Green & Sustainable Chemical Communication 綠色與永續化學通訊 2014年7月

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引言

這幾個月有兩則與「錯誤」有關的大新聞格外引人注目。其一為 IBM Almanden 研究中心研發高強度物質的團隊，因進行反應時少加了一個成份，製造出全新的可分解熱固性塑膠。傳統的熱固性塑膠耐高溫、化學穩定性高，多用於電子、汽車、航太用品。因非常穩定，回收不易，使用後只能棄置於掩埋場。此次發現能在強酸條件下變回單體的熱固性塑膠，實為一大突破。IBM 的研究員 Jeannette García 在少加了成份後，看到產物緊緊地卡在瓶底，沒有把瓶子丟掉重作實驗，反而是想盡辦法取出(最後以槌子解決)，研究到底做出了什麼產物及其各項性質，因此開啟熱固性塑膠新的一頁，可謂是美麗的錯誤。另一個錯誤就沒有這麼美麗了，UCLA Patrick Harran 教授的研究助理 Sheharbano Sangii，2008 年因取用在空氣中會自燃的 butyl lithium，不慎造成失火身亡。Harran 教授因此被告的案件在今年總算告一段落，除了須支付一萬美元的罰款，並且要在五年內於學校與醫院履行多項服務。如果五年後確認緩起訴書中的所有項目皆如實履行，洛杉磯檢調單位才會放棄起訴。

本期通訊除照例提供新聞與回顧論文的摘要，另有中興大學化學系李進發教授的專訪。李教授自 2008 年進入興大後，陸續發表利用銅和鐵等過渡金屬進行催化反應的研究成果。這兩種金屬毒性低、容易取得，因此他的表現受到多方矚目，得到國內外的獎項如傑出年輕金玉學者(2011)、Asian Core Program Lectureship Award(2012, 2013)、傑出青年化學獎(2013)、Thieme Chemistry Journal Award(2014)、中興大學興大之光(2011)與懷璧獎(2014)等。感謝李教授百忙之中回覆甘魯生教授的提問，讓我們對他的工作進展有進一步的瞭解。

目錄

Webinar

Endangered Elements: Critical Materials in the Supply Chain

Thursday, June 19, 2014 @ 2:00pm ET

To view visit https://www.youtube.com/watch?v=Zlht1h15q_0

The periodic table of elements is under siege. Modern materials use an ever-increasing number of elements, and some supplies are running short. This is presenting a number of supply chain risks: demand shocks due to new uses, supply uncertainties because of geographically concentrated production and geo-political risks, and reliance on co-production. Tune in to this special broadcast LIVE from the ACS Green Chemistry and Engineering Conference to discover how chemists are working to tackle these problems and showcase how innovators are creating chemistry that is resilient and conflict-free.

Conferences

1. **248th ACS National Meeting & Exposition**
   Chemistry & Global Stewardship
   August 10-14, 2014
   San Francisco, California, USA
   http://www.acs.org/content/acs/en/meetings/fall-2014.html

2. **5th IUPAC International Conference on Green Chemistry**
   August 17-21, 2014
   Durban, South Africa
   http://www.saci.co.za/greenchem2014/

Award

ACS Award for Affordable Green Chemistry

Arthur Ragauskas has worked on transforming biomass to fuels and materials such as nanocellulose composites and films. He is currently Georgia Tech's team leader at the Department of Energy's Bio-energy Science Center, based at Oak Ridge National Laboratory. Working with the center's investigators, he has explored the fundamentals of biomass recalcitrance, taking advantage of advances in imaging technology including Förster resonance energy transfer, time-of-flight secondary ion mass spectrometry, and matrix-assisted laser desorption/ionization mass spectrometry to analyze the surface chemistry of biomass during pretreatment and enzymatic deconstruction. His team, which includes 27 graduate students, also develops NMR techniques to characterize chemical conversions via catalysis.

http://cen.acs.org/articles/92/i5/ACS-Award-Affordable-Green-Chemistry.html

http://www.chemistry.gatech.edu/faculty/Ragauskas/

http://ipst.gatech.edu/faculty/ragauskas_art/bio_ragauskas_art.html

News

Lab Safety

Chemist Reaches Agreement with Prosecutors over Lab Death

Researchers express hope that UCLA case will spur safety improvements.

According to the terms of the agreement, approved today by Los Angeles County Superior Court Judge George Lomeli, Harran will pay US$10,000 to the burns unit where Sangji was treated; develop lab-safety training tools as part of an organic-chemistry summer class that he will teach for five years to underprivileged students about to enter university; speak to incoming UCLA students about the importance of lab safety; and conduct 800 hours of non-teaching community service at a hospital.

Neal Langerman, head of Advanced Chemical Safety in San Diego, California, would have preferred the settlement to require Harran to interact with members of the research community — for instance, by requiring him to speak to other chemists about his experience. He also says it is not clear who will oversee Harran's development of instructional materials on lab safety.

http://www.nature.com/news/chemist-reaches-agreement-with-prosecutors-over-lab-death-1.15444

Related links:
Patrick Harran and L.A. District Attorney Reach Deferred Prosecution Deal in Sheri Sangji Case
http://cen.acs.org/articles/92/web/2014/06/Patrick-Harran-L-District-Attorney.html
甘魯生,『實驗室安全』事件後續, 化學, 70, 193 (2012).
http://proj3.sinica.edu.tw/~chem/servxx6/files/paper_13965_1381212186.pdf
甘魯生,實驗室意外和實驗室安全, 化學, 68, 313-319 (2010).
http://proj3.sinica.edu.tw/~chem/servxx6/files/paper_13652_1292205748.pdf

Catalyst

Natural Gas Gets an Upgrade

Fuels & Chemicals: Main-group metals selectively oxidize alkanes to make commodity alcohol esters

A research team including Brian G. Hashiguchi and Roy A. Periana of Scripps Research Institute Florida and Daniel H. Ess of Brigham Young University has discovered that inexpensive main-group thallium and lead complexes work well at converting the typically unreactive alkanes in natural gas into alcohol esters (*Science* **2014**, DOI: 10.1126/science.1249357). The new chemistry operates more selectively and at much lower temperatures than conventional natural gas reforming methods that operate at about 900 °C.
http://cen.acs.org/articles/92/i11/Natural-Gas-Upgrade.html

Pair of Catalysts Builds Chiral Rings Using Visible Light

Photochemistry: Compact fluorescent bulbs power production of desirable building blocks featuring delicate bonds

By combining two catalysts, researchers have used photochemistry to build enantiomerically enriched rings in high yields. The advance could add to the tool kit for building motifs present in agrochemicals and pharmaceuticals.
http://cen.acs.org/articles/92/i17/Pair-Catalysts-Builds-Chiral-Rings.html

Carbon Capture

Carbon-Capture Breakthrough at Wellheads

Porous material polymerizes carbon dioxide at natural gas wellheads

Rice University scientists James Tour and Chih-Chau Hwang invent a porous material that pulls only carbon dioxide molecules from flowing natural gas and polymerizes them while under pressure naturally provided by the well. When the pressure is

released, the carbon dioxide spontaneously depolymerizes and frees the sorbent material to collect more. All of this work is in ambient temperatures, unlike current high-temperature capture technologies that use up a significant portion of the energy being produced. The recyclable material absorbs 82 percent of its weight in carbon dioxide.

http://www.chemeurope.com/en/news/148079/rice-university-produces-carbon-capture-breakthrough.html

Cross-Linked Polymer Captures CO_2

Carbon Capture: The low-cost material can effectively absorb the greenhouse gas, even under wet and acidic conditions like those found in power-plant gas streams

A material made of cross-linked benzene acts like a stiff sponge, swelling as it absorbs carbon dioxide. Unlike other carbon-capturing materials, it retains most of its absorbent ability under wet or acidic conditions (*J. Am. Chem. Soc.* **2014**, DOI: 10.1021/ja5031968). The polymer has one major advantage: It's cheap to make. The main disadvantage is that its capacity surpasses the other carbon-capture materials only at high pressures.

http://cen.acs.org/articles/92/web/2014/06/Cross-Linked-Polymer-Captures-CO2.html

Microbial Reactor Could Help Capture Carbon Sustainably

Electrochemical cell could lower cost of sequestering carbon dioxide as carbonate minerals

A new reactor powered in part by microbes can generate hydrogen gas while producing solutions of hydrochloric acid and sodium hydroxide for use in carbon dioxide sequestration (*Environ. Sci. Technol. Lett*. **2014**, DOI: 10.1021/ez500073q). The reactor's developers think the device could lower the cost of mineral sequestration, a method of that converts CO_2 into solid carbonate minerals by reacting the gas with natural deposits of silicate minerals. In nature this reaction occurs very slowly, but acid and base treatment steps can enhance the rate of carbonate formation.

http://cen.acs.org/articles/92/web/2014/04/Microbial-Reactor-Help-Capture-Carbon.html

Fuel & Energy Storage

Electrochemistry: Catalysis at the Boundaries

Copper-based materials have been found that efficiently convert carbon monoxide and water to ethanol using electricity. The discovery is a major advance towards storing renewable energy in the form of a liquid fuel.

http://www.nature.com/nature/journal/v508/n7497/full/nature13226.html

A Molecular Approach to Solar Power

Switchable material could harness the power of the sun — even when it's not shining.

The problem with solar power is that sometimes the sun doesn't shine. Now a team at MIT and Harvard University has come up with an ingenious workaround — a material that can absorb the sun's heat and store that energy in chemical form, ready to be released again on demand. The principle is simple: Some molecules, known as photoswitches, can assume either of two different shapes, as if they had a hinge in the middle. Exposing them to sunlight causes them to absorb energy and jump from one configuration to the other, which is then stable for long periods of time. These photoswitches can be triggered to return to the other configuration by applying a small jolt of heat, light, or electricity — and when they relax, they give off heat. In effect, they behave as rechargeable thermal batteries: taking in energy from the sun, storing it indefinitely, and then releasing it on demand.

http://newsoffice.mit.edu/2014/molecular-approach-to-solar-power

The Rechargeable Revolution: A Better Battery

Chemists are reinventing rechargeable cells to drive down costs and boost capacity.

In 2012, the US Joint Center for Energy Storage Research won US$120 million from the US Department of Energy to take a leap beyond Li-ion technology. Its stated goal was to make cells that, when scaled up to the sort of commercial battery packs used in electric cars, would be five times more energy dense than the standard of the day, and five times cheaper, in just five years. This news feature from the Nature magazine covers the recent advances in the search of rechargeable batteries.

http://www.nature.com/news/the-rechargeable-revolution-a-better-battery-1.14815

Trees Go High-Tech

Process turns cellulose into energy storage devices

OSU chemists have found that cellulose – the most abundant organic polymer on Earth and a key component of trees – can be heated in a furnace in the presence of

ammonia, and turned into the building blocks for supercapacitors.
http://www.chemeurope.com/en/news/147759/trees-go-high-tech.html

Polymer

Ball Mill Grinds Monomers into Polymer

Polymer Chemistry: Chemists use ball-milling to synthesize the conductive polymer poly(phenylenevinylene) without solvent

Smashing compounds together to get them to polymerize sounds more like desperation than effective organic chemistry. But chemists Timothy M. Swager of Massachusetts Institute of Technology and Jens B. Ravnsbæk, now of Aarhus University, in Denmark, have demonstrated that the technique works. They polymerized poly(phenylenevinylene) (PPV)—a conductive polymer used in organic light-emitting diodes—in minutes inside a ball mill, which grinds the reactants together (*ACS Macro Lett*. **2014**, DOI: 10.1021/mz500098r). They say the process is fast, requires no solvent, and yields more consistent chain lengths than wet-chemistry synthesis.
http://cen.acs.org/articles/92/web/2014/03/Ball-Mill-Grinds-Monomers-Polymer.html

Thermosets Built to Break Down

Polymers: Novel reaction creates strong plastics that can be unzipped with acid

Now, thanks to a new poly-merization reaction, chemists have made thermosets that can be returned to their constituent diamine monomers via exposure to low pH (*Science***2014**, DOI: 10.1126/science.1251484).A team led by Jeannette M. García and James L. Hed-rick of the IBM Almaden Research Center developed the reaction, which condenses a diamine monomer with paraformaldehyde. At low temperature, the reaction forms a hemiaminal dynamic covalent network. Turn up the heat, and this material will cyclize to form a poly(hexahydrotriazine).
http://cen.acs.org/articles/92/i20/Thermosets-Built-Break-Down.html

Toxicity

Down the Drain Doesn't Mean They're Gone

Pollution: Chemicals in consumer products can end up deep in fields fertilized with sewage sludge

Now, researchers have found that compounds in consumer products that go down the drain can move downward through soil after land is fertilized with treated

sewage sludge, says a federally funded study from the U.S. Geological Survey and Colorado State University, Pueblo (*J. Am. Water Resour. Assoc*. **2014**, DOI: 10.1111/jawr.12163).
http://cen.acs.org/articles/92/i20/Down-Drain-Doesnt-Mean-re.html

Ionic Liquids Could Enhance Spread of Antibiotic Resistance Genes

Green Chemistry: One of the alternative solvents increases the permeability of bacteria cell membranes, helping resistance genes to jump from microbe to microbe

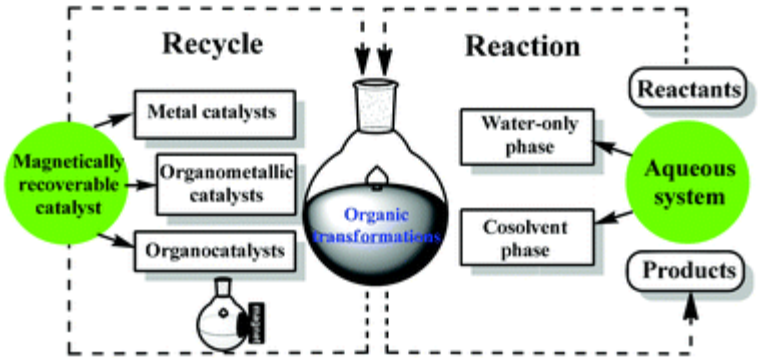
Some researchers in the field of green and sustainable chemistry have proposed replacing volatile organic solvents in industrial reactions with a class of solvents called ionic liquids. Most of these organic salts are not volatile, so they have been touted as a safe, environmentally friendly alternative to conventional solvents. But a new study shows that they could create problems of their own when released into the environment. Chinese researchers report that one ionic liquid helps bacteria share an antibiotic resistance gene, causing the gene to proliferate among the microbes (*Environ. Sci. Tech. Lett*., DOI: 10.1021/ez500103v).
http://cen.acs.org/articles/92/web/2014/04/Ionic-Liquids-Enhance-Spread-Antibiotic.html

Review

Catalysis

Magnetically Recoverable Nanoparticles as Efficient Catalysts for Organic Transformations in Aqueous Medium

Green Chem., **2014**, Advance Article **DOI:** 10.1039/C4GC00458B

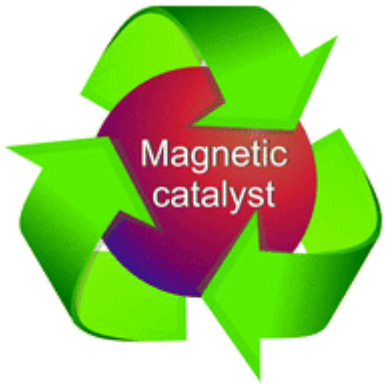


Development of magnetic nanoparticles (MNPs) for use as supports and exploration of their applications in aqueous catalysis represent an important branch of green chemistry as they enable environmentally friendly and sustainable catalytic processes. Besides the significant merit of easily recovering magnetic nanoparticles from reaction systems, various strategies through surface modification, grafting and self-assembly offer a broad range of approaches for constructing magnetically recoverable heterogeneous catalysts. In this review, we focus on the green catalytic processes and summarize recent advances in organic transformations catalyzed by magnetically recoverable catalysts (MRCs). This paper is divided into two main parts: the first part provides background information on the general preparation, modifications, and characterization, where the modifications of various magnetic nanoparticles through coating with silica, carbon, metal, or polymer are also presented. The second part provides a basic outline of aqueous catalysis based on water-only or water-and-organic solvent cosolvent systems, in which numerous types of organic transformations are catalyzed by magnetically recoverable catalysts. Lastly, perspectives for further development of magnetically recoverable heterogeneous catalysts in aqueous catalysis are addressed.

Magnetic Nanomaterials in Catalysis: Advanced Catalysts for Magnetic Separation and Beyond

Green Chem., **2014**, *16*, 2906–2933 **DOI:** 10.1039/C4GC00164H

While magnetic separation techniques have long been in use, intensive research into superparamagnetic nanomaterials has accelerated the development of magnetically recoverable catalysts. Preparation techniques are currently undergoing rapid development and magnetic separation has been studied to facilitate the handling and recovery of enzyme, organo-, metal complex-, and nanoparticle-catalysts. In this article, we emphasize the preparation of support materials, because the choice of the correct support and the immobilization strategy are of primary importance in the development of high-quality magnetically recoverable catalysts. We summarize the representative methods for the synthesis of well-defined uncoated and coated magnetic nanomaterials. Recent scientific progress on the preparation of surface-modified magnetic nanomaterials and the most common synthetic approaches to attach or immobilize non-magnetic catalytic active phases onto magnetic nanomaterials were discussed. Moreover, better control and understanding of the magnetic properties is now an essential tool not only in selecting the best preparation route for recoverable catalysts, but also for designing reactors (e.g., magnetic fluidized-bed reactors) and for developing magnetic field-driven technologies (e.g., changes in the catalytic output operating under an applied magnetic field).



Fast-Growing Field of Magnetically Recyclable Nanocatalysts

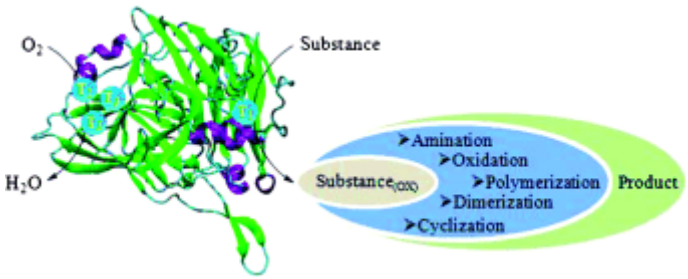
Chem. Rev., Article ASAP **DOI:** 10.1021/cr500134h

In this review, we briefly summarize the basic concepts and seminal studies of magnetically recoverable catalysts; then we highlight the new breakthroughs and trends in the area that have most recently appeared until 2014.

Laccase and Laccase-Mediated Systems in the Synthesis of Organic Compounds

Adv. Synth. Catal., **2014**, *356*, 897–927 **DOI:** 10.1002/adsc.201300960

Laccase, a blue multicopper oxidase, has recently received considerable attention because of its usefulness in oxidizing phenolic and non-phenolic compounds, as well as its suitability for organic synthesis, environmental pollutant treatment, and other biotechnological applications. This review covers recent studies on the structural properties, occurrence, reaction mechanisms, redox mediators of laccases and their application in organic synthesis procedures, such as dimerization, polymerization, oxidation, and amination. We also present a brief discussion on laccase activity in non-aqueous media. Given that the development of green protocols for the synthesis of pure compounds is one of the main goals of sustainable chemistry, the exploitation of laccases is expected to remain one of the most popular directions in future biocatalysis research.



Carbocatalysis by Graphene-Based Materials

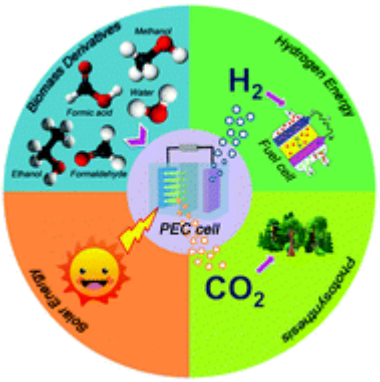
Chem. Rev., **2014**, *114*, 6179–6212 **DOI:** 10.1021/cr4007347

In the present review, we will focus on the use of graphene (G) and G-based materials (G-mat) as carbocatalysts. While there are many different types of carbon materials including amorphous and diamond NPs, herein we will deal with applications of 2D G-mat as carbocatalysts. The main purpose of the present review is to show the advantages and possibilities that G-mat offer in catalysis due to their 2D morphology and to the possibility of introducing heteroatoms and functional groups on the G sheet in such a way that they can act as catalytic centers. Our review covers the chemical literature on the use of G as catalyst or support up to end of 2013.

Biomass and CO_2 Related

Photoelectrochemical Hydrogen Production from Biomass Derivatives and Water

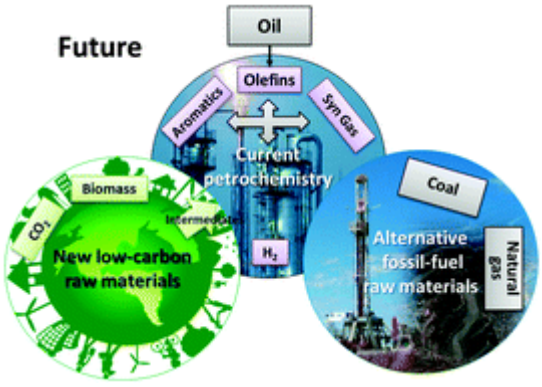
Chem. Soc. Rev., **2014**, Advance Article **DOI:** 10.1039/C3CS60392J



Hydrogen, a clean energy carrier with high energy capacity, is a very promising candidate as a primary energy source for the future. Photoelectrochemical (PEC) hydrogen production from renewable biomass derivatives and water is one of the most promising approaches to producing green chemical fuel. Compared to water splitting, hydrogen production from renewable biomass derivatives and water through a PEC process is more efficient from the viewpoint of thermodynamics. Additionally, the carbon dioxide formed can be re-transformed into carbohydrates via photosynthesis in plants. In this review, we focus on the development of photoanodes and systems for PEC hydrogen production from water and renewable biomass derivatives, such as methanol, ethanol, glycerol and sugars. We also discuss the future challenges and opportunities for the design of the state-of-the-art photoanodes and PEC systems for hydrogen production from biomass derivatives and water.

Catalysis for Biomass and CO_2 Use through Solar Energy: Opening New Scenarios for a Sustainable and Low-Carbon Chemical Production

Chem. Soc. Rev., **2014**, Advance Article **DOI:** 10.1039/C3CS60396B



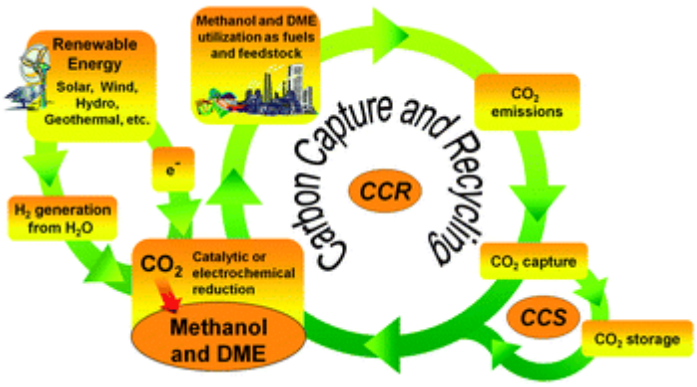
The use of biomass, bio-waste and CO_2 derived raw materials, the latter synthesized using H_2 produced using renewable energy sources, opens new scenarios to develop a sustainable and low carbon chemical production, particularly in regions such as Europe lacking in other resources. This tutorial review discusses first this new scenario with the aim to point out, between the different possible options, those more relevant to enable this new future scenario for the chemical production, commenting in particular the different drivers (economic, technological and strategic,

environmental and sustainability and socio-political) which guide the selection. The case of the use of non-fossil fuel based raw materials for the sustainable production of light olefins is discussed in more detail, but the production of other olefins and polyolefins, of drop-in intermediates and other platform molecules are also analysed. The final part discusses the role of catalysis in establishing this new scenario, summarizing the development of catalysts with respect to industrial targets, for (i) the production of light olefins by catalytic dehydration of ethanol and by CO_2 conversion via FTO process, (ii) the catalytic synthesis of butadiene from ethanol, butanol and butanediols, and (iii) the catalytic synthesis of HMF and its conversion to 2,5-FDCA, adipic acid, caprolactam and 1,6-hexanediol.

Recycling of Carbon Dioxide to Methanol and Derived Products – Closing the Loop

Chem. Soc. Rev., **2014**, Advance Article **DOI:** 10.1039/C4CS00122B

Starting with coal, followed by petroleum oil and natural gas, the utilization of fossil fuels has allowed the fast and unprecedented development of human society. However, the burning of these resources in ever increasing pace is accompanied by large amounts of anthropogenic CO_2 emissions, which are outpacing the natural carbon cycle, causing adverse global environmental changes, the full extent of which is still unclear. Even through fossil fuels are still abundant, they are nevertheless limited and will, in time, be depleted. Chemical recycling of CO_2 to renewable fuels and materials, primarily methanol, offers a powerful alternative to tackle both issues, that is, global climate change and fossil fuel depletion. The energy needed for the reduction of CO_2 can come from any renewable energy source such as solar and wind. Methanol, the simplest C_1 liquid product that can be easily obtained from any carbon source, including biomass and CO_2, has been proposed as a key component of such an anthropogenic carbon cycle in the framework of a "Methanol Economy". Methanol itself is an excellent fuel for internal combustion engines, fuel cells, stoves, etc. Its dehydration product, dimethyl ether, is a diesel fuel and liquefied petroleum gas (LPG) substitute. Furthermore, methanol can be transformed to ethylene, propylene and most of the petrochemical products currently obtained from fossil fuels. The conversion of CO_2 to methanol is discussed in detail in this review.



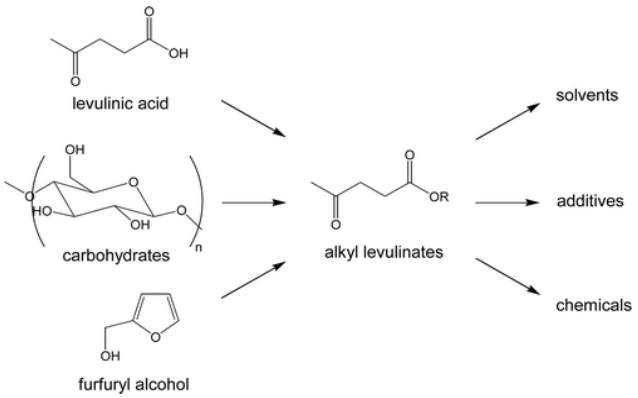
Always Look on the "Light" Side of Life: Sustainable Carbon Aerogels

ChemSusChem, **2014**, *7*, 670–689 **DOI:**10.1002/cssc.201300961

The production of carbon aerogels based on the conversion of inexpensive and abundant precursors using environmentally friendly processes is a highly attractive subject in materials chemistry today. This article reviews the latest developments regarding the rapidly developing field of carbonaceous aerogels prepared from biomass and biomass-derived precursors, highlighting exciting and innovative approaches to green, sustainable nanomaterial synthesis. A review of the state-of-the-art technologies will be provided with a specific focus on two complimentary synthetic approaches developed upon the principles of green chemistry. These carbonaceous aerogel synthesis strategies, namely the Starbon and carbogel approaches, can be regarded as "top-down" and "bottom-up" strategies, respectively. The structural properties can be easily tailored by controlling synthetic parameters such as the precursor selection and concentration, the drying technique employed and post-synthesis temperature annealing. In addition to these parameters, the behavior of these sustainable carbon aerogel platforms in a variety of environmental and energy-related applications will also be discussed, including water remediation and fuel cell chemistry (i.e., the oxygen reduction reaction). This review reveals the fascinating variety of highly porous, versatile, nanostructured, and functional carbon-based aerogels accessible through the highlighted sustainable synthetic platforms.

Synthesis and Applications of Alkyl Levulinates

ACS Sustainable Chem. Eng., **2014**, *2*, 1338–1352 **DOI:** 10.1021/sc500082n



Alkyl levulinates are biobased chemicals having a strong potential to be used in various applications, substituting current chemicals produced from petro-chemical routes. Dedicated literature has considerably increased in the past five years. This review describes state-of-the-art preparation routes and their main application fields. Alkyl levulinates are obtained in high yields and selectivities from simple biomass-derived products like levulinic acid or furfuryl alcohol. They are also obtained directly from lignocellulosic resources with generally limited yields. In all cases, the transformation needs a catalyst. Current efforts are now performed with developing efficient and recyclable catalysts. Alkyl levulinates found applications as

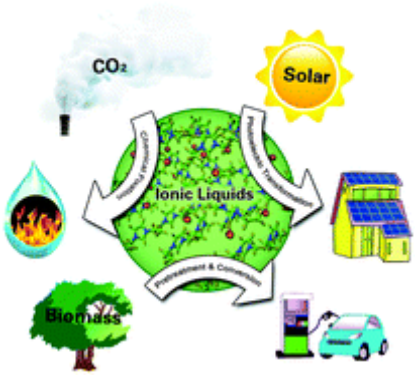
solvents and additives as well as in the area of chemical synthesis. The development of new preparation routes and applications of alkyl levulinates are contributing to future greener and sustainable processes.

Ionic Liquid

Ionic Liquid-Based Green Processes for Energy Production

Chem. Soc. Rev., **2014**, Advance Article **DOI:** 10.1039/C3CS60409H

To mitigate the growing pressure on resource depletion and environment degradation, the development of green processes for the production of renewable energy is highly required. As a class of novel and promising media, ionic liquids (ILs) have shown infusive potential applications in energy production. Aiming to offer a critical overview regarding the new challenges and opportunities of ILs for developing green processes of renewable energy, this article emphasizes the role of ILs as catalysts, solvents, or electrolytes in three broadly interesting energy production processes from renewable resources, such as CO_2 conversion to fuels and fuel additives, biomass pretreatment and conversion to biofuels, as well as solar energy and energy storage. It is expected that this article will stimulate a generation of new ideas and new technologies in IL-based renewable energy production.



Toxicity of Ionic Liquids: Eco(cyto)activity as Complicated, but Unavoidable Parameter for Task-Specific Optimization

ChemSusChem, **2014**, *7*, 336–360 **DOI:**10.1002/cssc.201300459

Rapid progress in the field of ionic liquids in recent decades led to the development of many outstanding energy-conversion processes, catalytic systems, synthetic procedures, and important practical applications. Task-specific optimization emerged as a sharpening stone for the fine-tuning of structure of ionic liquids, which resulted in unprecedented efficiency at the molecular level. Ionic-liquid systems showed promising opportunities in the development of green and sustainable technologies; however, the chemical nature of ionic liquids is not intrinsically green. Many ionic liquids were found to be toxic or even highly toxic towards cells and living organisms. In this review, we show that biological activity and cytotoxicity of ionic liquids dramatically depend on the nature of a biological system. An ionic liquid may be not toxic for particular cells or organisms, but may demonstrate high toxicity towards

another target present in the environment. Thus, a careful selection of biological activity data is a must for the correct assessment of chemical technologies involving ionic liquids. In addition to the direct biological activity (immediate response), several indirect effects and aftereffects are of primary importance. The following principal factors were revealed to modulate toxicity of ionic liquids: i) length of an alkyl chain in the cation; ii) degree of functionalization in the side chain of the cation; iii) anion nature; iv) cation nature; and v) mutual influence of anion and cation.

Ionic Liquids and Deep Eutectic Mixtures: Sustainable Solvents for Extraction Processes

ChemSusChem, **2014**, **DOI**: 10.1002/cssc.201301192

In recent years, ionic liquids and deep eutectic mixtures have demonstrated great potential in extraction processes relevant to several scientific and technological activities. This review focuses on the applicability of these sustainable solvents in a variety of extraction techniques, including but not limited to liquid- and solid-phase (micro) extraction, microwave-assisted extraction, ultrasound-assisted extraction and pressurized liquid extraction. Selected applications of ionic liquids and deep eutectic mixtures on analytical method development, removal of environmental pollutants, selective isolation, and recovery of target compounds, purification of fuels, and azeotrope breaking are described and discussed.

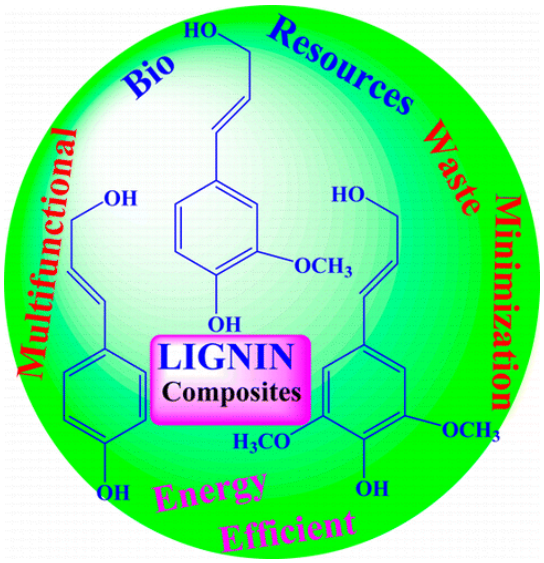
Polymer

Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review

ACS Sustainable Chem. Eng., **2014**, *2*, 1072−1092 **DOI:** 10.1021/sc500087z

Rising environmental concerns and depletion of petro-chemical resources has resulted in an increased interest in biorenewable polymer-based environmentally friendly materials. Among biorenewable polymers, lignin is the second most abundant and fascinating natural polymer next to cellulose. Lignin is one of the three major components found in the cell walls of natural lignocellulosic materials. Lignin is widely available as a major byproduct of a number of industries involved in retrieving the polysaccharide components of plants for industrial applications, such as in paper making, ethanol production from biomass, etc. The impressive properties of lignin, such as its high abundance, low weight, environmentally friendliness and its antioxidant, antimicrobial, and biodegradable nature, along with its CO_2 neutrality and reinforcing capability, make it an ideal candidate for the development of novel polymer composite materials. Considerable efforts are now being made to effectively

utilize waste lignin as one of the components in polymer matrices for high performance composite applications. This article is intended to summarize the recent advances and issues involving the use of lignin in the development of new polymer composite materials. In this review, we have made an attempt to classify different types of lignin-reinforced polymer composites starting from synthetic to biodegradable polymer matrices and highlight recent advances in multifunctional applications of lignin. The structural features and functions of the lignin/polymer composite systems are discussed in each section. The current research trends in lignin-based materials for engineering applications, including strategies for modification of lignin, fabrication of thermoset/thermoplastic/biodegradable /rubber/foam composites, and the use of lignin as a compatibilizer are presented. This study will increase the interest of researchers all around the globe in lignin-based polymer composites and the development of new ideas in this field.



Recycling of Polymers: A Review

ChemSusChem, **2014**, *7*, 1579–1593 **DOI**: 10.1002/cssc.201300898

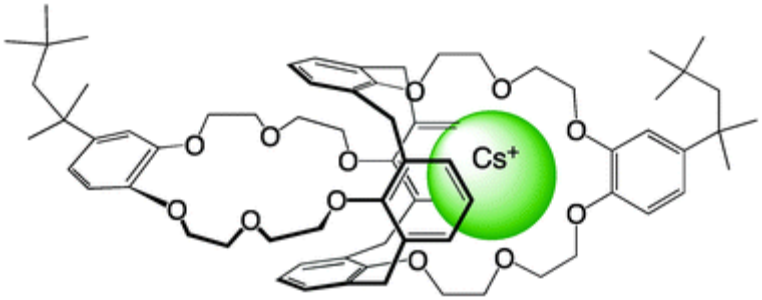
Plastics are inexpensive, easy to mold, and lightweight. These and many other advantages make them very promising candidates for commercial applications. In many areas, they have substantially suppressed traditional materials. However, the problem of recycling still is a major challenge. There are both technological and economic issues that restrain the progress in this field. Herein, a state-of-art overview of recycling is provided together with an outlook for the future by using popular polymers such as polyolefins, poly(vinyl chloride), polyurethane, and poly(ethylene terephthalate) as examples. Different types of recycling, primary, secondary, tertiary, quaternary, and biological recycling, are discussed together with related issues, such as compatibilization and cross-linking. There are various projects in the European Union on research and application of these recycling approaches; selected examples are provided in this article. Their progress is mirrored by granted patents, most of which have a very limited scope and narrowly cover certain technologies. Global introduction of waste utilization techniques to the polymer market is currently not fully developed, but has an enormous potential.

Metal Sustainability

Challenges to Achievement of Metal Sustainability in Our High-Tech Society

Chem. Soc. Rev., **2014**, *43*, 2451–2475 **DOI:** 10.1039/C3CS60440C

Achievement of sustainability in metal life cycles from mining of virgin ore to consumer and industrial devices to end-of-life products requires greatly increased recycling rates and improved processing of metals using conventional and green chemistry technologies. Electronic and other high-tech products containing precious, toxic, and specialty metals usually have short lifetimes and low recycling rates. Products containing these metals generally are incinerated, discarded as waste in landfills, or dismantled in informal recycling using crude and environmentally irresponsible procedures. Low recycling rates of metals coupled with increasing demand for high-tech products containing them necessitate increased mining with attendant environmental, health, energy, water, and carbon-footprint consequences. In this tutorial review, challenges to achieving metal sustainability, including projected use of urban mining, in present high-tech society are presented; health, environmental, and economic incentives for various government, industry, and public stakeholders to improve metal sustainability are discussed; a case for technical improvements, including use of molecular recognition, in selective metal separation technology, especially for metal recovery from dilute feed stocks is given; and global consequences of continuing on the present path are examined.



Flow Chemistry

Flow Approaches towards Sustainability

Green Chem., **2014**, Advance Article **DOI:** 10.1039/C4GC00410H

Green chemistry and flow chemistry are ideal partners for accessing novel chemical spaces and define highly efficient synthetic tools. In this review article contributions have been selected according to the advantages offered in terms of features that are not immediately related to classic green metrics such as minimization of reaction time, optimization for time screening, waste minimization, safety improvement, process intensification and easy scale up, energy and cost efficiency. Such features make processes in flow highly interesting in terms of developing a green and sustainable chemistry.

Microwave-Assisted Synthesis

Microwave-Assisted Preparation of Inorganic Nanostructures in Liquid Phase

Chem. Rev., **2014**, *114*, 6462−6555 **DOI:** 10.1021/cr400366s

In this review, we do not give an exhaustive coverage of the microwave-assisted synthesis of inorganic nanostructures in liquid phase, but mainly cover the significant research progress in the past decade. Many inorganic nanostructured materials including metals, semimetals, alloys, metal oxides, metal sulfides, metal selenides, metal tellurides, calcium-based salts and other oxysalts, inorganic/inorganic nanocomposites, and inorganic/organic nanocomposites, prepared by microwave heating in various solvents including water, polyols, ionic liquids, and mixed solvents, are classified and reviewed. The microwave-assisted self-assembly of inorganic nanostructures in liquid phase is discussed. In addition, the differences between microwave heating and conventional heating in the formation of inorganic nanostructures in liquid phase are compared. Finally, future prospects and challenges for microwave-assisted preparation of inorganic nanostructures in liquid phase are discussed. For the microwave-assisted synthesis of metallic nanostructures, we will focus on the progress made from 2005 upward, covering the new results that are not included in a previous review. For the microwave-assisted synthesis of nanostructured metal compounds, we will focus on metal oxides and metal chalcogenides for the reasons that they are very important functional materials both for the fundamental research and for practical applications and that there have been a large number of publications in the literature. However, fewer papers have been published on the microwave-assisted synthesis of other metal compounds such as metal halides and metal nitrides; thus, less coverage will be put on these nanostructured materials. The microwave-assisted synthesis of zeolite membranes and metal–organic frameworks has been reviewed by Li et al. and Klinowski et al., respectively, and these will not be included. In addition, the microwave-plasma

synthesis, microwave sintering, microwave processing, and microwave-assisted functionalization of materials are not the topics in this review.

專訪中興大學化學系李進發教授

李教授獲頒建大文教基金會的傑出年輕金玉學者獎

何時開始接觸綠色化學？契機為何？談談剛接觸到綠色化學時的感覺與想法。

十多年前，當我還是研究生時，我第一次聽到綠色化學這個名詞。當時心裡想著如果未來能以環保概念進行化學反應應該是很棒的研究。這是一個永續發展的研究課題！不過當時我的研究課題與綠色化學並無關聯。

什麼原因促使您開始以綠色化學的原則進行實驗構思與設計？

取得博士學位之後，我到美國耶魯大學以及英國愛丁堡大學進行博士後研究。我於 2008 年到中興大學化學系任教，當時正在思考自己的研究領域。過渡金屬催化耦合反應是一個極具競爭性的研究課題，可以有效地簡化合成上的製程，在學術界及工業界皆有重要的應用，舉凡 OLED（有機發光二極體）、光敏性太陽能電池、藥物中間體及抗癌藥物的合成等，過渡金屬催化皆為製程中重要的關鍵步驟，應用層面相當廣泛。2010 年諾貝爾化學獎就是頒給這一領域，其重要性可見一斑。鈀金屬是過渡金屬催化中最為重要的金屬，但是高毒性以及高價格是鈀金屬的缺點。我希望可以使用低毒性甚至無毒的過渡金屬為催化劑進行反應。以水當溶劑更是我們所期望的。

可否簡單分享研究成果與脈絡？研究方向著重於何處？像是避免浪費與毒物生成、提升合成效能、不使用有毒性之原料、觸媒設計等。

我們的研究方向是使用價格低廉及低毒性的銅金屬為催化劑。本實驗室於 2010 年與成功大學化學系林弘萍教授合作利用氧化銅的多孔性分子篩進行碳-硫鍵之

生成反應。此催化劑具有回收再利用的特性，相當環保。這項工作發表在重要期刊 Chem. Commun.後，至今已被引用 50 次。2011 年，更發現能利用半導體銅製程的廢液以及稻殼開發出新穎的催化劑，這種多孔性分子篩可以進行許多重要的催化反應。另外，鐵金屬無毒性且價錢便宜。本實驗室發現第一個鐵催化碳-硫鍵之生成反應，並於 2009 年發表在 Chem. Commun.，引用次數到目前為止已達 58 次。2013 年我們發現以氯化亞銅為催化劑，在氧化劑的作用下可以簡便地合成硫酯化合物，值得一提的是此催化系統中，水是最佳的溶劑！這項研究已經發表在 Green Chem.(I.F.=6.828)。是 Green Chem.網站 2013 年 7-9 月間點閱率最高的文章。今年我們以簡單又環保的方法生成硫-磷鍵。此成果也已發表在 Green Chem.。我們最新的結果發現氧化劑不需要過渡金屬的幫忙即可進行硫酯化合物的生成。此工作也已發表於 Green Chem.期刊。

若是以教學與培育人才的角度切入，在綠色化學方面，有沒有什麼特別想與老師或學生分享的想法？

CHEM-IS-TRY(Chemistry)—化學是實驗的科學！閱讀最新的研究是非常重要的。尤其大量閱讀綠色化學相關的研究報導是進入此研究領域最為重要的路徑。

附記：感謝中央研究院化學研究所甘魯生研究員提供訪談問題