Synthesis of Functional Hybrid Silica Scaffolds with Controllable Hierarchical Porosity by Dynamic Templating

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SUPPORTING INFORMATION

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(A) Materials

Tetraethyl orthosilicate (TEOS) and nonionic surfactant, nonaethylene glycol monododecyl ether ($C_{12}E_9$) sodium cyanoborohydride, 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane, Poly(ethylene glycol) diglycidyl ether**,** orange II, disodium banthophenanthroline sulfonate and copper iodide were used as received from Sigma Aldrich. Glutaraldehyde was purchased from Merck, India. All other chemicals were used as obtained from Sigma Aldrich. All the other solvents were purchased from Merck india. 3-Azidopropyltriethoxysilane (AzPTES), sodium dithiocarbamate were prepared as reported before.

(B) Experimental

(1) *Synthesis of Mesoporous Silica Nanoparticles Small Pore (MSN-S):*

Mesoporous Silica Nanoparticles (MSN) was prepared by following the procedure reported with slight modifications.[1] Cetyltrimethylammonium bromide (CTAB, 1.00 g, 2.74 × 10^{-3} mol) was dissolved in 480 mL of nanopure water. NaOH (aq) (2.00 M, 3.50 mL) was then added to CTAB solution, followed by adjusting the solution temperature to 80°C. Tetraethyl orthosilicate (5.0 mL, 21.9 mmol) were then added drop wise and the mixture was stirred vigorously at 80°C for 2 h. The resulting white precipitate was isolated by filtration, washed with abundant methanol, and dried under vacuum at 100°C for 12 h. Yield: 1.8 g

(2) *Synthesis of Mesoporous Silica Nanoparticles Large Pore (MSN-L):*

The large pore sized mesoporous silica nanoparticles was prepared by following the reported procedures with slight modifications.[2] Cetyltrimethylammonium bromide (CTAB, 1.0 g, 2.7 mmol) was dissolved in a solution of 480 mL nanopure water and NaOH (aq) (2M, 3.5 mL), mesitylene (7.0 mL, 50.30 mmol) were then added to the solution. The mixture was stirred vigorously at 80°C for 2 h. Tetraethyl orthosilicate (5.0 mL, 22.56 mmol) was then finally added dropwise. The reaction mixture was stirred vigorously at 80°C for another 2 h. The resulting white precipitate was isolated by filtration, washed with abundant methanol, and dried under vacuum at 100°C for 12 h. Yield: 1.95g

(3) *Synthesis of MSN-L-NH_2 and MSN-S-NH_2 by grafting of 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane onto MSN-L and MSN-S*

The grafting of organoamine was performed according to procedure reported before.[3] In a typical reaction, 500 mg of MSN particle (**MSN-S** or **MSN-L**) was added to 50 ml dry toluene and the reaction mixture was sonicated until it formed a clear dispersion. To this dispersion was added 3-[2-(2-aminoethylamino)ethylamino] propyltrimethoxysilane (0.200 ml; 0.75 mmol) and the resultant reaction mixture was heated at 85 °C for 16 hrs. After completion of the reaction, the resultant amine grafted MSN particles were washed several times with ethanol to remove the unreacted 3-[2-(2-aminoethylamino)ethylamino] propyltrimethoxysilane. Finally, the CTAB template was removed from these amine grafted MSN particles by treating the amine grafted MSN with 5 ml conc. HCl in 120 ml EtOH under reflux. After 2 hrs, the reaction mixture was centrifuged at 8000 rpm for 20 mins. The resultant solid powder was washed an additional three times with ethanol to afford amine grafted MSN particles **MSN-L-NH$_2$** and **MSN-S-NH$_2$**. These particles were stored as dispersion in ethanol for further usage.

Table1: Properties of MSN particles and scaffolds from BET measurements

Sample Name	M_{BET} (m^2/g)	Pore Diameter (nm)	Total Pore Volume (cm^3/g)
MSN-S-NH$_2$	836	2.5	1.44
Small Pore Scaffold	407	2.3	0.89
MSN-L-NH$_2$	842	3.7	1.47
Large Pore Scaffold	251	3.5	0.69

(4) Methodology for Assembly of Nanoparticles for Making a Self-Standing Scaffold:

(i) Using glutaraldehyde/NaCNBH$_3$ for cross-linking: Amine grafted mesoporous nanoparticles **MSN-L-NH$_2$** and **MSN-S-NH$_2$** were assembled into self-standing scaffold by using a dynamic templating procedure recently reported by our group.[4],[5] Typically, 165mg of 10% (by weight) dispersion of **MSN-S-NH$_2$** nanoparticles was added to surfactant $C_{12}E_9$ (135mg) and homogenized in a water bath at 50ºC such that the surfactant to water ratio was 1:1. To this, glutaraldehyde (10 mg, 25 wt% solution) was added and the sample was then cooled to room temperature in a feedback controlled convective oven. The particle concentration in the overall composite is ~ 9 wt %. The sample was then allowed to crosslink on standing at room temperature for a week. 0.1 M NaCNBH$_3$ was then added to the gel to reduce the imine groups formed upon crosslinking of amine and glutaraldehyde. Finally, the scaffold was washed repeatedly with ethanol and water (6-7 times) to remove the surfactant and afford the free-standing macroporous material. The silica scaffold was then dried in a vacuum oven at 120ºC.

(ii) Using Poly(ethylene glycol) diglycidyl ether as the cross-linker : To 165mg of 10% (by weight) dispersion of **MSN-S-NH$_2$** nanoparticles was added to surfactant $C_{12}E_9$ (135mg) and homogenized in a water bath at 50ºC such that the surfactant to water ratio was 1:1. To this poly(ethylene glycol) diglycidyl ether (10mg) was added and the sample was then cooled to room temperature in a feedback controlled convective oven. The particle concentration in the overall composite is ~ 9 wt %. The sample was then allowed to crosslink on standing at room temperature for 12 hrs. Finally, the scaffold was washed repeatedly with ethanol and water (6-7 times) to remove the surfactant and afford the free-standing macroporous material. The silica scaffold was then dried in a vacuum oven at 120ºC.

(5) One-pot Synthesis of Hierarchical Self-standing scaffold

(i) *Using glutaraldehyde/NaCNBH$_3$ for cross-linking:* To an aqueous solution of CTAB (166 mg, 0.00045 mol, 80 ml), NaOH (2M, 0.5833ml) and Tetraethyl orthosilicate (0.75 ml, 0.0036 mol) was added drop wise and the mixture was stirred vigorously at 80°C. After 30 mins, 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (0.1077 ml, 0.0004 mol) was added to the reaction mixture and stirred for 1.5 hrs further for amine grafting. After completion of reaction, 20 mg of particles was taken out and mixed with 90 mg of $C_{12}E_9$ and 90 mg of H_2O. The mixture was heated to 55^{o}C and to this glutaraldehyde was added and cooled to room temperature. The sample was then allowed to crosslink on standing at room temperature for a week. 0.1 M $NaCNBH_3$ was then added to the gel to reduce the imine groups formed upon crosslinking of amine and glutaraldehyde. Finally, the scaffold was washed repeatedly with ethanol and water (6-7 times) to remove the surfactant and afford the free-standing macroporous material.

(*ii) Using Poly(ethylene glycol) diglycidyl ether as the cross-linker:* To an aqueous solution of CTAB (166 mg, 0.00045 mol, 80 ml) NaOH (2M, 0.5833 ml) and Tetraethyl orthosilicate (0.75ml, 0.0036 mol) was added drop wise and the mixture was stirred vigorously at 80°C. After 30 mins, 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (0.1077 ml, 0.0004 mol) was added to the reaction mixture and stirred for 1.5 hrs more for amine grafting. After completion of reaction, 20 mg of particles was taken out and mixed with 90 mg of $C_{12}E_9$ and 90 mg of H_2O. The mixture was heated to 55^{o}C and to this Poly(ethylene glycol) diglycidyl ether was added and cooled to room temperature. The sample was then allowed to crosslink on standing at room temperature for 12 hrs. Finally, the scaffold was washed repeatedly with ethanol and water (6-7 times) to remove the surfactant and afford the free-standing macroporous material. The silica scaffold was then dried in a vacuum oven at 120ºC.

(C) Synthesis of Fe-Cat embedded hierarchical self-standing scaffold

(1) *Synthesis of MSN particles (N_3-MSN-S-NH_2) with organoazide and organoammine grafted in the inner and outer surface respectively:*

Scheme SI 1: The above schematic represents the formation of **N_3-MSN-S-NH_2** particles with organoazide and organoammine grafted in the inner and outer surface respectively.

MSN particles (**N_3-MSN-S-NH_2**) with organoazide grafted in the inner surface and organoammine grafted in outer surface was synthesized by grafting organoazides onto **MSN-S-NH_2** mesoporous nanoparticles.[3,6] In short, **MSN-S-NH_2** nanoparticle (500 mg) was dispersed in 50 ml dry toluene. In this reaction mixture azido-propyl trimethoxy silane (0.150 ml, 0.70 mmol) was added and refluxed at 85°C for 16 hrs. After the completion of reaction, the reaction mixture was centrifuged and the resultant solid powder was washed with an additional three times with ethanol to afford organoazide **N_3-MSN-S-NH_2**. The sample was stored in EtOH for further usage. Yield: 460 mg.

(2) *Synthesis of alkyne tagged Fe-Cat catalyst:*

The alkyne tagged Fe-Cat was synthesized by procedure reported elsewhere.[7]

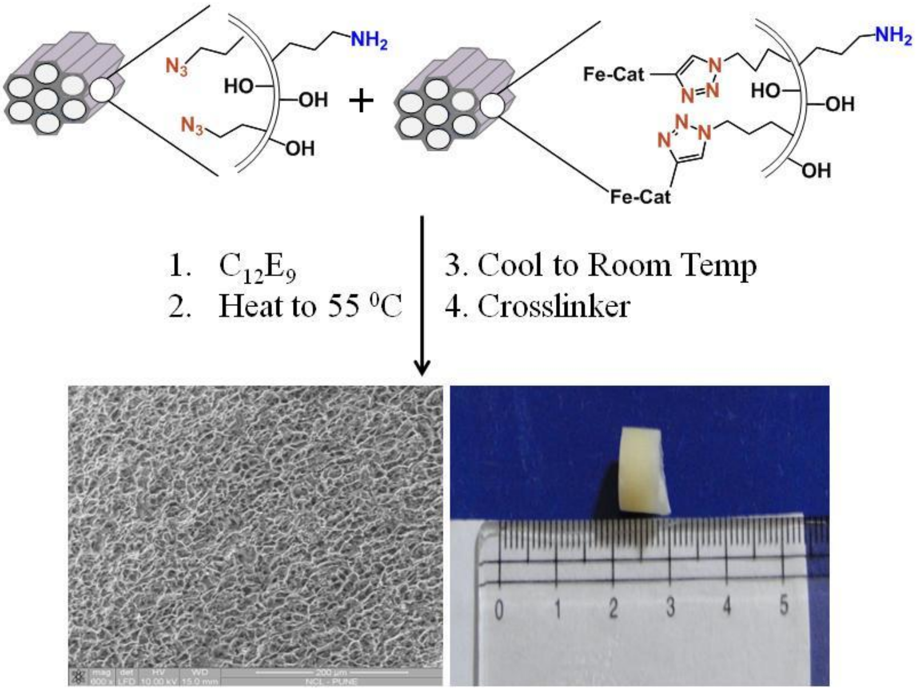
(3) Immobilization of Fe-Cat catayst on N_3-MSN-S-NH_2 to afford Fe-cat-MSN-S-NH_2:

Scheme SI 2: The above schematic represents immobilization of Fe-cat on **N_3-MSN-S-NH_2** particles with organoazide and organoammine grafted in the inner and outer surface respectively

Fe-Cat catalyst was immobilized on **N_3-MSN-S-NH_2** using "Click Chemistry" as has been reported before by our group.[8] For CuAAC, **N_3-MSN-S-NH_2** nanoparticles were incubated with 2 equivalents of the alkyne substituted Fe-Cat in a DMSO–H_2O solvent mixture (2:8) containing CuI (2.0 equivalents), disodium bathophenanthrolene sulfonate (2.0 equivalents), sodium ascorbate (4.0 equivalents). In a typical reaction, **N_3-MSN-S-NH_2** (10 mg) were incubated with alkyne substituted Fe-Cat (4 mg, 0.04 mmol, 2 eq.) in a DMSO/water mixture (1.6 ml H_2O + 0.4 ml DMSO) containing sodium ascorbate (0.016 g, 0.08 mmol, 4 eq.) and copper iodide (0.008 g, 0.0.04 mmol, 2 eq.) and disodium sulfonated bathophenanthroline (0.02 g, 0.04 mmol, 2 eq. The reaction mixture was subjected to three freeze–pump–thaw cycles for rigorous exclusion of dioxygen. The CuAAC was allowed to proceed for 24 h with stirring. After the completion of reaction, the reaction mixture was centrifuged and the solid residue was first washed with water twice and then sequentially washed with 0.1 M N,N-diethyldithiocarbamate sodium in PBS buffer (100 mM , pH 7.5), and acetone twice respectively. The last three washings were repeated thrice. Finally, the orange colored solid powder obtained (**Fe-Cat-MSN-S-NH_2***)* was dispersed in ethanol for further usage. The resultant **Fe-Cat-MSN-S-NH_2** was characterized by FT-IR (Figure SI 5(A)), ICP and EPR (Figure SI 5(B)). The EPR of the resultant solid displayed a resonance at g = 1.96 and 4.2 which is typical of such Fe(III) complexes having intermediate S=3/2. Yield: 8mg.

From semi quantitative IR, it was established that 50% of the available azides have been converted to the corresponding triazoles. This corresponds to 0.4 mmol of Fe-Cat /g of silica material. The percentage of catalyst immobilized was also calculated from ICP analysis and was determined to be 0.357 mmol of Fe-Cat /g of silica materials.

(4) *Synthesis of Fe-Cat embedded self-standing monolith type scaffold:*



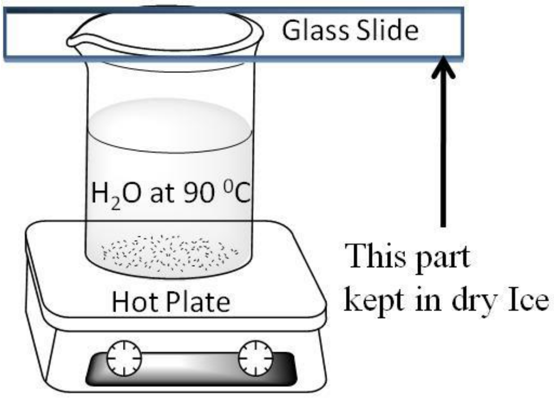
Scheme SI 3: The above schematic represents the synthesis of Fe-cat embedded self-standing monolith type scaffold. The SEM and optical picture of the resultant scaffold is also shown below.

To a mixture of **Fe-Cat-MSN-S-NH_2** (4mg) and **N_3-MSN-S-NH_2** (20mg) was added to surfactant $C_{12}E_9$/water mixture (1:1; 108 mg surfactant) at 50°C such that the amount of nanoparticles was 10 weight% by weight. These particles were assembled into macroporous networks in $C_{12}E_9$/water matrices, by cooling from 50^{o}C to below T_{HI}, and were cross-linked with poly(ethylene glycol) diglycidyl ether as described above. Subsequent to cross-linking, the surfactant was readily removed by washing with water, to afford catalyst embedded free standing scaffold. The amount of Fe-cat embedded in the monolith was estimated to be 0.027 mmol/g of monolith.

(5) Degradation of Orange II by Fe-Cat embedded scaffold

To a solution of Orange II (2 ml, 10^{-5} M) was added Fe-cat embedded scaffold. H_2O_2 (20 μL, 10^{-3} M) was added to start the reaction. 200 μL aliquot was taken out every time to measure the UV. After completion of reaction (6 min), the scaffold was thoroughly washed with water and the above reaction was carried out four more times.

(D) Temperature Gradient Experiments:



Scheme SI 4: The above schematic represents control of macroporosity within a single sample, simply by imposing a spatial variation in cooling rates.

To obtain a stable temperature gradient across a glass slide, we held a glass slide over a beaker containing water maintained at 90°C. One end of the slide was maintained in dry ice. We observed that the arrangement resulted in a temperature gradient from 60°C to -10°C over a ~8cm length of the slide. On the slide, we deposited a uniform thin film of the MSN containing $C_{12}E_9/H_2O$ sample at 60°C using a micropipette.

(E) Material Characterization:

Samples were imaged using a Quanta 200 3D scanning electron microscope (SEM). An LSM 710 Carl Zeiss laser scanning confocal microscope (LSCM) was used to image the fluorescent samples. We have used a He–Ne laser (543 nm) and an Argon-ion laser (488 and 514 nm) for our experiments. TEM measurements were done at 100 kV on an FEI Technai F30.The TEM samples was prepared by embedding the scaffold in the epoxy resin and microtome to view the sample under HRTEM. Optical microscopy was performed using an Olympus-BX 50 equipped with a crossed polarizer setup. FT-IR spectra were recorded on a Perkin Elmer FT-IR spectrum GX instrument by making KBr pellets. Pellets were prepared by mixing 3 mg of sample with 97 mg of KBr. The catalytic reaction was monitored by UV-vis spectra on a Jasco-V-570 UV-vis/NIR spectrophotometer operated at a resolution of 2 nm. Nitrogen adsorption and desorption studies at -196^{o}C were carried out using an Quadrasorb SI instrument. Before the nitrogen adsorption measurements, the samples were degassed overnight under vacuum using a FloVac Degasser at 100^{o}C (for modified silicas). Multipoint BET surface area was obtained from the nitrogen adsorption isotherm in the relative pressure range from 0.15 to 0.5.

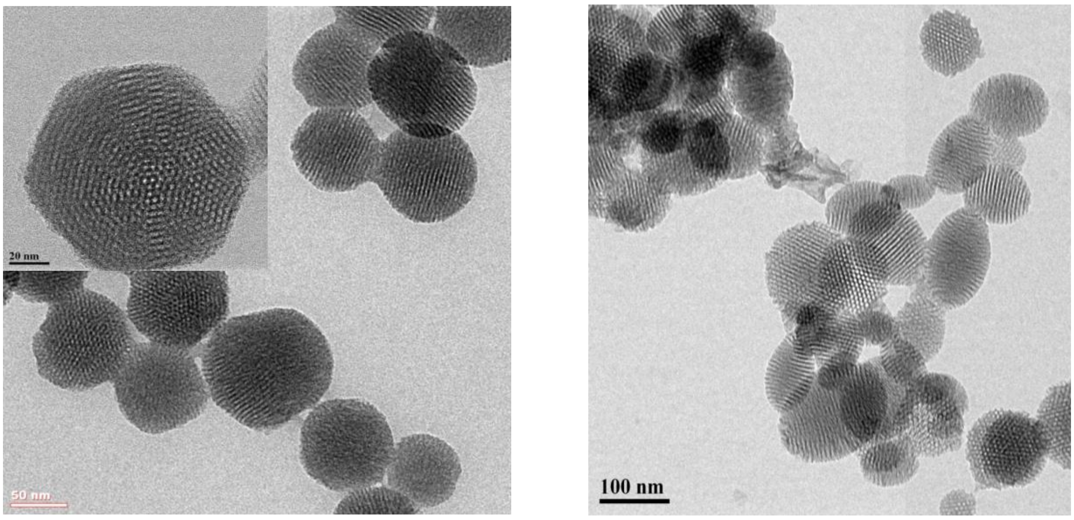


Figure SI 1: (A) HRTEM of Small Pore Mesoporous Silica Nanoparticles (B) HRTEM of Large Pore Mesoporous Silica Nanoparticles

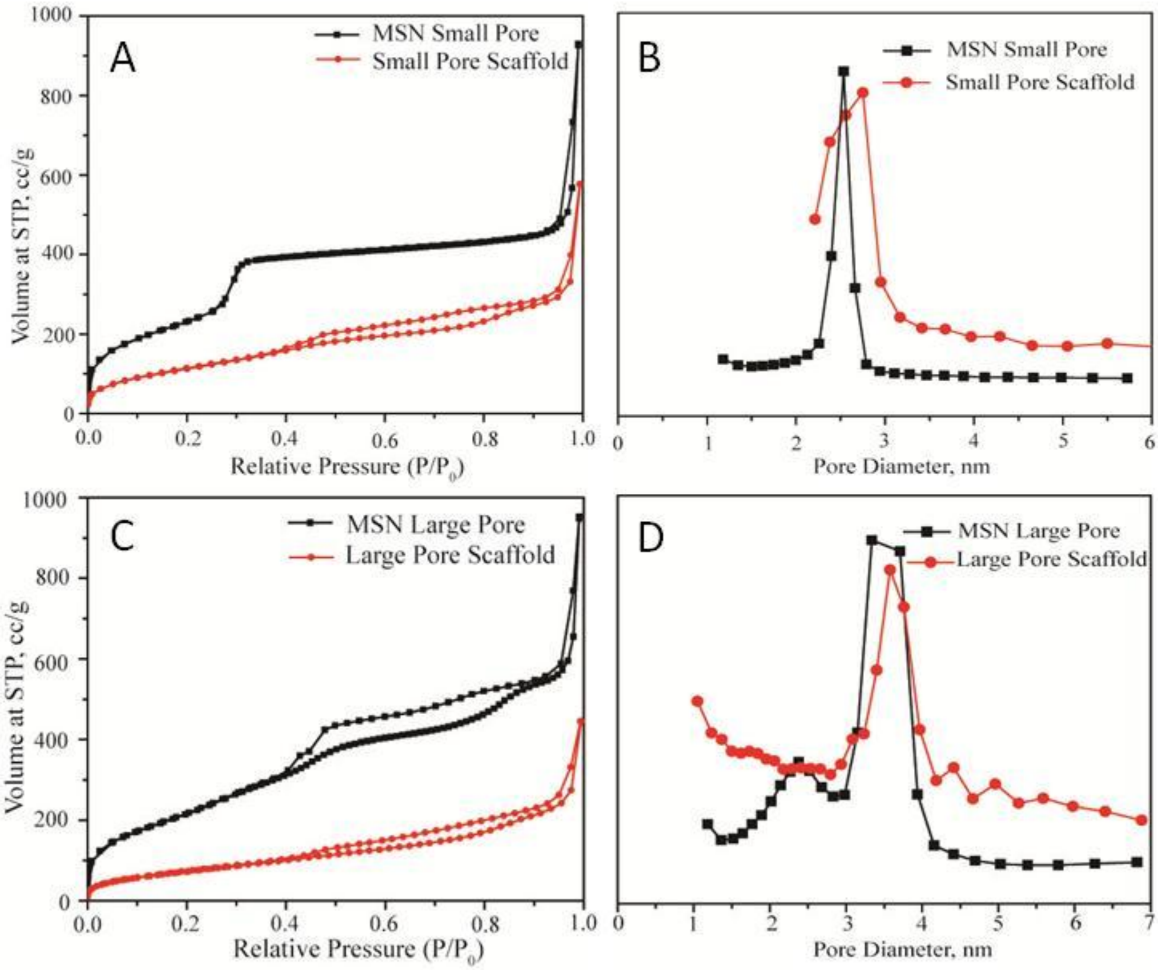


Figure SI 2: (A) N_2 absorption isotherm of MSN-S-NH_2 and small pore scaffold. (B) Pore size distribution of MSN-S-NH_2 and small pore scaffold. (C) N_2 absorption isotherm of MSN-L-NH_2 and large pore scaffold. (D) Pore size distribution of MSN-L-NH_2 and large pore scaffold.

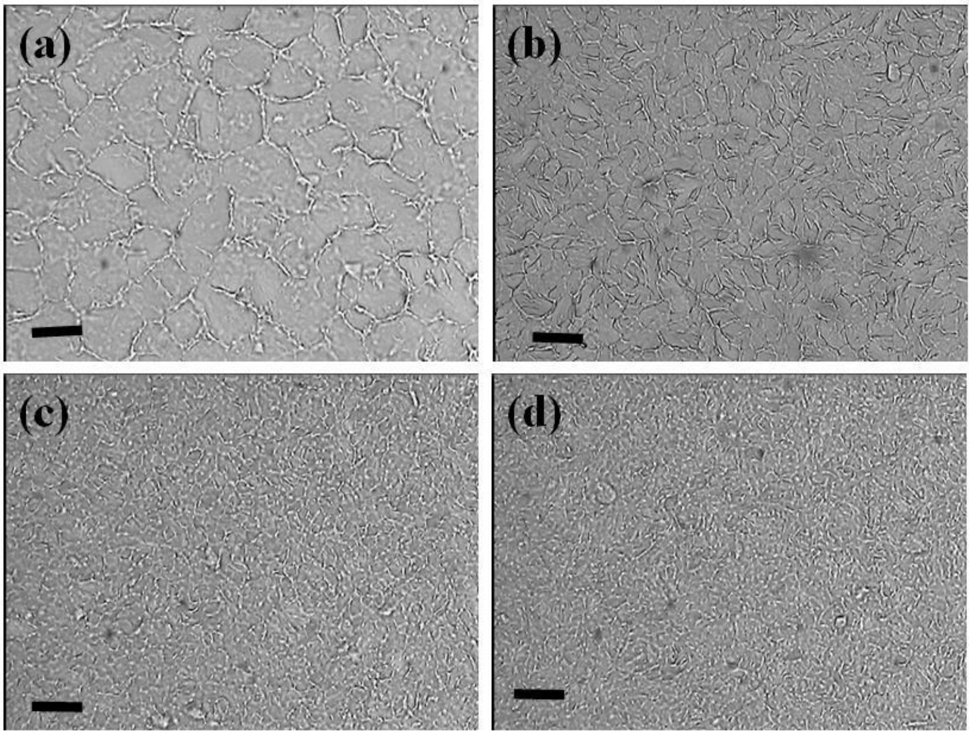


Figure SI 3: Temperature dependent optical micrograph. (a) 0.5 ^{0}C per minute (b) 5 ^{0}C per minute (c) 10 ^{0}C per minute (d) 20 ^{0}C per minute. The scale bar corresponds to 50 microns

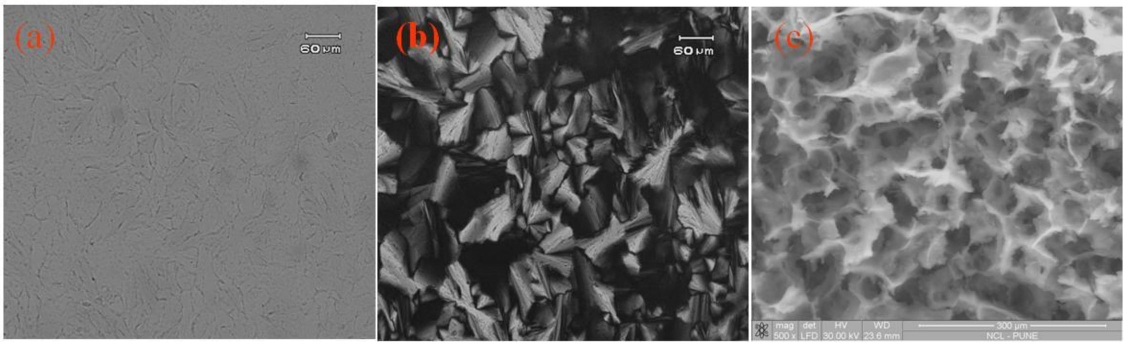
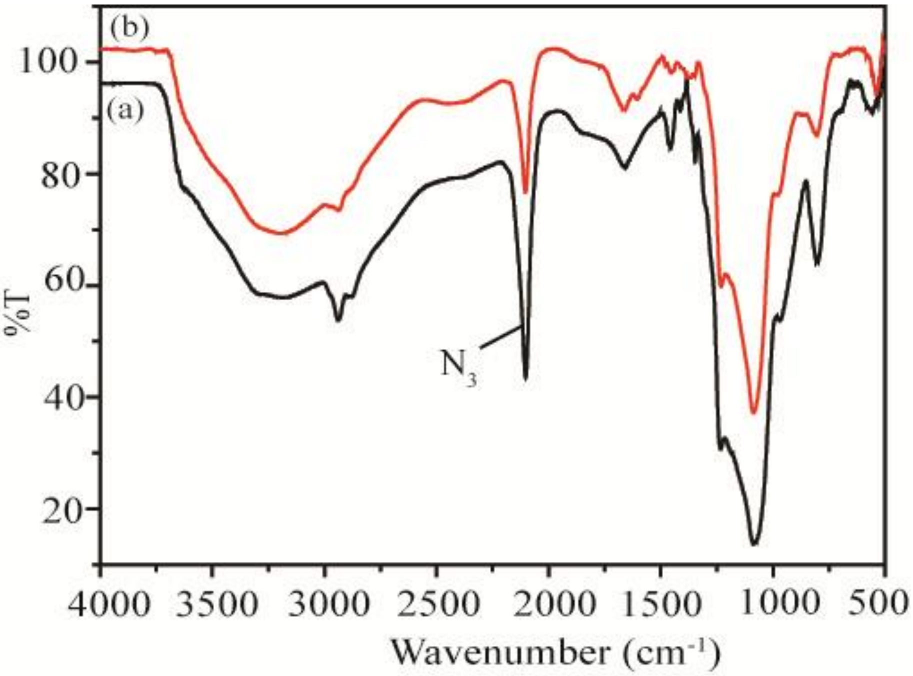


Figure SI 4: Optical micrographs and SEM images of Scaffold obtained by one pot synthesis. (a) Corresponding optical micrograph under parallel polarizers showing the phase separated mesoporous silica particles forming a network at the boundaries of the birefringent domains. (b) Corresponding crossed optical microscope image (showing birefringence due to different domains of the H1 phase. (c) SEM of the scaffold obtained by one pot synthesis.



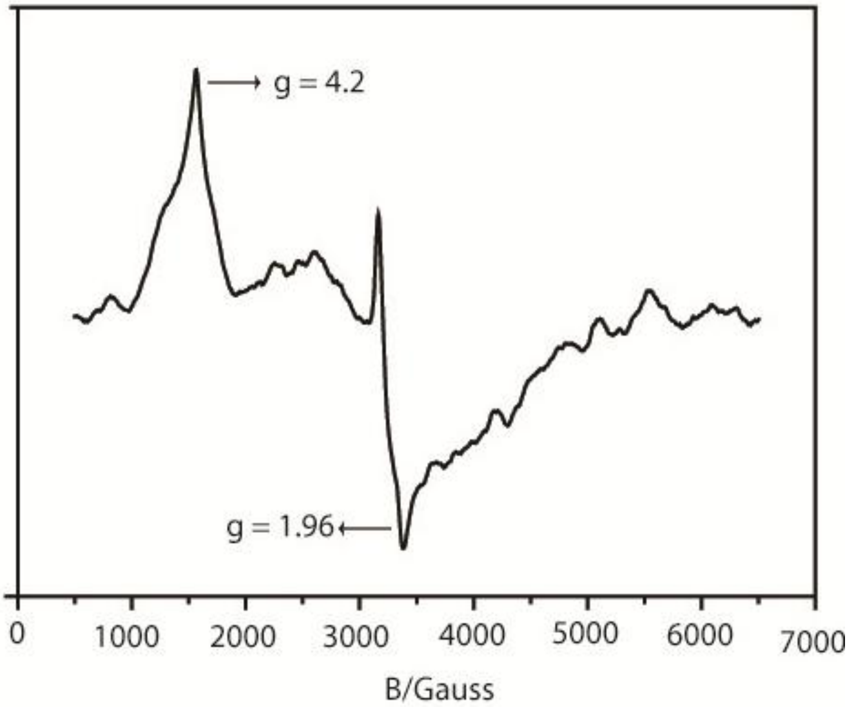


Figure SI 5: (A) Infrared spectra of (a) N_3-MSN-S-NH_2 (b) Fe-Cat-MSN-S-NH_2. (B) X-band EPR spectrum of solid Fe-Cat-MSN-S-NH_2 at 109K.

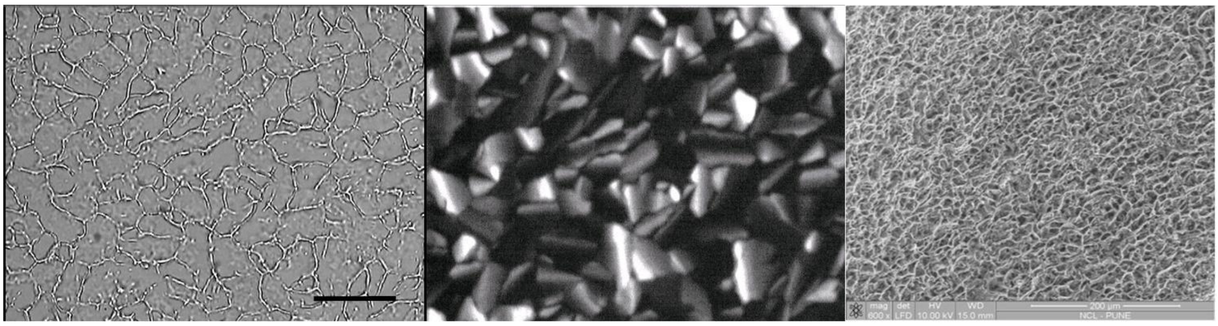


Figure SI 6: Optical micrographs and SEM of catalyst embedded scaffold (a) Corresponding optical micrograph under parallel polarizers showing the phase separated mesoporous silica particles forming a network at the boundaries of the birefringent domains. The scale bar represents 50 microns. (b) Corresponding crossed optical microscope image (showing birefringence due to different domains of the H1 phase. (c) SEM of the Fe-Cat embedded scaffold.

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