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Research breakthroughs

(This section is cited from Green Chemistry News Issue 31. [http://www.rsc.org/chemsoc/gen/pdf/Newsletter31.pdf](http://www.rsc.org/chemsoc/gen/pdf/Newsletter31.pdf))

We also welcome the domestic researchers to send the research results about “Green Chemistry” to us.

**Green cement**

A remarkable 6% of the carbon dioxide we release into the atmosphere comes from cement manufacture. Portland cement is produced at ca. 1500°C and for every tone produced, 100 kg of fossil fuel is consumed and one tone of carbon dioxide is generated. Some types of waste or low value biomass contain significant amounts of silicates – the primary constituent of cement. For example, rice hulls which are produced in enormous quantities in many parts of the world including the USA, China and Brazil contain about 10% silicate; this can be relatively easily produced by burning the hulls at 600°C followed by further processing which is complete at 800°C.


**Reducing the environmental footprint of chemicals**

The manufacturing processes for chemicals can make large contribution to their environmental footprints. In the case of speciality products such as pharmaceuticals, manufacturing can be especially onerous – in many cases only 1% of the resource input ends up in the product. One of the major environmental impacts in chemical manufacturing is the use of organic solvents. In a recent publication from Israel, water is shown to be an effective replacement for organic solvents in some chemical syntheses. In particular it is shown that one of the most important chemical reactions, oxidation, can be carried out using water and air.


**Safer and greener foods**

Consumers are demanding safer foods but also foods that use natural rather than synthetic additives. Spices and essential oils are being researched as natural agents for food preservation. In a recent publication from the USA, seven citrus essential oils
were screened for antibacterial activity against 11 strains of Salmonella. Good inhibiting activity was shown by several oils with terpenes from orange essence showing the highest activity. Analysis of this substance showed it was mostly composed of d-limonene.


**Bio-deicing**

De-icing fluids are widely used on roads, airport runways and other large scale applications. Currently used substances include glycols but there are concerns about the impact of such substances in large volumes, on the environment. In a recent US Patent, a group from the Batelle Memorial Institute in Ohio report the use of a novel, non-hazardous anti-icing agent based on a bio derived freezing point depressant such as glycerol which can be mixed with other bio-polyols as well as a surfactant and an anti-oxidant (e.g. citric acid). A polymer, typically PVP, can also be part of the formulation.


**Green waxes**

Plants are coated with chemicals which have a multitude of functions depending on their environment and time of year. These “waxes” can be extracted and then used in a variety of applications. In research published by the Green Chemistry Centre at York, the surface waxes from low value wheat straw have been extracted using low environmental impact supercritical carbon dioxide. Furthermore, the chemicals in the waxes can be simultaneously fractionated to give specific products with value in areas including cosmetics, nutraceuticals and insect repellents. The low environmental impact of these products, coupled with increasing consumer demands for natural, non-animal derived products makes these attractive green products.


**Wine waste is good for you as well!**

Once again the “food vs. fuel vs. feed” is being avoided by the ingenious use of waste agricultural products. This time researchers in Canada and Turkey have used the grape cane waste from Pinot Noir wine production (and a mighty fine production it is too!) as a source of valuable phytochemicals that have shown significant activity against animal diseases such as cancer, cardiovascular complaints and they can also act as
anti-oxidants as well. These chemicals, trans-resveratrol and trans-viniferin, are isolated using an environmentally benign solvent mixture of ethanol and water. The researchers have calculated that if all the Pinot Noir cane in the world, all 8 million tons of it, were extracted and these compounds isolated the global economic value would be ~£30 billion! So the next time you have a glass of Pinot Noir, you can drink easier knowing you are saving both animals and the planet!


**Green synthesis of silver and palladium nanoparticles at room temperature using coffee and tea extract**

An extremely simple green approach that generates bulk quantities of nanocrystals of noble metals such as silver (Ag) and palladium (Pd) using coffee and tea extract at room temperature is described. The single-pot method uses no surfactant, capping agent, and/or template. The obtained nanoparticles are in the size range of 20–60 nm and crystallized in face centered cubic symmetry. The method is general and may be extended to other noble metals such as gold (Au) and platinum (Pt).


**Microwave-assisted rapid facile “green” synthesis of uniform silver nanoparticles: self-assembly into multilayered films and their optical properties**

We report an environmentally benign process for the synthesis of nearly monodisperse silver nanoparticles in large quantities via a microwave-assisted “green” chemistry method in an aqueous system, using basic amino acids, such as L-lysine or L-arginine, as reducing agents and soluble starch as a protecting agent. The presence of amino acids with basicity such as L-lysine or L-arginine, having two amino groups in each
molecule, is indispensable for the synthesis of uniform silver nanoparticles. The current synthetic process can be readily applied to large-scale production, for example, a reaction yielding 0.1 g of nearly monodisperse silver nanoparticles can be performed in a 80 mL microwave sealed vessel. This combination of solvent, renewable reactants, and microwave irradiation seem to make it clear that green chemical synthesis of metal nanoparticles with well-controlled shapes, sizes, and structures has practical potential. Self-assembly of starch-capped silver nanoparticles results in multilayered mirrorlike films forming on the glass slide surface. The surface plasmon transmission of the films has blue-shifted with decreasing silver atom concentrations of the films. The silver films offer great surface enhancement for 4-mercaptobenzoic acid (4-MBA) molecules, and the surface enhancement factor can be efficiently changed by the silver atom concentrations of the films.


**A green route to water soluble carbon nanotubes and in situ loading of silver nanoparticles**

A green approach has been developed to synthesize water soluble multi-walled carbon nanotubes (MWNTs). Ag nanoparticles have been loaded on the as-synthesized MWNTs via the in situ solution method. The strategy is based on the introduction of hydroxyl and carboxyl groups through a mild modification of MWNTs via polycondensation of citric acid and D-sorbitol, improving the water solubility of MWNTs, giving rise to preferred sites of Ag nucleation, and providing mild in situ reducing agents. The modification of MWNTs and loading of Ag nanoparticles on MWNTs were demonstrated by Fourier transform infrared spectroscopy, thermogravimetric analysis, transmission electron microscopy, and scanning electron microscopy.


**Green synthesis of 1–2 nm gold nanoparticles stabilized by amine-terminated ionic liquid and their electrocatalytic activity in oxygen reduction**

Stable gold nanoparticles with average size 1.7 nm synthesized by an amine-terminated ionic liquid showed enhanced electrocatalytic activity and high stability.

Selective growth of gold nanoparticles onto tellurium nanowires via a green chemical route

In this paper, we describe a green chemical route for highly selective growth of Au tips onto Te nanowires (NWs). We carefully selected the pH values to vary the redox reaction potential between Au$^{3+}$ and Te NWs, allowing control of nucleation and growth rates of Au nanoparticles (NPs). In the presence of 10 mM CTAB, we obtained Au-Te and Au-Te-Au NWs at pH 4.0 and 5.0, respectively. Photovoltaic data revealed that the resistance of the Te NW-based thin films is controlled by the degree of deposition of Au NPs. We suspect that Au-Te and/or Au-Te-Au NWs hold great potential for use in the fabrication of electronic devices.


One-step “green” synthesis and stabilization of Au and Ag nanoparticles using ionic polymers

Generally, metal nanoparticles are prepared by a variety of chemical methods that are not environmentally friendly. We report on the use of aqueous solutions of ionic polymers containing arsonic acid groups for the green synthesis of Au and Ag nanoparticles of intriguing shapes at room temperature without using additional reducing reagent. Our results indicate that these ionic polymers are not only capable of reducing metal ions but also can protect the nanoparticles in the colloidal solutions. In general, the process of metal ions reduction using these ionic polymers is very slow, but the ability of the polymers to protect the Au and Ag nanoparticles permits us to obtain colloidal solutions that are stable for several months. This method would be very much useful for the preparation of other metal nanoparticles.


Green preparation and catalytic application of Pd nanoparticles

A green strategy for the facile preparation and effective stabilization of Pd nanoparticles has been developed by using D-glucose as the reducing and stabilizing agents. The UV/vis absorption spectroscopy, transmission electron microscopy (TEM),
X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and zeta potential measurements were used to characterize the as-prepared Pd nanoparticles. It was found that the D-glucose concentration and pH value had an important effect on the size distribution and stability of the nanoparticles. Further, the Pd nanoparticles exhibited good catalytic properties in the degradation of azo dyes.

L. Xu et al., *Nanotechnology*, 2008, 19, 305603.

**Biopolymer-assisted green synthesis of iron oxide nanoparticles and their magnetic properties**

Magnetite nanoparticles were fabricated using a biopolymer (sodium alginate)-assisted route via redox-based hydrothermal method using FeCl₃·6H₂O and urea as the starting materials. The morphology, composition, and phase structure of as-prepared powders were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The results show that biopolymer plays dual roles, reduction, and stabilization, in the formation of the products. This method can be easily controlled and is expected to be applicable for the preparation of other metal oxides. The sample demonstrated a typical ferromagnetic behavior from a direct current SQUID magnetometer (Quantum Design MPMS).


**A facile and green preparation of high-quality CdTe semiconductor nanocrystals at room temperature**

One chemical reagent, hydrazine hydrate, was discovered to accelerate the growth of semiconductor nanocrystals (cadmium telluride) instead of additional energy, which was applied to the synthesis of high-quality CdTe nanocrystals at room temperature and ambient conditions within several hours. Under this mild condition the mercapto stabilizers were not destroyed, and they guaranteed CdTe nanocrystal particle sizes with narrow and uniform distribution over the largest possible range. The CdTe nanocrystals (photoluminescence emission range of 530–660 nm) synthesized in this way had very good spectral properties; for instance, they showed high photoluminescence quantum yield of up to 60%. Furthermore, we have succeeded in detecting the living *Borrelia burgdorferi* of Lyme disease by its photoluminescence image using CdTe nanocrystals.

A green process for coupling manganese oxides with titanium(IV) dioxide

MnO$_2$ nanoparticle-loaded TiO$_2$ prepared by a green process capable of removing harmful MnO$_4^-$ ions from water exhibits catalytic activity for a test reaction, H$_2$O$_2$ decomposition, in the dark with its activity enhanced by UV light irradiation.

Green electricity production with living plants and bacteria in a fuel cell

The world needs sustainable, efficient, and renewable energy production. We present the plant microbial fuel cell (plant-MFC), a concept that exploits a bioenergy source in situ. In the plant-MFC, plants and bacteria were present to convert solar energy into green electricity. The principal idea is that plants produce rhizodeposits, mostly in the form of carbohydrates, and the bacteria convert these rhizodeposits into electrical energy via the fuel cell. Here, we demonstrated the proof of principle using Reed mannagrass. We achieved a maximal electrical power production of 67 mW m$^{-2}$ anode surface. This system was characterized by: (1) nondestructive, in situ harvesting of bioenergy; (2) potential implementation in wetlands and poor soils without competition to food or conventional bioenergy production, which makes it an additional bioenergy supply; (3) an estimated potential electricity production of 21 GJ ha$^{-1}$ year$^{-1}$ (5800 kWh ha$^{-1}$ year$^{-1}$) in Europe; and (4) carbon neutral and combustion emission-free operation.

Fuel cell cathode catalyst layers from “green” catalyst inks

Fuel cell cathode catalyst layers deposited from a water-based catalyst ink formulation, using high water content and minimum volatile organic compounds, are investigated. Cathodes fabricated from a dispersion medium containing 96 wt% water are compared with cathodes fabricated from conventional alcohol-based inks containing 1-propanol–water 3:1 (w/w). The morphology of the two catalyst layers are similar, as are electrochemically-active surface areas at relative humidities of 100, 70 and 30%
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Oxygen reduction kinetics obtained under fully humidified H2/O2 conditions exhibit similar Tafel slopes, 67 ± 3 mV per dec. However, cathodes prepared from water-based inks exhibit a lower H2/air fuel cell performance under 100, 70 and 30% RH while its porosity, obtained using mercury porosimetry, is slightly higher. EIS measurements obtained under high current density indicate that the mass transport resistance of the water-based catalyst layer is lower, which is consistent with porosimetric data, and suggests that factors other than mass transport limit the performance of the water-based cathode. The protonic resistance of the catalyst layers was found to be 105 and 145 mΩ cm² for the propanol- and water-based catalyst layers, respectively. The differences are more pronounced when RH is decreased from 100 to 30%. This trend is consistent with the observed decrease in fuel cell performance under conditions of lower RH, and indicates that the higher proton resistance of the water-based catalyst layer is the cause of its lower fuel cell performance.


**Copper zeolites as green catalysts for multicomponent reactions of aldehydes, terminal alkynes and amines: an efficient and green synthesis of propargylamines**

CuI-modified zeolites, especially CuI-USY, have proved to be very efficient catalysts in multicomponent reactions, allowing for a solvent-free synthesis of propargylamines from aldehydes, amines, and terminal alkynes. With a heterogeneous catalyst and in the absence of solvent, this process is among the greenest ever reported. A mechanism has been proposed for this three-component reaction.


**One-pot green synthesis of propylene oxide using in situ generated hydrogen peroxide in carbon dioxide**

In the one-pot green synthesis of propylene oxide using *in situ* generated hydrogen peroxide, a propylene oxide yield of 23% with 82% selectivity was achieved over a (0.2%Pd + 0.02%Pt)/TS-1 catalyst by using compressed (supercritical or liquid) carbon dioxide as the solvent and small amounts
of water and methanol as co-solvents. The addition of an inhibitor effectively suppressed a number of common side-reactions, including the hydrogenation of propylene, the hydrolysis of propylene oxide and the reaction between propylene oxide and methanol. This suppression effect is due to the interaction between the inhibitor and TS-1 leading to the neutralization of its surface acidity.


**Green composites reinforced with hemp nanocrystals in plasticized starch**

New nanocomposite films were prepared from a mixed suspension of hemp cellulose nanocrystals (HCNs) and thermoplastic starch, or plasticized starch (PS), by the casting and evaporating method. The morphology, thermal behavior, mechanical properties, and water sensitivity of the films were investigated by means of scanning electron microscopy, wide-angle X-ray diffraction, differential scanning calorimetry, tensile testing, contact angle measurements, and water absorption. The results indicate that the cellulose nanocrystals dispersed in the PS matrix homogeneously and resulted in an increase in the glass-transition temperature ascribed to the fact that the flexibility of the starch molecular chains in the starch-rich phase was reduced because of the strong intermolecular interactions between the starch and stiff HCNs. The films exhibited significant increases in the tensile strength and Young's modulus, from 3.9 to 11.5 MPa and from 31.9 to 823.9 MPa, respectively, with increasing HCN content from 0 to 30 wt%. In addition to the improvement in mechanical properties, the incorporation of HCNs into the PS matrix also led to a decrease in the water sensitivity of the final composite materials. Therefore, the HCNs played an important role in improving the mechanical properties and water resistance of the starch-based material.


**Mechanical properties of green composites with polycaprolactone and wheat gluten**

Wheat gluten (WG) was incorporated into polycaprolactone (PCL) (up to 50% w/w) as a filler to form a biodegradable polymer composite. A microscopic examination showed a well-dispersed particle-matrix system. The composite was evaluated for its tensile properties. The tensile strength of the composite decreased linearly with increasing WG content from 20 (0% WG) to 6 MPa (50% WG). However, the reduction of the tensile strength did not fit the Nicolais-Narkis model, and this indicated that some adhesion between WG and PCL occurred. High elongation (> 900%) was observed in PCL-WG composites with up to 20% WG; it decreased to 400% with 35% WG and finally to less than 100% with 40-50% WG. There was a
particle-induced transition at a calculated critical volume of 0.3 corresponding to 30% WG by weight with respect to PCL.

**Clean and green bioplastic composites: comparison of calcium sulfate and carbon nanospheres in polylactide composites**

Two environmentally friendly fillers, carbon nanospheres (CNS) derived from cellulose and calcium sulfate anhydrite (CaSO₄), a by-product of the polylactide (PLA) production process, are compared as nucleating agents in commercial-grade PLA. CNS and CaSO₄ are compounded with PLA using solution blending. Additionally, CaSO₄ is melt mixed with PLA. Crystallization kinetics are explored using differential scanning calorimetry (DSC) and polarized optical microscopy. Mechanical properties are examined using dynamic mechanical thermal analysis (DMTA) and morphology is determined using field-emission scanning electron microscopy (FE-SEM). It is found that the filler does not increase the PLA crystallization rates significantly at loadings up to 15 wt% (CNS) or 20 wt% (CaSO₄). The lack of effect on crystallization kinetics is attributed to the high D-lactic acid content of commercial-grade PLA, and also to poor dispersion of the fillers in the PLA matrix. The glassy shear storage modulus of the composites is found to increase by 50% in the highest weight loadings tested. These clean and green bioplastic composites may be able to offset the use of fossil resource-based materials.

**Environmental decision support for the construction of a “green” mountain hut**

The construction of a modern mountain hut near the mountains Matterhorn and Dufourspitze in the Swiss Alps is investigated from an environmental point of view. A prospective environmental assessment was performed to minimize the environmental impact already in the planning phase of the new building; construction will start in autumn 2008. An energy balance of the existing hut was made to detect optimization
potentials and to predict the necessary energy generating systems of the new building. In addition to energy supply, the environmental impacts of materials and processes were compared and evaluated with the help of Life Cycle Assessment. Although energy use will increase in the new building, mainly due to the installation of a wastewater purification system, total greenhouse gas emissions will decrease. M. Goymann et al., Environ. Sci. Technol., 2008, 42, 4060 – 4067.

**Sustainability as an emerging design criterion in nanoparticle synthesis and applications**

The precepts of green chemistry have been spreading since the mid-1990s, concomitant with advances in nanomaterial synthesis. Recently these two communities have begun to significantly converge. Nanomaterial synthesis groups are developing greener, more sustainable production methods, while nanoparticle application groups are exploring sustainable energy sources and environmental remediation as end goals. C.J. Murphy, J. Mater. Chem., 2008, 18, 2173 – 2176.

**Green energies and the environment**

Globally, buildings are responsible for approximately 40% of the total world annual energy consumption. Most of this energy is for the provision of lighting, heating, cooling, and air conditioning.Increasing awareness of the environmental impact of CO2 and NOx emissions and CFCs triggered a renewed interest in environmentally friendly cooling, and heating technologies. Under the 1997 Montreal Protocol, governments agreed to phase out chemicals used as refrigerants that have the potential to destroy stratospheric ozone. It was therefore considered desirable to reduce energy consumption and decrease the rate of depletion of world energy reserves and pollution of the environment. This article discusses a comprehensive review of energy sources, environment and sustainable development. This includes all the renewable energy technologies, energy efficiency systems, energy conservation scenarios, energy savings and other mitigation measures necessary to reduce climate change. A.M. Omer, Rene. Sust. Energy Rev. 2008, 12, 1789 – 1821.
Crops: a green approach toward self-assembled soft materials

To date, a wide range of industrial materials such as solvents, fuels, synthetic fibers, and chemical products are being manufactured from petroleum resources. However, rapid depletion of fossil and petroleum resources is encouraging current and future chemists to orient their research toward designing safer chemicals, products, and processes from renewable feedstock with an increased awareness of environmental and industrial impact. Advances in genetics, biotechnology, process chemistry, and engineering are leading to a new manufacturing concept for converting renewable biomass to valuable fuels and products, generally known as the biorefinery concept. The swift integration of crop-based materials synthesis and biorefinery manufacturing technologies offers the potential for new advances in sustainable energy alternatives and biomaterials that will lead to a new manufacturing paradigm. This Account presents a novel and emerging concept of generating various forms of soft materials from crops (an alternate feedstock). In future research, developing biobased soft materials will be a fascinating yet demanding practice, which will have direct impact on industrial applications as an economically viable alternative. Here we discuss some remarkable examples of glycolipids generated from industrial byproducts such as cashew nut shell liquid, which upon self-assembly produced soft nanoarchitectures including lipid nanotubes, twisted/helical nanofibers, low-molecular-weight gels, and liquid crystals. Synthetic methods applied to a “chiral pool” of carbohydrates using the selectivity of enzyme catalysis yield amphiphilic products derived from biobased feedstock including amygdalin, trehalose, and vitamin C. This has been achieved with a lipase-mediated regioselective synthetic procedure to obtain such amphiphiles in quantitative yields. Amygdalin amphiphiles showed unique gelation behavior in a broad range of solvents such as nonpolar hexanes to polar aqueous solutions. Importantly, an enzyme triggered drug-delivery model for hydrophobic drugs was demonstrated by using these supramolecularly assembled hydrogels. Following a similar biocatalytic approach, vitamin C amphiphiles were synthesized with different hydrocarbon chain lengths, and their ability to self-assemble into molecular gels and liquid crystals has been studied in detail. Such biobased soft materials were successfully used to develop novel organic–inorganic hybrid materials by in situ synthesis of metal nanoparticles. The self-assembled soft materials were characterized by several spectroscopic techniques, UV–vis, infrared, and fluorescence spectrophotometers, as well as microscopic methods including polarized optical, confocal, scanning, and transmission electron
microscopes, and thermal analysis. The molecular packing of the hierarchically assembled bilayer membranes was fully elucidated by X-ray analysis. We envision that the results summarized in this Account will encourage interdisciplinary collaboration between scientists in the fields of organic synthesis, soft materials research, and green chemistry to develop functional materials from underutilized crop-based renewable feedstock, with innovation driven both by material needs and environmentally benign design principles.


Conference information

1. 7th Green Chemistry Conference Barcelona, Spain, November 12-13, 2008
   http://www.iuct.net/chem/7/index.html

2. Advances in Green Science and Technology Atlanta, Georgia, USA, November 14-15, 2008
   http://www.enviroexpousa.com/

   http://www.aiche.org/Conferences/AnnualMeeting/index.asp

   owconfdets

5. ACHEMA 2009: 29th International Exhibition-Congress on Chemical Engineering, Environmental Protection and Biotechnology Frankfurt am Main, Germany, May 11-15, 2009
   http://www.achema.de

6. 5th International Conference on Renewable Resources & Biorefineries Ghent, Belgium, June 10-12, 2009
   http://www.rrbconference.com/

7. 2nd International Congress on Green Process Engineering, GPE 2009 Venice, Italy, June 14-17, 2009
   http://www.gpe-epic2009.org/