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Research breakthroughs

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Putting nano into paints – the green way

Nanoparticles are attracting a lot of interest as providing highly active and efficient sources of various, typically metal, additives for many consumer products. One of the concerns about this is that the current methods of producing nanoparticles of a metal such as silver are onerous and wasteful. Silver can be highly antimicrobial and can be used to stabilize various products against bacteria; its compounds have quite low human toxicity, good stability to heat and are not volatile although they are quite expensive. Using nanoparticulate silver should make it more efficient (higher particle surface area) and require smaller quantities. In a recent publication from groups in New York, an environmentally friendly chemistry approach to make paint doped with nano-silver is described. The approach took advantage of the natural drying process of the vegetable oil based binder in paint to both produce the silver nanoparticles (by reduction using free radicals) and disperse them in the paint. The resulting modified paints can be directly applied to various types of materials (wood, glass, steel, etc) as a strong biocidal coating.

Kumar et al., *Nat. Mater.*, **2008**, *7*, 236 – 241.

The preparation of nanoparticles using green chemistry principles rather than the traditional resource intensive, wasteful and often hazardous processes, is also the subject of other, more fundamental research work such as that recently reported by a group of researchers based in France. Their article describes the preparation of silver nanoparticles in water.

G. Zhang et al., *Chem. Mater.*, **2007**, *19*, 5821 – 5823.

Green chemistry for greener dyes

Dyes represent some of the greatest challenges for green chemistry. Many are derived from increasingly scare petroleum resources and may present serious problems at end-of-life, when typically contaminated waste streams need extensive treatment to make them safe and environmentally compatible. In many cases, however, the most troublesome step in the product lifecycle is the manufacturing, which can itself lead to large quantities of hazardous waste as well as being resource intensive.

In a joint publication from Bulgaria and Spain, a new greener route to styryl dyes described. These types of dyes are widely used in the photographic industry. By avoiding the use of solvents as process auxiliaries and by using energy-efficient microwave heating, both resource consumption and process wastes are reduced.

A. Vasilev et al., *Dyes Pigment.*, **2008**, *77*, 550 – 555.

Using peanut shells to capture waste metal

While the "food vs. fuel vs. feed" debate rages over the use of primary agricultural land and of food-quality products, we can avoid the controversy by using the agricultural food products that currently have little value. We have previously looked at crab shell-derived chitin and cashew nut-derived aromatic chemicals, in a recent article from Turkey, peanut shells are used to remove copper from wastewater. Copper is widely used in many industries including the manufacture of fertilizers, in paper mills and in metal planting; the copper-rich waste streams from such activities are harmful to marine systems. Peanut shells are naturally ionic and this property can be exploited to capture metal ions such as copper ions, although the process only works best under mildly acidic conditions.

H. Duygu Ozsoy et al., *Int. J. Enviorn. Pollut.*, **2007**, *31*, 125 – 134.

Self-cleaning fibers

The use of simple photo-catalysts that use sunlight to provide energy to clean various surfaces such as pavements and buildings is one of the areas likely to benefit from nanotechnology – if we can get the processing right and if we can make final material stable enough. In an interesting article from groups in Australia and Hong Kong, this method is applied to fibers such as wool. Keratin, a class of biological fibers proteins, can be chemically modified to enable it to bind anatase (titanium oxide) nanocrystals. This means that self-cleaning fibrous proteins such as wool can be produced by a relatively simple process.

W.A. Daoud et al., *Chem. Mater.*, **2008**, *20*, 1242 – 1244.

Sustainable deodorants

Greening personal care products is becoming a popular goal for many cosmetic companies, retailers and producers (see recent issue of Cosmetics and Toiletries, March 2008). These products invariable contain several different chemical substances, each providing a function such as binding, stabilization, and odor as well as more specific functions particular to the product type. Many of these chemical substances are petroleum derived and can involve substantial processing with associated resource consumption and process wastes. Deodorants commonly contain petroleum-derived glycols as but it has recently been proven that bio-derived propanediol, now being produced in large quantities for making new biopolymers, can be an effective alternative. The company Terra Naturals is

using this as part of it policy to "green" cosmetics.
A. Pichon, *Biofuels, Bioprod. Bioref.*, **2007**, *1*, 240.

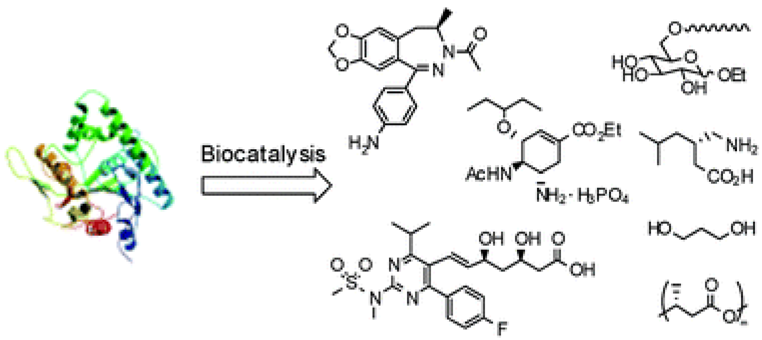
Detecting carbon dioxide

While so much public attention is focused on the danger of uncontrolled increases in the quantities of carbon dioxide in the atmosphere, we should also remember that carbon dioxide can be a valuable gas, for example, to enable accelerate food growth, to prolong the shelf life of fresh food, and, in its supercritical form, to decaffeinate coffee and produce the flavor for beers. In all cases, the detection and measurement of the gas is important – in greenhouses and workplaces as well as in natural environments. New carbon dioxide sensors with simple optical read-outs and with the flexibility to respond to a wide range of concentrations are needed. In a recent article from groups in Austria and Germany, a new carbon dioxide sensor is described which has adjustable sensitivity and good stability although not to photodegradation. The sensor is based on non-volatile ionic liquid solvents, which have been widely studied as greener alternatives to traditional volatile solvents.
S.M. Borisov et al., *Chem. Mater.*, **2007**, *19*, 6187 – 6194.

Catalysts with ionic tag and their use in ionic liquids

The concept of homogeneous supported catalysts has emerged as a useful alternative to homogeneous as well as heterogeneous catalysis, possibly combining positive aspects of both. Designing catalysts with respect to not only their catalytic activity but also their physical-chemical properties, appears to be a possible way towards sustainable chemical synthesis. Such tailored catalytic systems would ideally have high catalytic activities and some property enabling their efficient recycling. We reviewed the field of specifically designed ionic catalysts used mostly in ionic liquids.
R. Šebesta et al., *Green Chem.*, **2008**, *10*, 484 – 496.

Recent applications of biocatalysis in developing green chemistry for chemical synthesis at the industrial scale

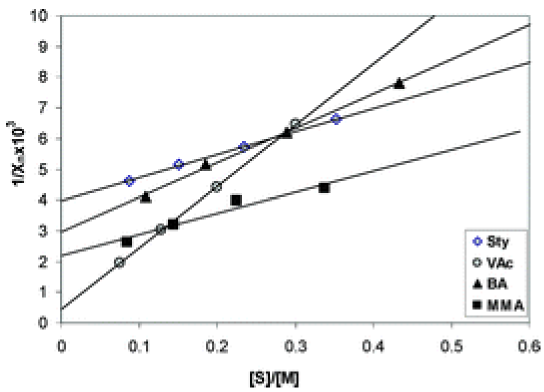


Application of the twelve principles of green chemistry can deliver higher efficiency and reduce the environmental burden during chemical synthesis. As a result of recent advances in genomics, proteomics and pathway engineering, biocatalysis is emerging as one of the greenest technologies. Enzymes are highly efficient with excellent regioselectivity and stereoselectivity. By conducting reactions in water under ambient reaction conditions, both the use of organic solvents and energy input are minimized.

N. Ran et al., *Green Chem.*, **2008**, *10*, 361 – 372.

Biodiesel: A green polymerization solvent

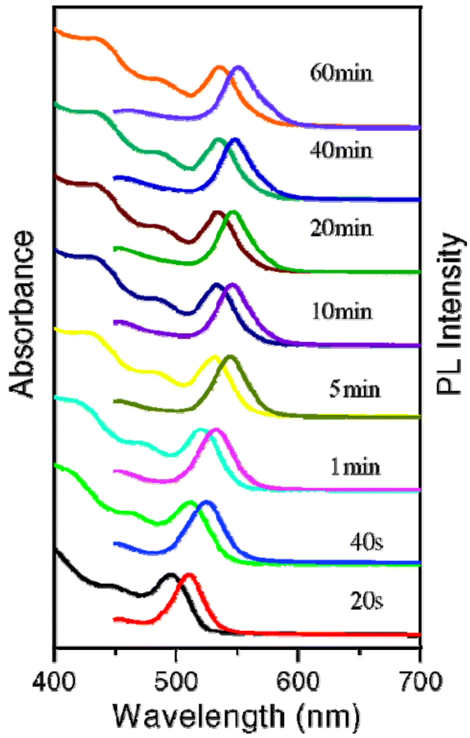
In an effort to use clean technologies, fatty acid methyl esters (FAME) produced from canola have been used as a polymerization solvent. Solution polymerizations of four commercially important monomers have been studied using FAME as a solvent. A series of methyl methacrylate (MMA), styrene (Sty), butyl acrylate (BA) and vinyl acetate (VAc) homopolymerizations in FAME were carried out at 60°C at different solvent concentrations. Chain transfer to solvent rate constants were obtained using the Mayo method. The transfer constants increased in the order: MMA < Sty < BA < VAc. Under the conditions studied, the MMA solution polymerization in FAME was observed to behave as a precipitation polymerization. The estimated chain transfer to solvent rate constants were employed in a polymerization simulator to predict the polymerization rates and



average molecular weights.

S. Salehpour et al., *Green Chem.*, **2008**, *10*, 321 – 326.

Green chemistry for large-scale synthesis of semiconductor quantum dots



Large-scale synthesis of semiconductor nanocrystals or quantum dots (QDs) with high concentration and high yield through simultaneously increasing the precursor concentration was introduced. This synthetic route conducted in diesel has produced gram-scale CdSe semiconductor quantum dots (In optimal scale-up synthetic condition, the one-pot yield of QDs is up to 9.6 g). The reaction has been conducted in open air and at relatively low temperature at 190−230°C in the absence of expensive organic phosphine ligands, aliphatic amine and octadecene, which is really green chemistry without high energy cost for high temperature reaction and unessential toxic chemicals except for Cd, which is the essential building block for QDs.

J.-H. Liu et al., *Langmuir*, **2008**, *24*, 5241 – 5244.

Synthesis and mechanism of particle- and flower-shaped ZnSe nanocrystals: Green chemical approaches toward green nanoproducts

A nontoxic, simple, cheap, and reproducible strategy, which meets the standard of green chemistry, is introduced for the synthesis of ZnSe nanoparticles and nanoflowers. The production of these green nanomaterials can be readily scaled up and performed directly at ambient condition without affecting their qualities. The experimental results show that the as-synthesized ZnSe nanoparticles and nanoflowers with a zinc blende structure have a narrow size distribution without

resorting to any postsynthetic size-selective procedure. A systematic study of the nanocrystal formation process indicates the following properties. (i) The amount of precursors plays a greater role in the determination of the nanoparticle size than other reaction parameters. Variation of this parameter allows us to tune the nanoparticle size in the high-temperature annealing process. This tunability is interpreted well by the growth kinetics. (ii) The limited ligand protection mechanism cannot be employed to explain the formation of our nanoflowers. Instead, a new growth mechanism is proposed. Upon heating at high temperature, a mononuclear Zn complex converts to a polynuclear Zn complex with multiple Zn atoms. Each Zn atom grows into one ZnSe nanoparticle after the injection of Se solution. These nanoparticles closely connect and thus look like nanoflowers.
Q. Dai et al., *J. Phys. Chem. C*, **2008**, *112*, 7567 – 7571.

Green synthesis applicable for industrial-scale preparation of efaproxiral sodium

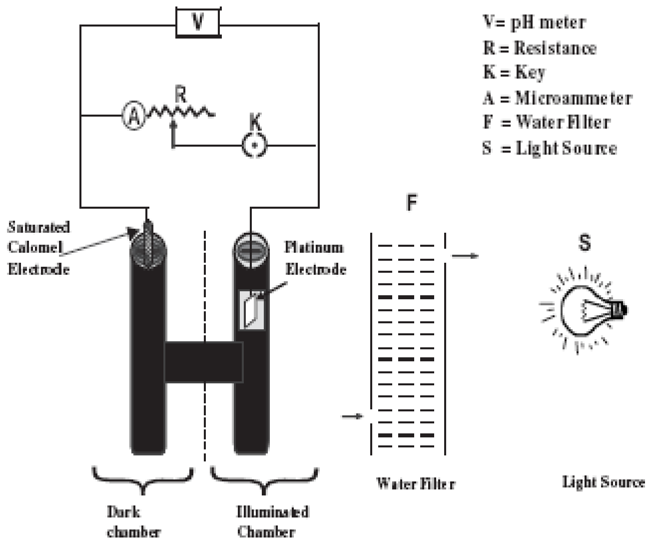
In this article we proposed a novel procedure for the synthesis of efaproxiral sodium, including two reaction steps, condensation, and O-alkylation. In the condensation step, a convenient method was adopted to eliminate the use of solvents, i.e., 4-hydroxyphenylacetic acid and 3,5-dimethylaniline were heated at 150-180°C for 3-5 h, and the reaction was successfully carried out. The yield of anilide in 4-hydroxyphenylacetic acid was 90-93%. In the O-alkylation step, the old circuitous process was avoided, and high-quality sodium salt was directly obtained with a yield of 90%. The final product of efaproxiral sodium was crystallized in water, yielding a new crystalline form containing a unique X-ray powder diffraction pattern with only one peak of 3.7° ± 0.2° in 2θ. The quality of the final product is high with a content of 99.51% according to high-performance liquid chromatographic detection. The present study provided a new environmentally friendly procedure for the preparation of efaproxiral sodium with high yield, low cost, and a short reaction pathway.
H. Shi et al., *Ind. Eng. Chem. Res.*, **2008**, *47*, 2861 – 2866.

Lysozyme-dextran core-shell nanogels prepared via a green process

A novel method has been developed for preparing nanogels with a lysozyme core and dextran shell. The method involves the Maillard dry-heat process and heat-gelation process. First, lysozyme-dextran conjugates were produced through the Maillard reaction. Then, the conjugate solution was heated above the denaturation temperature of lysozyme to produce nanogels. The nanogels are of spherical shape having a hydrodynamic diameter of about 200 nm and swelling ratio of about 30. The nanogel solutions are stable against long-term storage as well as changes in pH and ionic strength. Ibuprofen has been used as a drug model to study the electrostatic and hydrophobic interactions with these nanogels at different pH values. The study reveals that the nanogels are more suitable for loading protonated ibuprofen. We have verified that the knowledge of the formation mechanism of lysozyme-dextran nanogels can be applied to prepare other globular protein-dextran nanogels.

J. Li et al., *Langmuir*, **2008**, *24*, 3486 – 3492.

Photogalvanic cell: A new approach for green and sustainable chemistry



A comparative study of anionic, cationic, and nonionic surfactants on photogalvanic effect was studied in a photogalvanic cell containing dioctyl sulfosuccinate (DSS), cetyltrimethylammonium bromide (CTAB), and TritonX-100 as surfactants, rhodamine 6G as photosensitizer, and oxalic acid as reductant. Observed values of photopotential, photocurrent, fill factor, conversion efficiency, and storage capacity for DSS–rhodamine 6G–oxalic acid system was, respectively, 880.0mV, 200μA, 0.41, 0.86%, and 131.0min, for CTAB–rhodamine 6G–oxalic acid system,

414.0mV, 90.0μA, 0.45, 0.24%, and 68.0min, and for TritonX-100–rhodamine 6G–oxalic acid system, 672.0mV, 165.0μA, 0.38, 0.55%, and 96.0min. The effects of different parameters on electrical output of the cell were observed and a tentative mechanism has also been proposed for the generation of photocurrent in photogalvanic cell.
K.R. Genwa et al., *Sol. Energy Mat. Sol. Cells*, **2008**, *92*, 522 – 529.

Superheated water chromatography – A green technology for the future

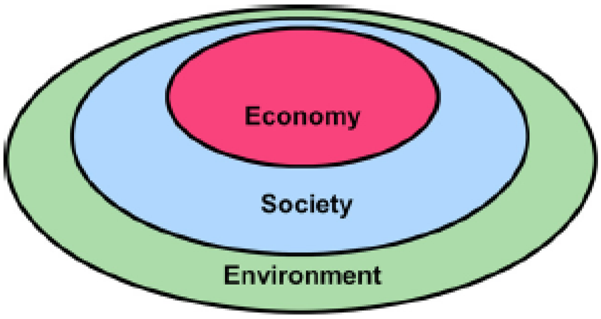
Reversed phase liquid chromatography using superheated water as the mobile phase, at temperatures between 100 and 250°C, offers a number of advantages for the analyst. It is an environmentally clean solvent, reducing solvent usage and disposal costs. It has advantages in detection, allowing UV spectra to be monitored down to short wavelengths, as well as a compatibility with universal flame ionization detection and mass spectroscopy. By employing deuterium oxide as the eluent, solvent free NMR spectra can be measured. The development of newer more thermally stable stationary phases, including hybrid phases, have expanded the analytes that can be examined and these now range from alkylbenzenes, phenols, alkyl aryl ketones and a number of pharmaceuticals to carboxylic acids, amino acids, and carbohydrates. Very few compounds have been found to be unstable during the analysis. The separation methods can be directly coupled to superheated water extraction providing a totally solvent free system for sample extraction and analysis.
R.M. Smith, *J. Chromatogr. A*, **2008**, *1184*, 441 – 455.

Green electronics through legislation and lead free soldering

Management of used electrical and electronic equipment (EEE) is becoming a major issue as each year around 20 to 50 million tonnes of electronic waste (e-waste) is generated worldwide. EEE contains over 1000 materials of which lead (Pb) has been one of the targets of the regulators forcing manufacturers to adopt lead free products. Industry has come up with several lead free solders with preference given to alloys containing tin, silver, and copper but there is no ‚drop-in' substitute to leaded solder. Issues with lead free solders such as temperature, intermetallics, tin whisker, tin pest, and reliability are yet to be resolved. The paper investigated the contribution of lead free soldering to green electronics in a holistic way. Global lead free movement has reached a point of no return. However, it is necessary to make sure that life span of EEE is not shortened thereby resulting in an unforeseen increase in e-waste or problem shifting does not occur by shifting a problem from one life cycle to another or from one category/media to another.

S. Heart, *Clean*, **2008**, *36*, 145-151.

Frontiers in green chemistry: Meeting the grand challenges for sustainability in R&D and manufacturing



Green Chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment. It is an innovative, non-regulatory, economically driven approach toward sustainability. The unequivocal value of Green Chemistry to the business and to the environment is illustrated through industrial examples. Green Chemistry must be recognized for its ability to address sustainability at the molecular level. By designing for sustainability at this fundamental level, Green Chemistry challenges innovators to design and utilize matter and energy in a way that increases performance and value while protecting human health and the environment. The principles of Green Chemistry today need to become the core for tomorrow's chemistry, integrating sustainability into science and its innovations.

J.B. Manley et al., *J. Clean Prod.*, **2008**, *16*, 743 –750.

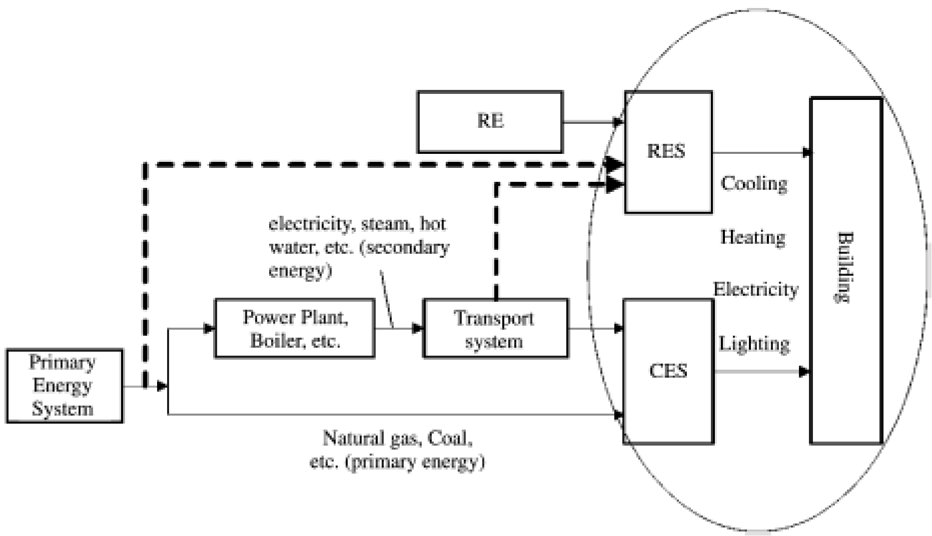
The 24 Principles of green engineering and green chemistry: “IMPROVEMENTS PRODUCTIVELY”

Samantha Tang, Richard Bourne, Richard Smith and Martyn Poliakoff suggest a condensed 24 Principles of Green Chemistry and Green Engineering, with the mnemonic “IMPROVEMENTS PRODUCTIVELY”

Principles of Green Engineering	Principles of Green Chemistry
I - Inherently non-hazardous and safe	**P** - Prevent wastes
M - Minimize material diversity	**R** - Renewable materials
P - Prevention instead of treatment	**O** - Omit derivatization steps
R - Renewable material and energy inputs	**D** - Degradable chemical products
O - Output-led design	**U** - Use safe synthetic methods
V - Very simple	**C** - Catalytic reagents
E - Efficient use of mass, energy, space & time	**T** - Temperature, Pressure ambient
M - Meet the need	**I** - In-Process Monitoring
E - Easy to separate by design	**V** - Very few auxiliary substances
N - Networks for exchange of local mass & energy	**E** - E-factor, maximize feed in product
T - Test the life cycle of the design	**L** - Low toxicity of chemical products
S - Sustainability throughout product life cycle	**Y** - Yes it's safe

S.Y. Tang et al., *Green Chem.*, **2008**, *10*, 268 – 269.

Renewable energy utilization evaluation method in green buildings

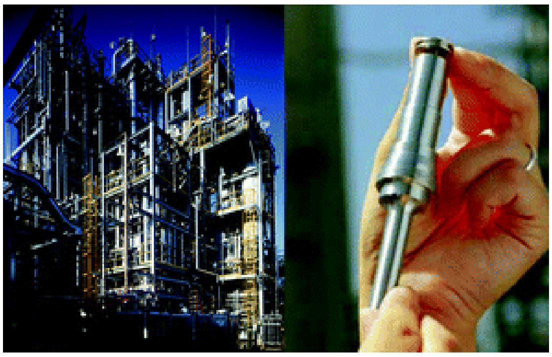


Utilizing renewable energy (RE) is an important part of the design and development of green buildings. However, it is unreasonable to assess renewable energy utilization (REU) only with the net ratio of end-use energy provided by the renewable energy system to a building’s total energy consumption, but ignoring the system efficiency of REU with the necessary extra conventional energy consumption, such as electricity. In this paper, the energy quality coefficient

(EQC) is introduced to describe the quality of energy, while the energy conversion coefficient (ECC) is applied to evaluate energy system efficiency. The indexes and their expressions were developed based on energy analysis. Based on these two indexes, an effective substitution ratio (ESR) was developed for the evaluation of REU. Furthermore, the ESR of utilizing RE to substitute for single type and multiple types of conventional energy is discussed. Finally, case studies were conducted and some conclusions were drawn from the results for application of RE in buildings.

X. Chunhai et al., *Renew. Energy*, **2008**, *33*, 883 – 886.

Applications of ionic liquids in the chemical industry



In contrast to a recently expressed, and widely cited, view that "Ionic liquids are starting to leave academic labs and find their way into a wide variety of industrial applications", we demonstrate in this critical review that there have been parallel and collaborative exchanges between academic research and industrial developments since the materials were first reported in 1914 (148 references)

N.V. Plechkova et al., *Chem. Soc. Rev.*, **2008**, *37*, 123 – 150.

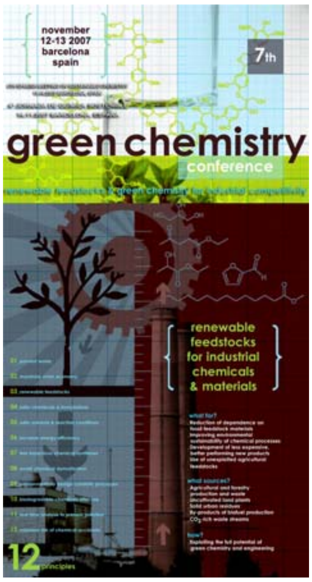
Conference information

1. Gordon Research Conference on Green Chemistry
   Lewiston, Maine, USA, August 3-8, 2008
   http://www.grc.org/programs.aspx?year=2008&program=green
2. UConn GSSPC symposium: Transitioning into Green Chemistry
   Philadelphia, PA, USA, August 17-21, 2008
   http://chemistry.uconn.edu/gsspc/index.html
3. 2nd International IUPAC Conference on Green Chemistry

Moscow, Russia, September 14-20, 2008
http://www.icgc2008.ru/

4. Green Solvents – Progress in Science and Application
http://events.dechema.de/en/Events/Green%2BSolvents%2B_%2BProgress%2Bin%2BScience%2Band%2BApplication-p-123244.html

5. 7th Green Chemistry Conference
Barcelona, Spain, November 12-13, 2008
http://www.iuct.net/chem/7/index.html



Google map for green chemists

As part of their Green Education Materials for Green Chemists, the University of Oregon has created a google map on the worldwide green chemistry community. You can add your details at http://greenchem.uoregon.edu/Pages/MapDisplay.php