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Generalized Syntheses of Periodic Surfactant/Inorganic Composite Materials

by

Q. Huo, D. I. Margolese, P. Feng, T. E. Gier, P. Sieger, G. D. Stucky,
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Generalized Syntheses of Periodic Surfactant/Inorganic Composite Materials

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We have recently proposed (1) that the matching of charge density at surfactant/inorganic interfaces governs the cooperative assembly of periodic silica-based mesophase materials such as MCM-41 and MCM-48 from basic solution (2,3). If the concepts describing these materials could be generalized, transition metal oxide mesostructures that offer the possibility of forming nanocomposite electrochromic or solid electrolyte devices (4,5), as well as high surface area redox active catalysts (6) and bio-separation substrates would be accessible via such routes. In addition, co-organization of organic and inorganic phases plays a crucial role in biomineralization processing (7) and mimicking such processes in the synthesis of bio-relevant composite phases with intricate microstructural assemblies would be a major achievement. Here we demonstrate a generalized approach to describe the synthesis of transition and other metal oxide mesophases with cationic and anionic surfactants under variable conditions of pH. We show that tailoring the metal-ion speciation and charge density results in cooperative assembly by electrostatic complementarity at the inorganic/organic interface. Two general

synthetic pathways are described: (I) direct co-condensation with surfactants of opposite charge and (II) indirect co-condensation of similarly charged species mediated by the intercalation of counterions at the surfactant/inorganic interface. The latter route has been used to produce, for the first time, organized periodic porous silica structures at room temperature in concentrated acid solution.

Four pathways to the synthesis of mesostructured surfactant-inorganic biphase arrays are depicted in Fig. 1. The first route involves the direct co-condensation of anionic inorganic species with a cationic surfactant (S^+I^-), the syntheses of MCM-41 and MCM-48 (1-3) are prototypic examples. A similar route to periodic tubular non silica structures, but involving cooperative condensation of a cationic inorganic species with an anionic surfactant (S^-I^+) is demonstrated for the first time. This possibility had already been predicted in (1), although no examples were known. By contrast, routes three and four involve condensation of ionic inorganic species in the presence of similarly charged surfactant molecules. These pathways are mediated by counter ions of opposite charge to that of the surfactant head group (solution species ($S^+X^-I^+$) where $X^- = Cl^-, Br^-$; or, ($S^-M^+I^-$) where $M^+ = Na^+, K^+$).

Lamellar, MCM-41 and MCM-48 periodic porous silicates (S^+I^-) are obtained under basic conditions by the self-assembly of anionic silicates and cationic surfactant molecules(1-3,8). According to (1) such a mechanism should work for other oxides as well, if the pH is chosen to adjust the charge density of the metal oxide polyanions. Thus, we were able to synthesize lamellar tungsten(VI) oxide (d_{100} = 31 Å) at pH above 8, and lamellar and hexagonal tungsten(VI) oxide phases (d_{100} = 40 Å) at pH 4-8 (Fig. 2) using cationic surfactants. As another example, both cubic (Ia3d, pH = 6.5 - 7.0) and hexagonal (pH = 6.0 - 6.5) antimony(V) oxide mesostructures were synthesized in lower pH windows for the anionic inorganic phase. By choosing inorganic species (e.g., antimony or tungsten oxides) that are more acidic than silicic acid, the cooperative biphase templating can be carried out at neutral and lower pH values to obtain a match of the charge density of the oxide to that of the respective surfactant phase.

A similar approach was taken in a charge reversed situation, where an anionic surfactant was used to direct the condensation of cationic oxide species (S^-I^+). $C_{16}H_{33}SO_3H$ was used in the synthesis of Fe- and Pb-oxides, giving a hexagonal phase (d_{100}= 45.8Å for Pb) and different lamellar phases (e.g., 38.5 Å for Pb and 41.0 Å for Fe). Lamellar phases were obtained depending on the synthesis conditions (pH 1-5), using Mg, Al, Mn, Fe, Co, Ni and Zn oxides with $C_{12}H_{25}PO_4H_2$ as the surfactant. An interesting example is aluminum oxide with sodium dodecylbenzenesulfonate at 70°C and pH = 3.5 which slowly rearranges to increase the layer spacing (28.9Å to 32.1Å in 8 hrs to 9 days). It should be noted that the anionic polar head group can be a part of the inorganic framework in these materials.

Surprisingly, the formation of mesophases was possible by the cooperative assembly of cationic inorganic species with cationic surfactants. Generally lamellar, hexagonal and Pm3n cubic (Fig.1) were prepared by addition of tetraethyl-orthosilicate (TEOS) at room temperature to an acidic (e.g., HCl) solution of surfactant. After stirring for 30 minutes or longer the solid product was recovered by filtration and studied by X-ray diffraction and high resolution TEM (Figs 2,3). High quality samples of the three phases can be formed in a wide range of strongly acidic conditions (1M to 7M HCl or HBr). We found that HCl favors the formation of all three phases while HBr favors the formation of the hexagonal and not the cubic phase. In contrast to the synthesis conditions used previously (1-3) for M41S silicate mesophases, extreme acidic medium, low temperature, short synthesis times and low concentrations of surfactant were employed. Zwitterionic and lipid-like surfactants were successfully used in this synthesis. Silica polymerization proceeds in this pH range through the condensation of cationic intermediates (9,10)

The new cubic silica phase, first reported here (Figs 1-3), was prepared using surfactants with larger head groups (e.g., alkyltriethylammonium, cetylethylpiperdinium) as the template. This was done to decrease the value of the surfactant packing parameter to generate maximum surface curvature (11,12). The XRD data closely matches (intensities and indexing) that for the I_1 (Pm3n) phase of cetyltrimethylammonium chloride and cetylpyridinium chloride in formamide (13). This phase consists of a packing of two types of discrete micellar aggregates (13-17) in globular-like cages, with one large cage of ~30Å giving a clathrasil-like structure. Removal of the $C_{16}TEA^+$ template by calcination to 500°C resulted in a reduction of the unit cell 89.9 Å to 78.2 Å.

The surfactant-silica mesophases exhibit different unit cell parameters when surfactants with differing alkyl chain lengths were used (Fig. 5). Moreover, the XRD data (Fig. 5), show clearly that similar surfactants at $pH < 0$ produce mesostructures with similar, but slightly larger d-spacings than those obtained by basic ($pH > 9$) medium synthesis. For the $C_{16}TMA^+$ hexagonal phase product formed in acidic media, chemical analysis gave (wt%): SiO_2, 39.7; $C_{16}TMA^+$, 46.38; Cl, 5.75. The product surfactant/Cl ratio is therefore 1.0:1.0, a feature that distinguishes these mesostructure phases from hexagonal phase MCM-41 formed in alkaline solution that has no significant halide content using the same surfactant halide starting materials. Since in the acid mesophase product the template cationic charge is exactly balanced by a halide anion, the template should be removable without providing an exchangeable cation as required for the anionic frameworks of MCM-41(18). Indeed, it was found that greater than 85% of the template could be removed from the material as-synthesized by stirring in pure ethanol at room temperature or by overnight reflux. The removal of the template was also possible by calcination. The calcined hexagonal phases (at 500°C) had surface areas greater than 1000 m^2/g and average pore diameters of 18.6, 26.5, and 33.2 Å for C_{14}, C_{16} and $C_{18}TMA^+$, respectively, as determined by N_2 BET measurements.

29Si MAS NMR data (Fig. 4), were used to determine the degree of polymerization and the concentration of silanol, as measured by the ratio Q3/Q4 (Q3 = #Si with one terminal Si-OH or Si-O-; Q4 = #Si with four bridging Si-O-Si linkages). At long reaction times, for the hexagonal phase, Q3/Q4 decreases due to increased polymerization, however for a given reaction time, the Q3/Q4 ratio is approximately the same (0.55) as for the hexagonal material precipitated from basic medium.

As proposed for the co-condensation of oligomeric polysilicate and cationic surfactant molecules in alkaline solution (pH > 9) (1-3), we believe that the main driving force for self-assembly in strong acid media is electrostatic. We postulate that the interactions between cationic silica species and halide-cationic surfactant headgroups are mediated by the halide ions which hydrogen bond to protonated silanols such as $\equiv Si(OH_2)^+$ (10). At high concentrations of hydrohalogen solutions, the cationic surfactant hydrophilic region is surrounded by halide ions forming an electrical double layer (S^+X^-) with the periphery negatively charged. As cooperative assembly and precipitation proceeds, the protons associated with the silica species along with associated excess halide ions are excluded until a neutral inorganic framework remains.

This model is supported by: (i) the cationic silica species that are present at $pH<2$ (9,10) and the fact that the solution $[H^+]$ does not change during synthesis, (ii) the 1:1 surfactant to chlorine ratio in the hexagonal product, (iii) the easy removal of the template with ethanol and (iv) the observation that TEOS and $SiCl_4$ hydrolyze and form mesophase products while Cab-O-Sil (SiO_2) which does not dissociatively hydrolyze in acidic conditions, forms no mesophase products. Clearly the template mechanism for ($S^+X^-I^+$) synthesis is not the same as that for (S^+I^-) synthesis.

We have applied the above approach to the synthesis of organized Zn-containing phosphate mesostructured materials. At least four lamellar $(C_nTMA)^+X^-[HZnPO_4]$ ($X = Cl^-, Br^-$) phases with different d-spacings and surfactant packing, including monolayer and bilayer geometries can be generated by controlling composition and pH. One of them was formed from solutions containing $[H_2ZnPO_4]^+$ (pH ~2.5) (Figs 3,5) and like the acid silica phases contains one halide ion per surfactant molecule. In this structure there are three-dimensional ordering and excellent lateral ordering of layers. Comparison with the determined structures of the layered $MH(ZnPO_4)_2$ (M = Na, Cs) (19) strongly supports a template model similar to that for the acid synthesized silica phases, with the cationic surfactant indirectly coordinated to the $HZnPO_4$ walls via hydrogen bonding to the anion (Cl^- or Br^-).

Finally, we have explored the possibility of synthesizing periodic biphase arrays from negatively charged surfactants and inorganic species (S^-I^-). For instance, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$ and $Zn_2(OH)_6^{2-}$ are the predominant species above a 0.1M solution of ZnO (pH=10-14) (20). The anionic surfactant $CH_3(CH_2)_{16}COO^-M^+$ gives a lamellar zinc oxide phase (d_{001}= 48.8Å, 50.3Å; $M^+ = Na^+, K^+$, respectively) above pH = 12.5 (TMAOH without surfactant under the same reaction conditions gives only ZnO), consistent with a mediated templating ($S^-M^+I^-$) pathway. Anionic surfactants compete with oxide/hydroxide groups for framework metal atom coordination sites and under similar conditions phosphates such as $C_{12}H_{25}OPO_3Na_{2-x}H_x$ (x=0-1) appear to coordinate directly to the zinc atom, thus becoming part of the framework with no sodium ions present in the final product. In another example, at pH > 8 using an anionic aluminate species in solution lamellar (d_{001} = 33.6Å) $[C_{12}H_{25}OPO_3NaH]_3 \cdot Al(OH)_3 \cdot 4H_2O$ {observed and calculated Al (2.5%, 2.5%); P(8.6%, 8.6%); C(40.2%, 39.7%); H(7.7%, 8.9%); Na(5.56%, 6.35%)} is formed in contrast to lamellar $[C_{12}H_{25}OPO_3] \cdot Al(OH) \cdot 2H_2O$ {observed and calculated Al(7.9%, 8.2%); P(9.3%, 9.5%); C(44.4%, 44.2%); H(8.6%, 8.6%)} which forms at pH < 5. The former is consistent with a ($S^-M^+I^-$) solution pathway and no framework phosphate, while in the latter the (S^-I^+) chemistry prevails with surfactant framework participation.

The results presented here confirm the feasibility of using the synergistic interface chemistry of inorganic and organic species to create periodic mesostructures with cationic or anionic inorganic species including transition metal oxides and cationic or anionic surfactants. A variety of surfactants including lipids and zwitterionic types were used so that this chemistry becomes directly applicable to biomimetics. These periodic biphasic arrays, as described in this paper, are to be contrasted with silica (21) and iron oxide (22) deposited organic tubules with bulk inorganic phases grown on a charged lipid substrate. Charge matching of the biphasic arrays can be accomplished through the four pathways shown in Fig 1. but even these may not be exclusive since charge matching also might be accomplished through a combination of both direct and mediated linkages. Ultimately temporal and spatial control of the relative rates of the biphase and interface assembly processes in cooperative templating might be used to impose microscopic long range modulation of the periodic composite array morphology in a manner directly relevant to biomaterial synthesis (23,24).

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Figure Captions

Fig. 1. A general scheme for the self-assembly reaction of different surfactant and inorganic species. The mesostructured phases can be synthesized by direct pathways or mediated pathways using different charged surfactant molecules and inorganic solution species in certain pH conditions. Some surfactants other than alkyltrimethylammonium ions are also good templates for mesoporous materials syntheses. Each surfactant can template the formation of one or more mesostructures in different reaction conditions. The topology of the composite mesostructures reflects the final geometry adopted by the organized organic array so that regardless of the inorganic framework composition, liquid crystal morphologies have been observed and can be expected. The dimensionless effective surfactant packing parameter $g = V/a_0l$ determines the product structure (11, 12, 25).

Fig. 2. Transmission electron micrographs of (i) acid phase hexagonal silica (left is SEM), (ii) hexagonal tungsten oxide, periodicity 40Å, (iii) lamellar tungsten oxide, periodicity 36Å, and (iv) direction [210] of the cubic Pm3n silica, v=78Å, w=35Å.

Fig. 3. Powder x-ray diffraction (XRD) patterns of silica and zinc phosphate mesostructures precipitated from acidic medium. Beginning at the bottom of the figure are (i) lamellar silica; $a_o = 39.8$ Å, (ii) hexagonal silica (MCM-41); $a_o = 47.6$ Å and (iii) cubic Pm3n silica; $a_o = 89.9$ Å, and (iv) lamellar zinc phosphate, with the high 2Θ region shown in the inset. These peaks (iv) could be indexed in an orthorombic cell having a = 6.49 Å, b = 6.57 Å and c = 28.08 Å. Typical preparation of the silica mesophases from acidic medium was carried out with the following molar ratios: (i) lamellar: 0.12 $C_{20}TMABr$: 1 TEOS : 4.9 HCl : 130 H_2O; (ii) hexagonal: 0.12 $C_{16}TMABr$: 1 TEOS : 9.2 HCl : 130 H_2O and (iii) cubic: 0.13 $C_{16}TEABr$: 1 TEOS : 10.4 HCl : 130 H_2O. The lamellar zinc phosphate phase shown here (iv) was synthesized by crystallization of a reaction mixture with molar composition of 3.0 $Zn(NO_3)_2$: 3.5 H_3PO_4: 5.0 $C_{16}TMABr$: 4.5 TMAOH : 1000 H_2O at 4° C for 18 days (pH = 2) to give a final composition of $[(C_{16}H_{33})N(CH_3)_3{}^+Br^-]\cdot HZnPO_4$, [obs,calc: Zn(12.4%,12.5%); Br(15.4%,15.2%); N(2.9%,2.7%); and P(5.5%,5.9%)}. By varying pH and dilution other lamellar structures can be obtained with spacings of 63 Å, 37.3Å and 29.7Å and surfactant chain length to lattice spacing variation which suggests a surfactant bilayer configuration for the first of these. In these lamellar phases, the residue obtained after thermal analysis to 900 °C is $Zn_2P_2O_7$.

Fig. 4. ^{29}Si MAS NMR of the as-synthesized silica mesophases. For all four of the materials the two major peaks shown are Q^3 at (-101 to -102 PPM) and Q^4 at (-110 to -111 PPM) (26). %Q^3 measures the number of ^{29}Si of the type $(SiO)_3\equiv\underline{Si}\text{-OH}$ and %Q^4 measures the number of ^{29}Si of the type $(SiO)_3\equiv\underline{Si}\text{-O-Si}\equiv$. The estimated error in the

values of Q^3 and Q^4 are ±5% of their value. Hexagonal phase A was run at short reaction time (30 min.) and hexagonal phase B was run under the same synthesis conditions except for long reaction time (2 hours). The Q^3/Q^4 ratio measures the extent of silanol condensation indicating for material B a more condensed framework than material A. Q^3/Q^4 for the hexagonal phase and for the lamellar phase in acidic media is similar to that found for materials precipitated from basic media which are 0.55 and 1.2 respectively.

Fig. 5 The relationship between unit cell parameter and number of carbon atoms in surfactant chain. Silica (Pm3n) phase was synthesized by using alkyltriethylammonium as template at room temperature for 1 hr. Hexagonal silica and silicate phases were obtained in the presence of alkyltrimethylammonium at room temperature in acidic and basic media, respectively. Only $C_{20-22}TMA^+$ led to the formation of lamellar silica in acidic medium at room temperature. Lamellar $ZnPO_4$ was prepared by using alkyltrimethylammonium as template from acidic medium (pH = 2.5). Estimated error is 1 Å in d-spacing of highest peak (d_{210} for Pm3n phase and d_{100} for hexagonal and lamellar phases).

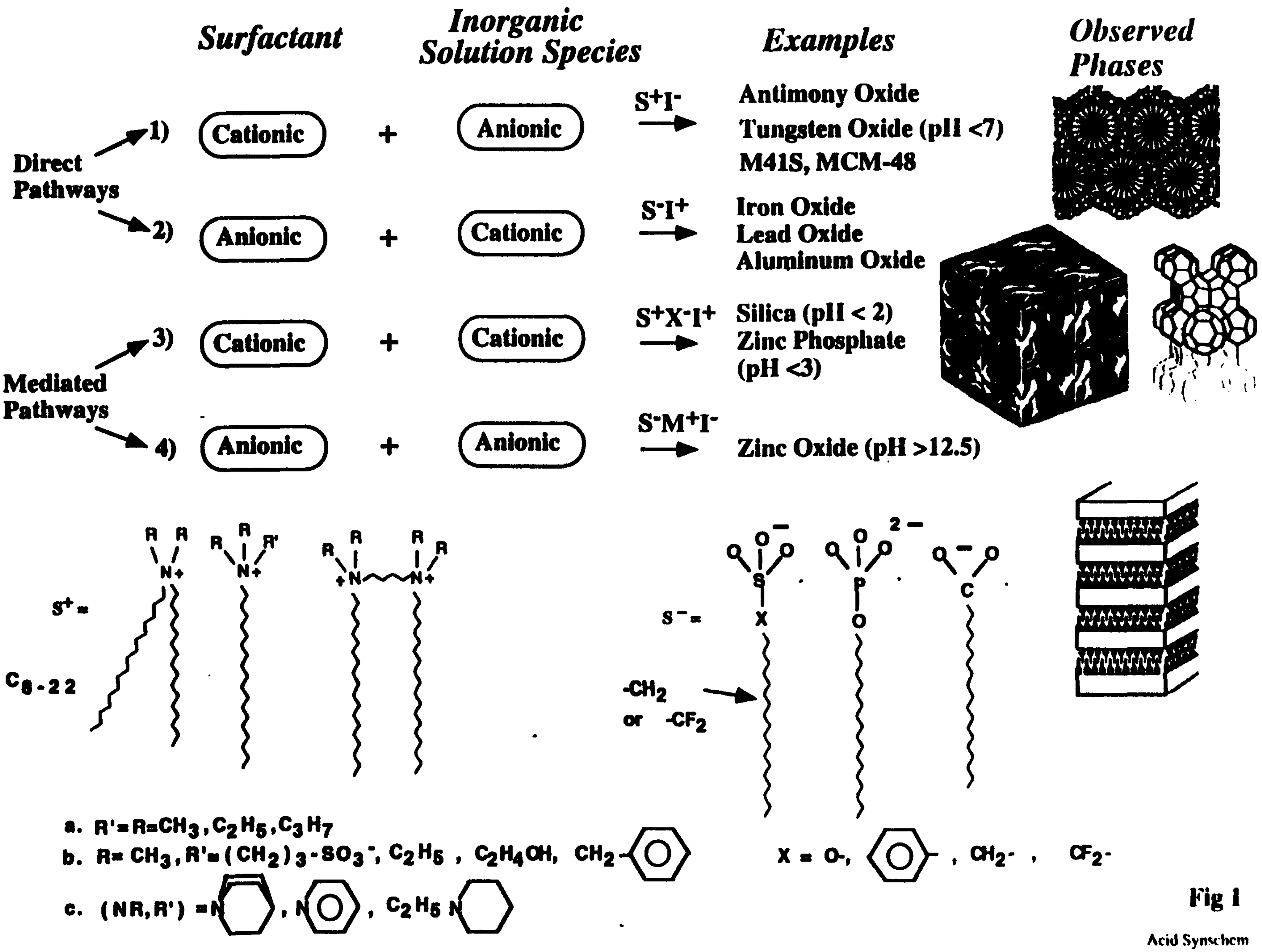
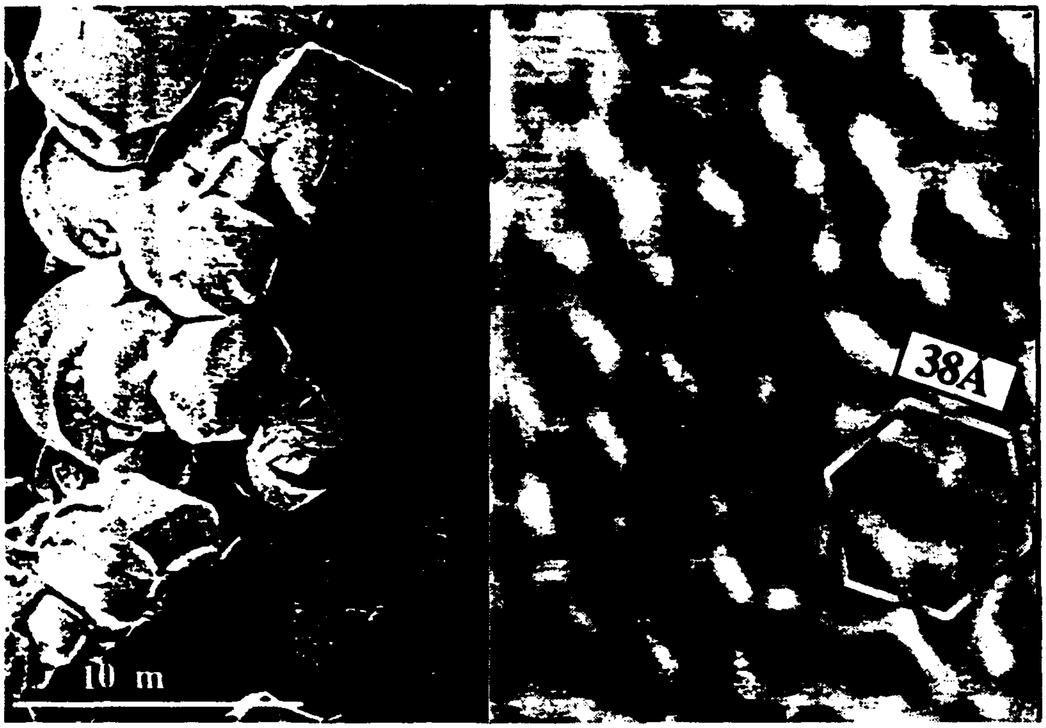


Fig 1

Acid Synschem

acidhex..TEMxtal



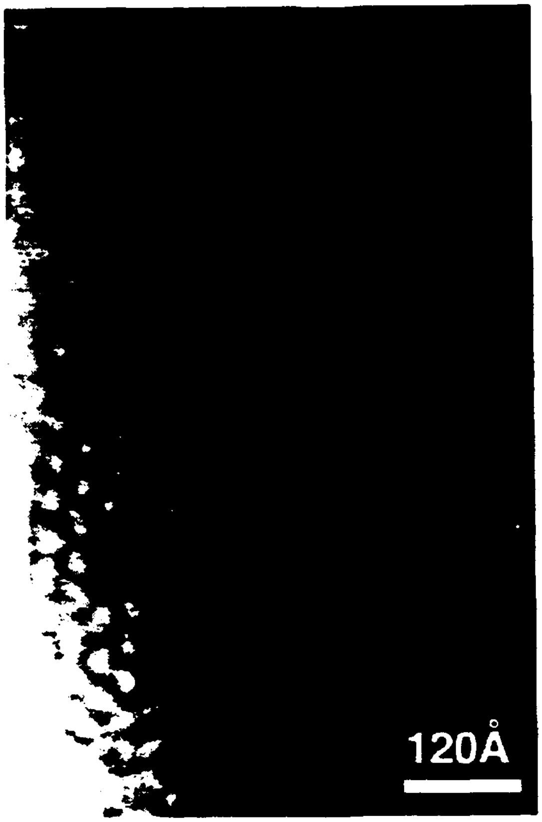


Fig 2ii

WO3TEMhex

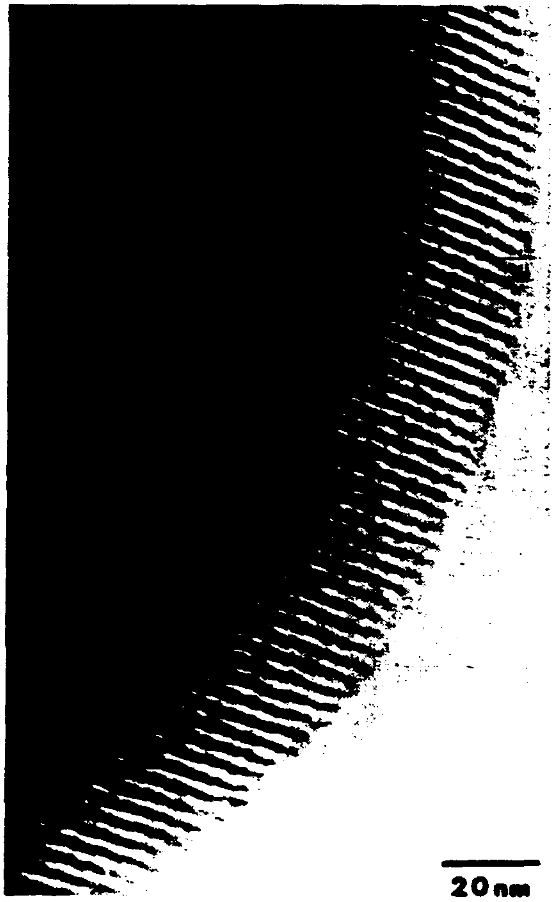
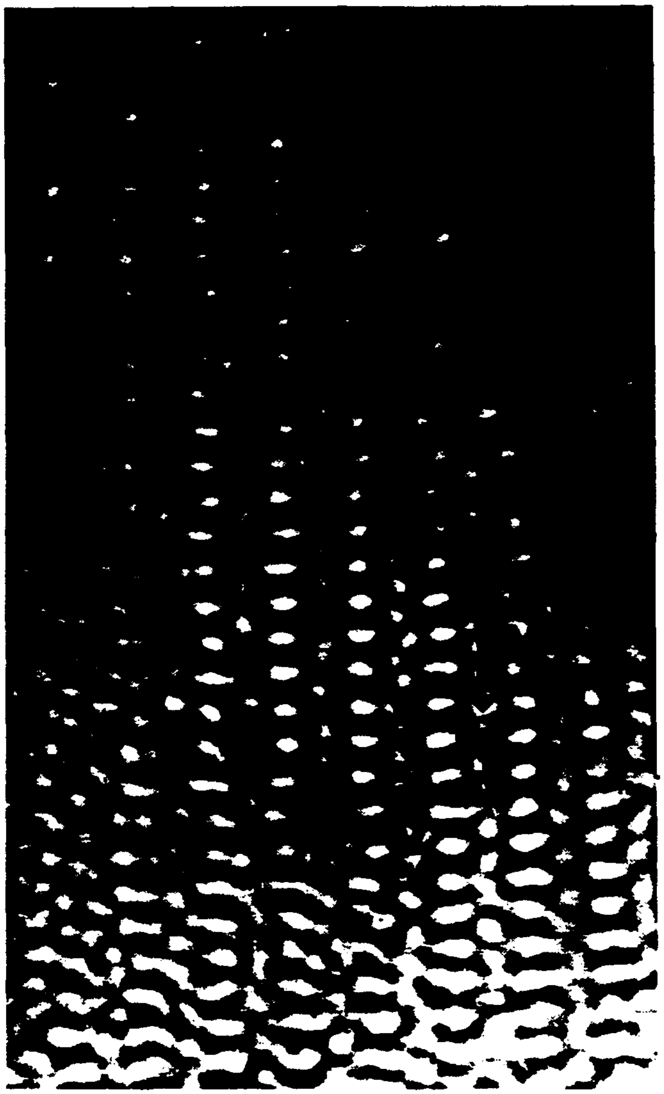
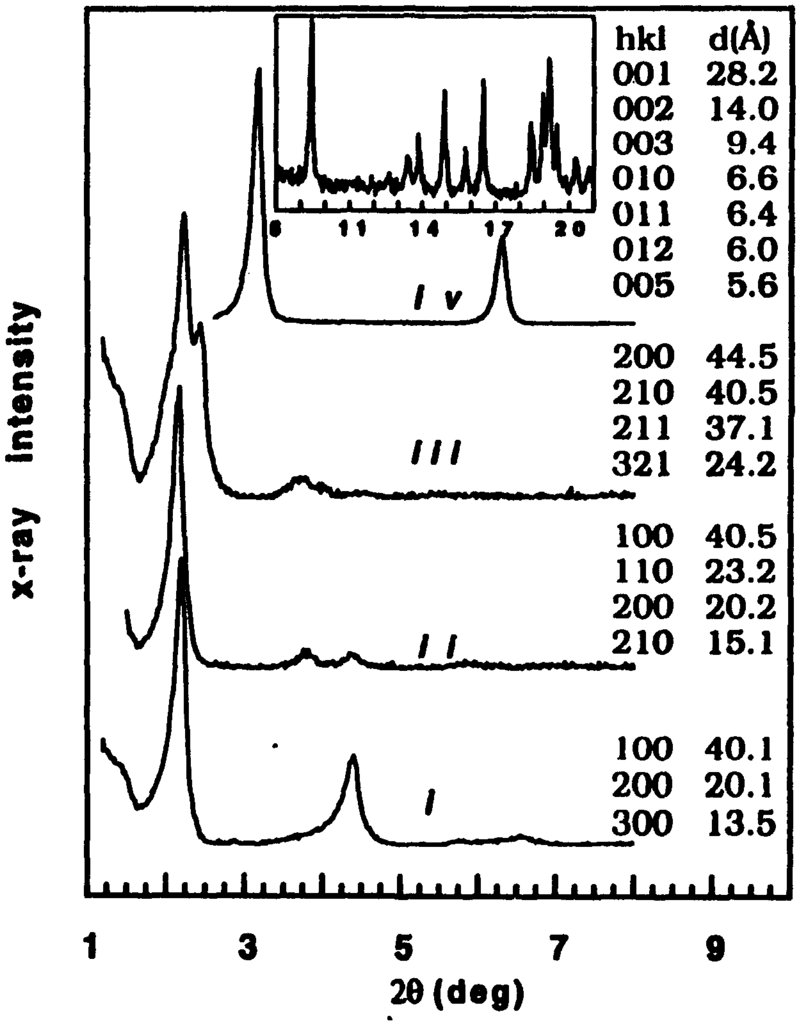


Fig 2iii

WO3TEMlam




x-ray Intensity
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7
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8
11
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IV
III
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I
hkl d(Å)
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002 14.0
003 9.4
010 6.6
011 6.4
012 6.0
005 5.6
200 44.5
210 40.5
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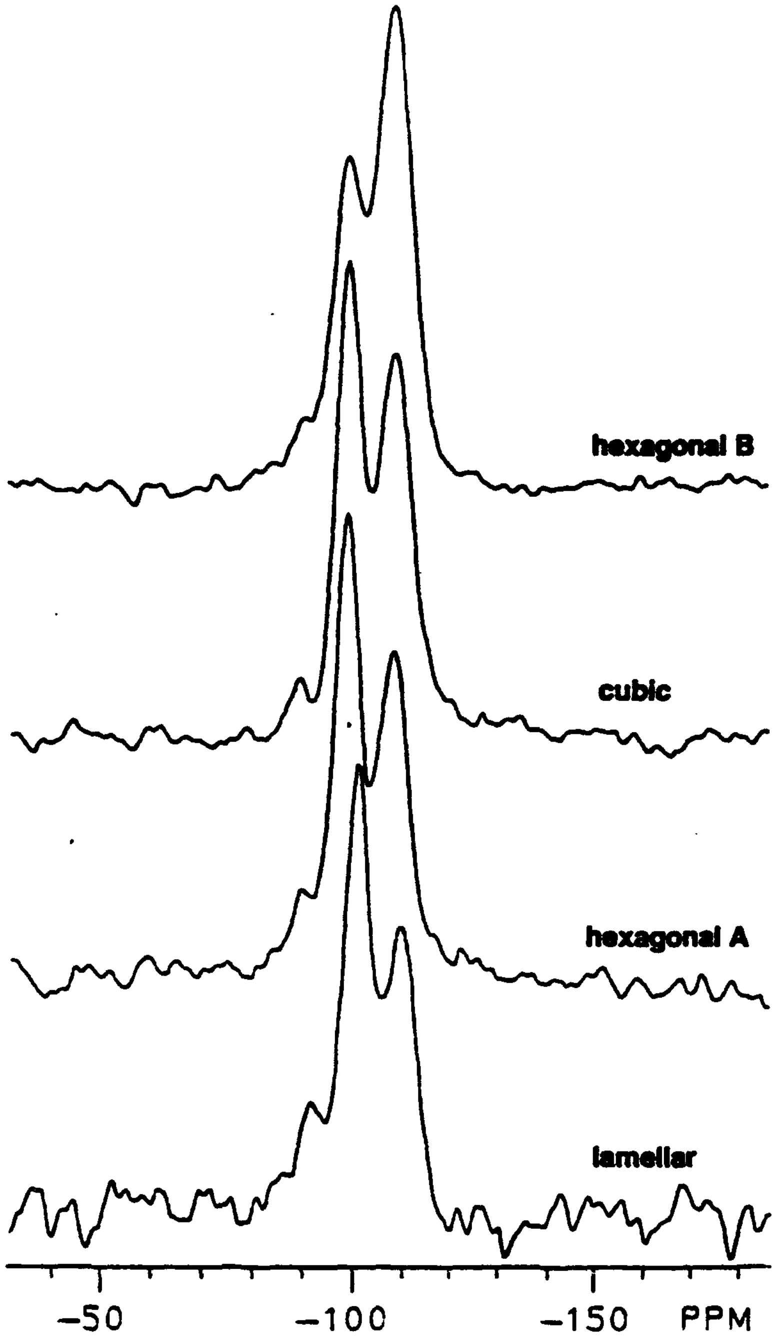
Fig 3



	$\%Q^3$	$\%Q^4$	Q^3/Q^4
hexagonal B	36	61	0.59
cubic	51	47	1.1
hexagonal A	53	47	1.1
lamellar	56	41	1.4

Fig 4

NMR

Fig. 5

uccll#car