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Recent Chemistry of Advanced Inorganic and Hybrid Materials at the MacDiarmid Institute

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Introduction

The work of the MacDiarmid Institute falls into five themes of which the fifth is concerned with the development of innovative advanced inorganic and nanostructured materials. The impact of such materials is broad and ranges from technologies for energy conversion and storage, environmental protection and sustainability to new materials for sensors, engineering, electronics, and biotechnology. The MacDiarmid research in this area seeks to design, synthesize, and determine the chemical and physical properties of new materials, with special emphasis on their nano and microstructures, to exploit new approaches to controlling the surface functionality of these new materials, and to understand the reaction mechanisms, phase transformations and other processes in these materials.

Vital to this work is the availability of world-class competencies and instrumental techniques, including multinuclear solid-state NMR, X-ray powder diffraction, scanning electron microscopy (SEM), ion beam analysis, thermal analysis, and superconducting quantum interference device (SQUID) magnetometry. Contacts and agreements provide additional access to international centres of neutron diffraction and synchrotron techniques.

Templated Nanostructures for Hydrogen Filters

Widespread adoption of hydrogen as a fuel ultimately will depend on the resolution of issues regarding its generation, separation, storage, and utilization. One possible strategy for separation and purification is to use devices fabricated from nanoporous ceramic membranes containing aligned arrays of high aspect ratio pores. An anodic technique for growing such aluminium oxide membranes with narrow pore dimensions has been developed.[1] These new materials are highly ordered and more robust than commercially available alternatives. The pores are perfectly straight and narrow (33 nm i.d.), have aspect ratios of 10,000:1 (Fig. 1), and are thermally stable above 800°C with thermal analysis, multinuclear solid state NMR, and high resolution SEM confirming suitability for high temperature applications. Techniques for growing aligned nanocrystals of the microporous aluminium phosphate AlPO¬-5 within the pores of these anodic alumina membranes have also been developed and provide what could be highly efficient H_2 filters.[2]

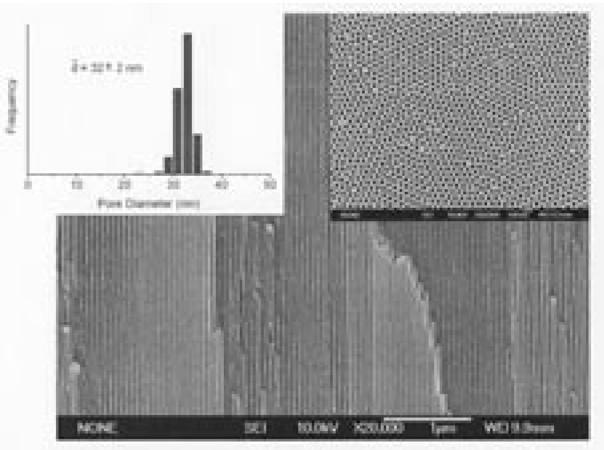

Fig. 1. Cross-section of an anodically grown aluminium oxide nanoporous membrane showing highly aligned 32 nm i.d. pores (left-hand inset)and pore-size distribution of the top surface (right-hand inset).

Another application that exploits the unique porous structure of these anodic alumina substrates involves chemical deposition to coat the pore walls with a TiO_2 gel precursor that can then be converted to the anatase form of TiO_2. The alumina substrate is subsequently removed by dissolution, leaving a product shown by electron microscopy to consist of anatase nanotubes (Fig. 2) that have possible photocatalytic activity.[3]

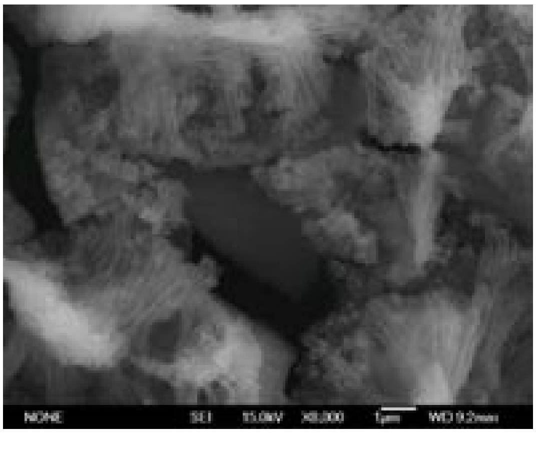

Fig. 2. Arrays of TiO_2 nanotubes formed by chemical deposition.

Novel Hybrid Composites of Conducting Polymers and Organic Materials

A series of novel hybrid materials have been developed to exploit the electronic properties of the conducting polymers polypyrrole and polyaniline. In one composite, the cellulose fibres of Kraft (*pinus radiata*) are fully coated with polymer to produce a novel hybrid material that combines the strength and flexibility of the fibres with the conductivity and redox properties of the polymer coating.[4,5]

The cellulose fibres or wood surfaces are treated with pyrrole or polyaniline monomer that is then oxidized with ferric chloride or ammonium persulfate to achieve polymerization. After removal of residual free polymer by sonication and washing, SEM shows the polypyrrole-containing material to consist of fused nano-sized spheres (100-150 nm dia.) that fully coats the individual fibres or wood surface (Fig. 3); polyaniline behaves similarly giving spheres of 50-200 nm size shown by UV-Vis spectroscopy to be in the emeraldine salt form. The fibre/polypyrrole composites have electrical conductivities up to *ca*. 0.1 S/cm while those of the polyaniline analogues are about one order of magnitude less. The redox properties of these polymers can be exploited to recover metal ions such as gold or silver from solution (redox coupling) by depositing them as metal films or nanoparticles directly onto the surfaces of the composites. Deposited silver nanoparticles exhibit significant antimicrobial properties when tested against *Staphylococcus aureus* (Fig. 4). The electrically conducting fibre surfaces also allow for electrochemical deposition of thin metal coatings that retain the underlying morphology of the fibre or wood surfaces. This opens the possibility of a range of novel metallized wood materials for new industry and consumer applications.[5]

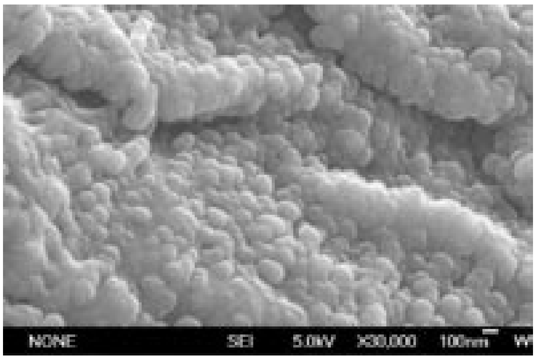

Fig. 3. SEM of cellulose fibres coated with polypyrrole.

Fig. 4. Antimicrobial properties of Ag nanoparticles deposited on a cellulose fibre-conducting polymer composite; clear areas define inhibited *Staphylococcus aureus* growth regions.

The techniques developed for preparing conducting cellulose fibres apply to natural protein fibres, *e.g.* merino wool and possum fur, using the same conducting polymers. Again, SEM shows the polypyrrole coatings to consist of individual spheres (0.10-0.15 µm). These are fused together to give a continuous sheet that coats the entire fibre (Fig. 5).[6] The resulting electrically conducting, coated wool and fur fibres allow variously sized gold nanoparticles to be deposited as stable colorants, thus opening an exciting opportunity to utilize the gold nanoparticles as stable colorants on high-quality fabrics. With gold particles at colloidal or nano-size, strong visible absorption occurs and gives a variety of colours that depend on the actual size and shape of the nanoparticles. At 2-5 nm size the colour is red but, as size increases or agglomerates form, the colour changes through the spectrum to violet with a size of 50-70 nm. The colour is due to phenomenon of surface plasmon resonance absorption of light and the technique has been used to colour NZ Merino wool, pointing to the possibility of a high-technology, high-value fashion product.[7]

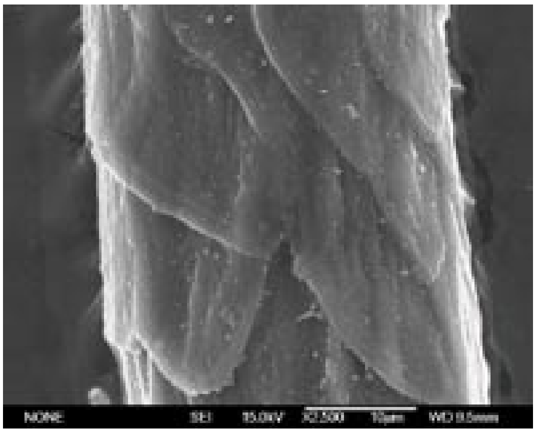

Fig 5. SEM Merino wool fibre fully coated with conducting polypyrrole.

Hybrid Materials of Cellulose Fibres with Magnetic Nanoparticles

A new method has been developed for coating Kraft fibres with magnetic (magnetite and cobalt ferrite) nanoparticles and the products retain the tensile strength and flexibility inherent in the fibre. The method for applying the coating differs from literature methods,[8] as it binds the magnetic particles securely to the fibre surface; they survive successive washings and even sonication. They can be fabricated into paper sheets with magnetic properties thus offering new concepts for papermaking and packaging, security paper, and information storage. SEM shows the fibre surfaces to be completely encapsulated by nanoparticles of ~15 nm for magnetite and ~80 nm for cobalt ferrite. SQUID magnetometry confirms the composites as ferrimagnetic with remnant magnetization at 10 K (Fig. 6). These magnetically responsive materials have potential in electromagnetic shielding, magneto-graphic printing, and magnetic filtering.

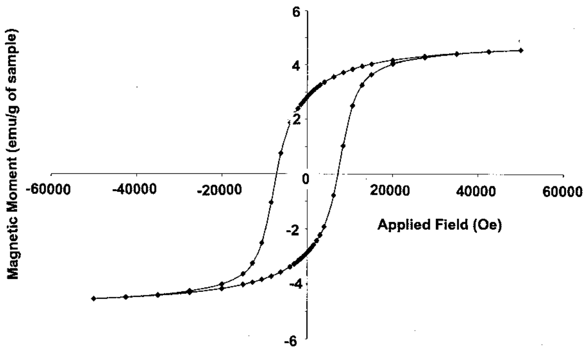

Fig.6. Hysteresis loop from Kraft fibres coated with $CoFe_2O_4$ nanoparticles.

New Developments in Inorganic Polymers

Inorganic or geopolymers are generally aluminosilicates formed by polycondensation of tetrahedral aluminate and silicate units at high pH and ambient temperatures, and they are X-ray amorphous. Interest in these materials is mainly as environmentally friendly substitutes for conventional calcium silicate cement-based building materials; production of aluminosilicates does not generate the large quantities of CO_2 that come from the pyrolysis of limestone or burning of fossil fuels. Other possible uses are as fireproof vehicles body panels and the encapsulation of radioactive and heavy metal wastes prior to disposal. We have previously studied the fundamental chemistry and formation mechanism of these materials that are (conventionally) synthesised from a solid dehydroxylated clay and sodium silicate solution. Recent research has focussed on solution phase preparation of such polymers from sodium aluminate and sodium silicate such that other tetrahedral components, *e.g.* phosphate and borate, could be incorporated within the structure. A phosphate geopolymer could be used in bioactive materials for hard tissue prostheses providing calcium can also be incorporated into the structure. Borates regulate the setting rate of the geopolymer. Moreover, successful liquid-phase syntheses could allow for gallium and germanium analogues with potentially interesting electronic properties.

Results to date are promising. A full liquid-phase synthesis of a solid product showing all the key geopolymer characteristics has been achieved[9] and geopolymers with some of the tetrahedral aluminosilicate units replaced by phosphate (Fig. 7) or boron (Fig. 8) have been obtained.[10] The structures of all these compounds are confirmed from use of solid-state multinuclear and magic angle spinning (MAS) NMR. Work on the incorporation of Ca in the structure suggests success. The extremely low natural abundance of ^{43}Ca (0.143%) makes it very difficult to detect by NMR, but ^{43}Ca solid-state MAS studies (collaboratively with staff at Warwick University) suggest that it may occupy sites in the pore water of the gel structure.

Novel Nanoporous Materials for Environmental Protection

It is known[11] that a range of materials with hydrophobic slit-shaped nanopores can be produced by selective acid-leaching of the octahedral layers from thermally-activated aluminosilicate clay minerals (Fig. 9). Now, a new range of X-ray amorphous aluminosilicate compounds has been synthesized from the leachate (Fig. 10). These have the

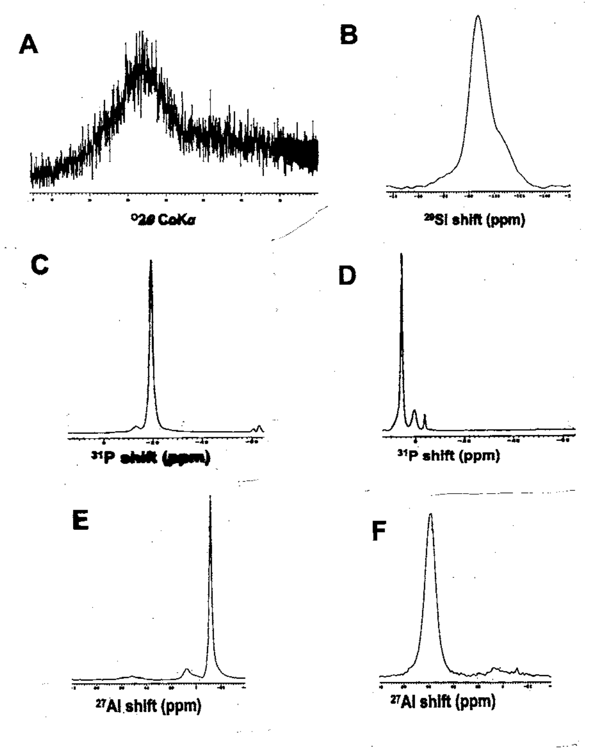

Fig. 7. A: XRD powder diffraction pattern showing typical amorphous geopolymer characteristics of a phosphate-substituted aluminosilicate inorganic polymer; B, D, and F: solid state MAS NMR spectra of the polymer with all species in tetrahedral coordination; C and E: ^{31}P and ^{27}Al MAS NMR spectra of the unpolymerized mixture.

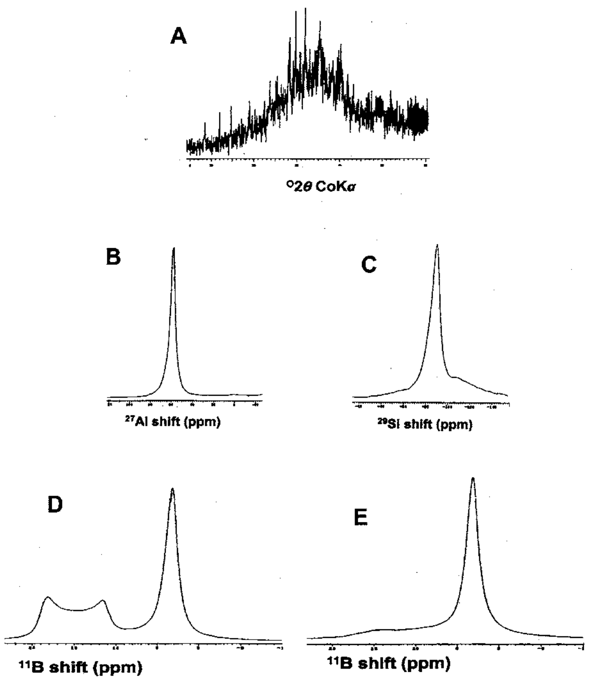

Fig.8. (A) XRD powder diffraction pattern showing typical amorphous geopolymer characteristics of a borate-substituted aluminosilicate inorganic polymer; (B, C and E) solid state MAS NMR spectra the polymer with all species in tetrahedral coordination; D, E, ^{11}B MAS NMR spectrum of the monomer mixture showing both BO_4 (right) and BO_3 species (left quadrupolar resonance).

unusual property of functioning simultaneously as cation and anion absorbers and is particularly effective for the phosphate and ammonium ions that are implicated in the eutrophication of rural waterways.[11] Recent collaborative work[12] has shown that Ca incorporation into these amorphous aluminosilicate hydrates, either by solid state reaction of $CaCO_3$ with an aluminosilicate clay, or using industrial waste paper sludge ash, produces an even more useful material. It has a strong adsorption capacity not only for phosphate and ammonium ions,[13] but also for transition metal ions such as Ni^{2+}.[14]

A new composite of activated carbon and zeolite has been developed from recycled waste paper. Thermally-carbonised paper is physically activated by exposure to humid nitrogen or CO_2 and then subjected to hydrothermal treatment in alkaline solution. This converts the inorganic paper fillers (typically aluminosilicate clays) to zeolite that becomes located on the carbon layers (Fig. 11). The composite has the combined adsorption properties of activated carbon (slit-shaped hydrophobic 0.6 nm pores) and zeolite (cylindrical hydrophobic or hydrophilic (depending on Al content) <2 nm pores), giving dual functionality product from a recycled waste material.

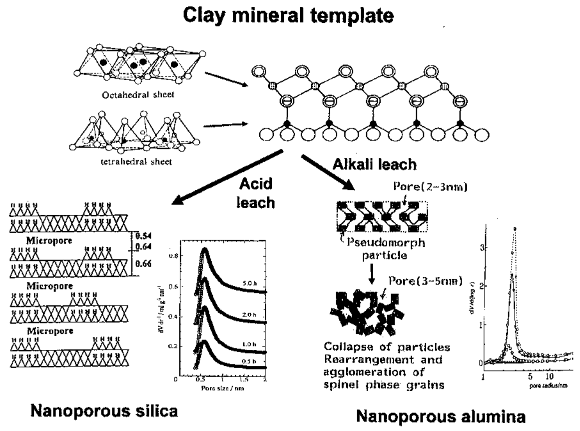

Fig.9. Nanopore formation by acid and alkali-leaching with insets showing measured pore-size distributions.

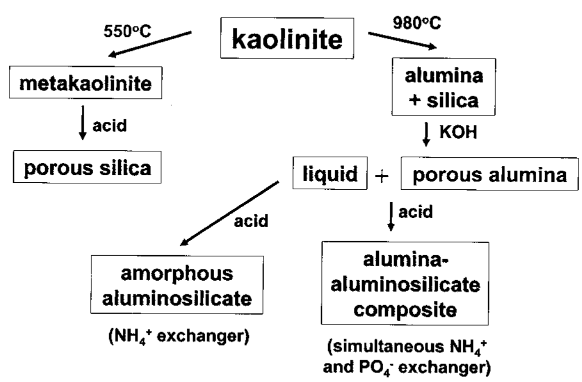

Fig.10. Nanoporous adsorbent materials from a 1:1 clay mineral.

New High-Performance Nano-Structured Calcium Silicates

The development of new nano-structured calcium silicate materials with high pore volumes (up to 600 g oil/100 g) and high surface areas (up to 700 m^2/g)[15] has provided novel applications. The structure (Fig. 12), consisting of nano-sized platelets joined into an open framework, gives a high oil adsorption capacity and makes the material an ideal filler for high grade papers with reduced print–through, sharper images, and superior light scattering qualities.[16] The sorbent properties of the nano structure allow for biocidal, antiseptic, anticorrosive, heat storage, photochemical, or electrical conductivity character to be incorporated, and, in turn, transferred to a paper filled with the material. The formation of these materials with the new calcium silicates suggests composites with carbon nanotubes[17] to influence both the electronic properties and mechanical strength of the resulting material, and those with inorganic polymers for a range of new bioactive materials. The calcium silicates possess an ability to take up various ionic species, *e.g.* Cu^{2+},[18] or, if functionalised with polyaniline, to act as a sorbent for rhenium.[19]

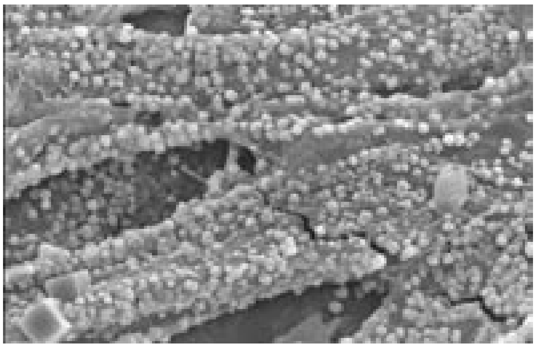

Fig.11. SM of activated carbon-zeolite composite absorber from recycled waste paper; carbon laths coated with *in-situ*-formed zeolite spheres.

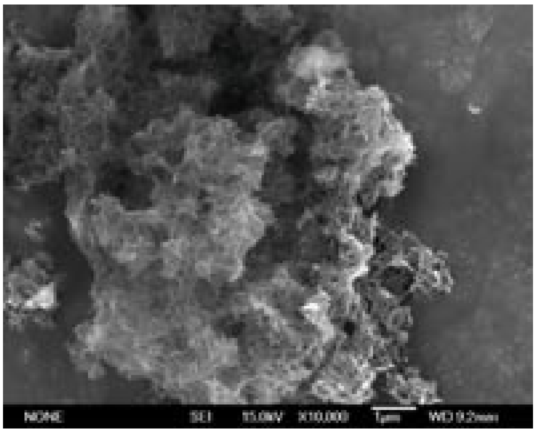

Fig.12. SEM of nanostructured calcium silicate showing interlocking platelets responsible for the large pore volume and high surface area.

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