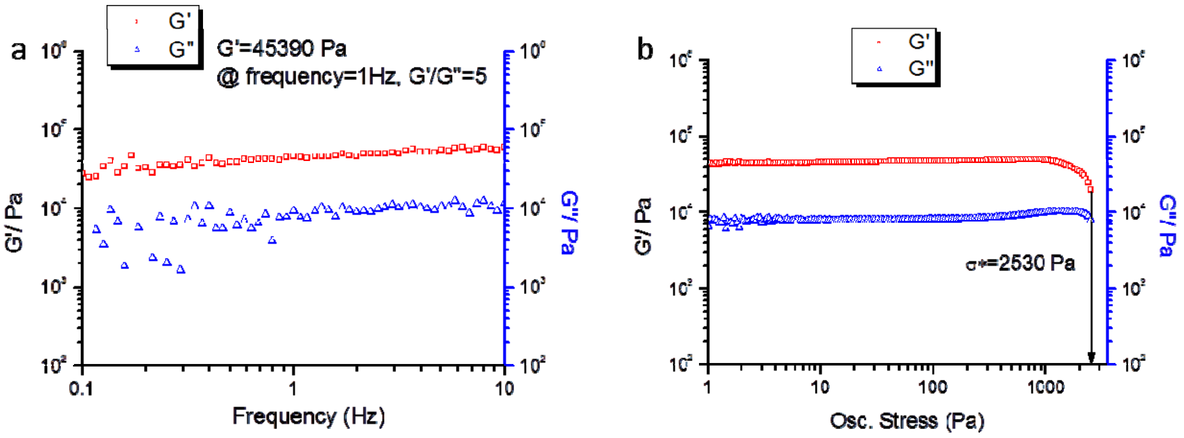

Fig. S2 Dynamic rheological studies of copper choalte hydrogel (10/30 mM): (a) frequency sweep test @ a fixed stress of 1.0 Pa and (b) stress sweep test @ a fixed frequency of 1.0 Hz. Value of $G' = 45390$ Pa, $G'/G'' = 5$ and $\sigma^* = 2530$ Pa.

For rheological studies either the gel was scooped up and placed on the rheometer plate (copper cholate) or sonicated for 15 sec and the solution was transferred on the rheometer plate and allowed to form gel (cobalt cholate).

4. Crystallization of cholic acid from copper cholate hydrogel

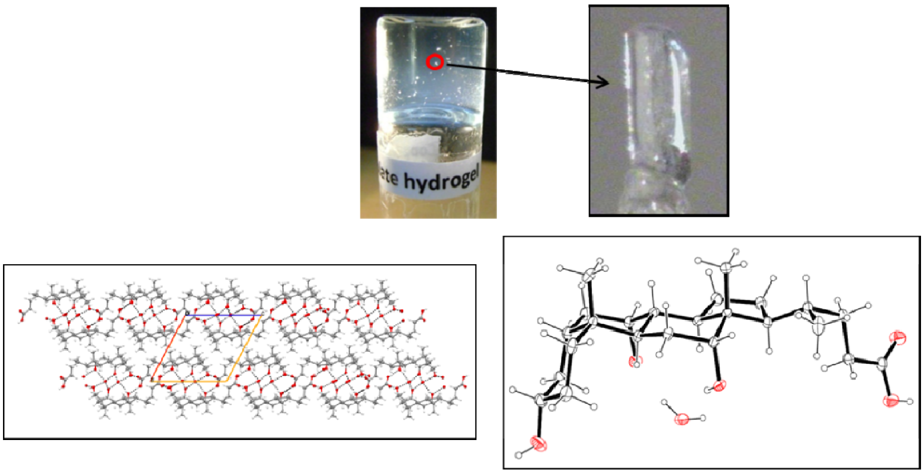

Fig. S3 Formation of block like crystals isolated from copper cholate hydrogel (Cu^{2+}/NaCh=1.2 mM/3 mM).

Table S1 Crystal structure information of cholic acid monohydrate (block like crystals) isolated from copper cholate hydrogel[a]

Compound reference	ac84251a/ Cholic acid
Chemical formula	$C_{24}H_{40}O_5{\bullet}H_2O$
Formula Mass	426.58
Crystal system	Monoclinic
a/Å	12.7763(7)
b/Å	8.1473(3)
c/Å	12.8625(7)
α/°	90
β/°	117.652(7)
γ/°	90
Unit cell volume/Å^3	1185.96(13)
Temperature/K	298
Space group	$P2_1$
No. of formula units per unit cell, Z	2
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	0.084
No. of reflections measured	14267
No. of independent reflections	4655
R_{int}	0.0444
Final R_1 values ($I > 2\sigma(I)$)	0.0484
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0963
Final R_1 values (all data)	0.074
Final $wR(F^2)$ values (all data)	0.1095
Goodness of fit on F^2	1.025
CCDC number	CCDC 860004

[a] M. Shibakami, M. Tamura and A. Sekiya, *J. Am. Chem. Soc,* 1995**, 117***,* 4499.

5. Additional POM/ SEM images of metal cholate and hybrid gels

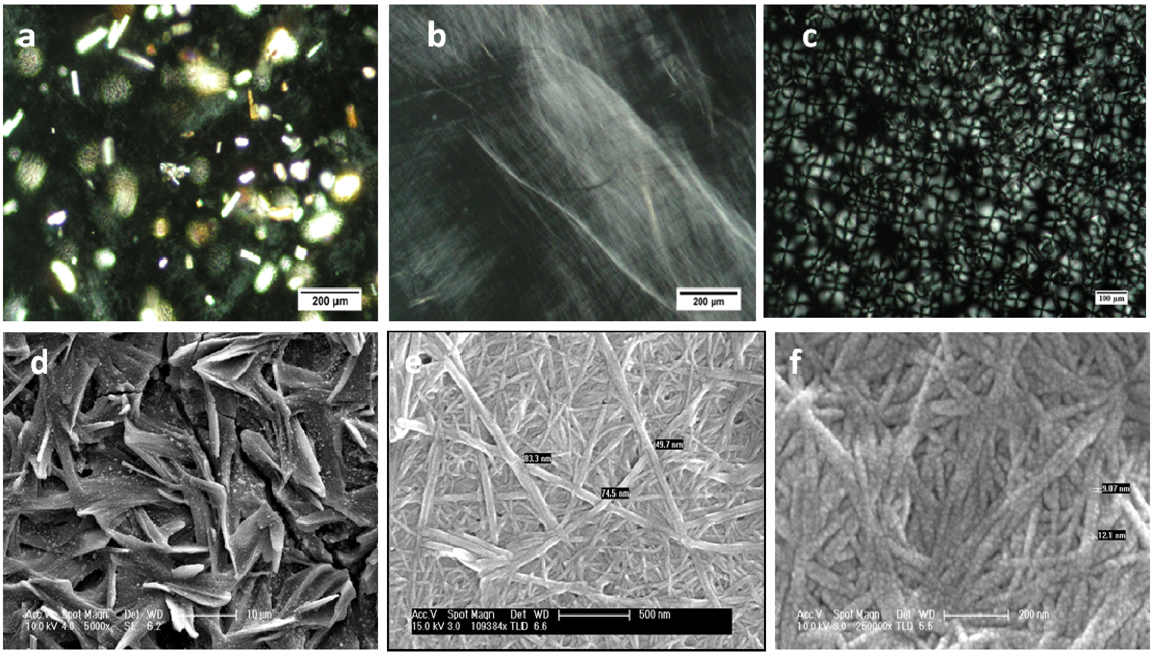

Fig. S4 POM images of (a) copper cholate hydrogel showing microcrystals (10/20 mM, scale bar 200 μm), (b) zinc cholate hydrogel (7.5/ 30 mM, scale bar 200 μm) and (c) AuNP/ calcium cholate hybrid gel (scale bar 100 μm); SEM images of (d) mercury cholate hydrogel (60/ 30 Mm, scale bar 10 μm), (e) ZnS/ CaCh hybrid gel (scale bar 500 nm) and (f) CdS/ CaCh hybrid gel (scale bar 200 nm).