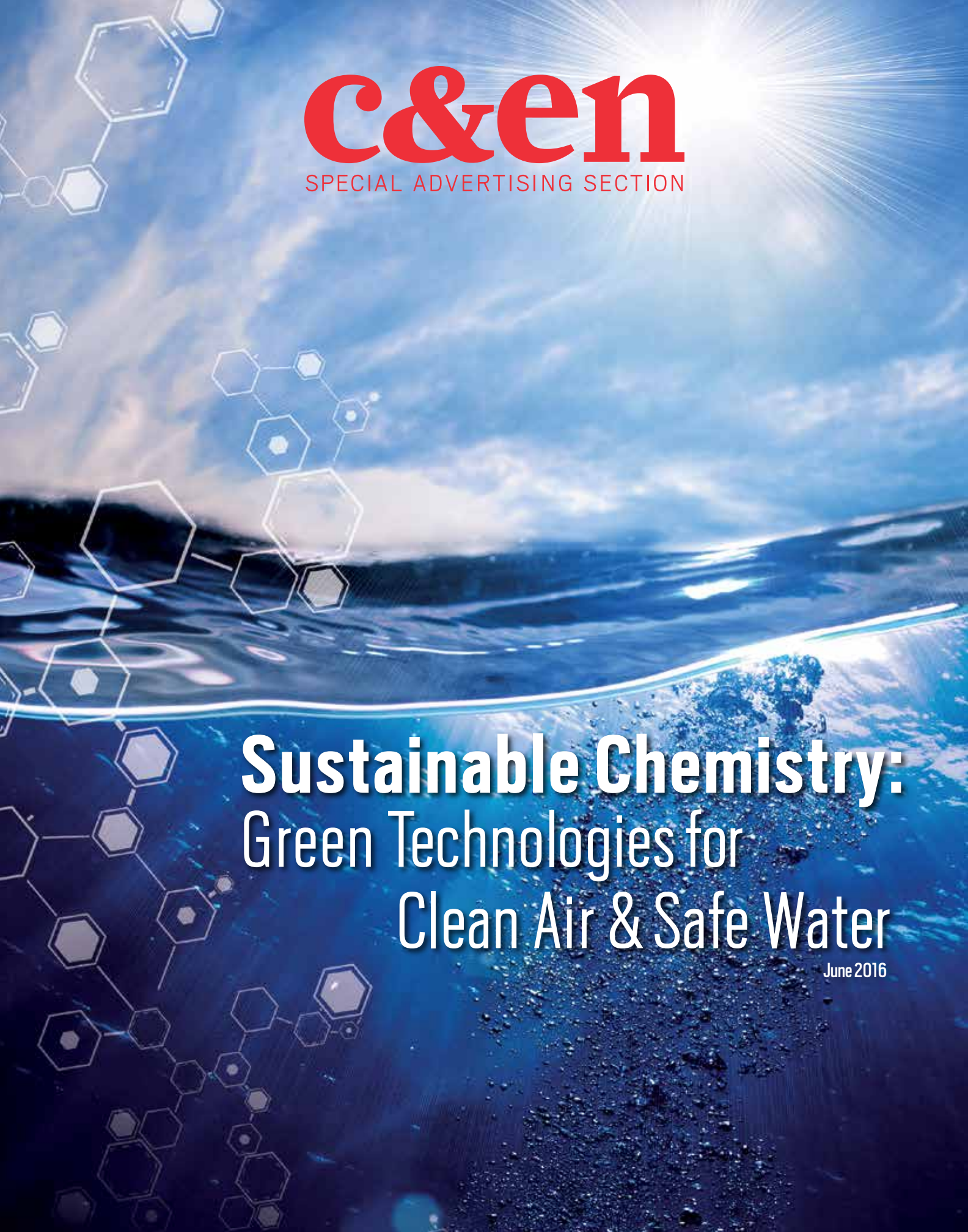

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June 2016

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HELPING INDUSTRY TO GO GREEN

Michael Eisenstein

2016 MARKS a major anniversary for the field of sustainable—or green—chemistry. Twenty years ago, the American Chemical Society Green Chemistry Institute held its inaugural Green Chemistry & Engineering (GC&E) Conference, bringing together experts from across the country to present research into how chemical processes might be rendered more efficient, safe and environmentally-friendly without impairing industrial productivity and innovation.

A year later, Paul Anastas and John Warner formally codified the aims of this still-nascent field as the 12 Principles of Green Chemistry.[1] These guidelines include focusing on the prevention of waste production rather than remediation, striving for safer synthetic reagents and solvents, and developing chemical products that degrade harmlessly after use rather than persisting in the environment.

Today, these goals are more relevant than ever, amid mounting public concern over access to clean drinking water and arable land, protecting fragile ecosystems, and mitigating the increasingly apparent effects of anthropogenic climate change. Accordingly, green chemistry is now a thriving subfield, with the 20th GC&E Conference mere weeks away and dozens of scientific journals dedicated to topics related to sustainability in chemical research, engineering, and manufacturing.

In the roster of Top 10 Articles presented here, we have highlighted popular recent articles from three leading journals in this space—*Environmental Science & Technology*, *Environmental Science & Technology Letters,* and *ACS Sustainable Chemistry & Engineering*—that help advance the principles outlined by Anastas and Warner in 1998.

For example, consider the problem of pharmaceutical pollution. Many drugs find their way into wastewater, as a natural consequence of both appropriate use and inappropriate disposal. Even after treatment, still-active pharmaceutical compounds can make their way back into the drinking water supply or the larger environment. Although the extent of the problem is ill-defined, there are some troubling datapoints—in 2010, for example, Associated Press reporters obtained scientific data showing that 24 major US cities had detectable levels of pharmaceuticals in their water supplies.[2] In one of our highlighted articles, the authors offer proof of concept for a 'design for degradation' approach for rationally modifying existing drugs in a way that renders them biodegradable without impeding their therapeutic efficacy.[3]

Others are tackling the problem of waste prevention, and making efforts to ensure that manufacturing resources are used as efficiently as possible. The production of colored textiles, for example, normally produces large quantities of highly toxic wastewater laden with salt and unused dye compounds. By employing a hybrid approach based on nanofiltration and bipolar membrane electrodialysis, researchers were successfully able to recover the excess dye and salt from such wastewater, enabling more productive use of these compounds and reduced environmental impact.[4]

Although the 12 Principles are fundamentally geared toward avoiding environmental damage, much of the work ongoing in the green chemistry field is focused on remediating the current consequences of industrialization. For example, one recent paper from *ACS Sustainable Chemistry & Engineering* demonstrates an extremely affordable solution for removing toxic contaminants from drinking water. The authors showed that chemical groups present on the surface of various fruit peels can bind to and extract dissolved lead, nickel, and chemical dyes and that treatment under acidic conditions is sufficient to 'recharge' these peels for repeat use.[5]

We hope that you enjoy this special focus on Sustainable Chemistry, which highlights these studies as well as other research efforts now underway to achieve improved global health and environmental stability through smarter chemical research and manufacturing processes.

References

1 Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice,* Oxford University Press: New York, 1998; pp 30.

2 Donn, J.; Mendoza, M; Pritchard, J. *The Associated*

Press, http://hosted.ap.org/specials/interactives/pharmawater_site/day1_01.html
3 Rastogi, T.; Leder, C.; Kümmerer, K *Environ. Sci. Technol.* **2015**, *49* (19), 11756–11763.
4 Lin, J.; Ye, W.; Huang, J; Ricard, B.; Baltaru, M.-C.; Greydanus, B.; Balta, S.; Shen, J.; Vlad, M.; Sotto, A.; Luis, P.; Van der Bruggen, B. *ACS Sustainable Chem. Eng.*, **2015**, *3* (9), 1993–2001.
5 Mallampati, R.; Xuanjun, L.; Adin, A.; Valiyaveettil, S. *ACS Sustainable Chem. Eng.*, **2015**, *3* (6), 1117–1124.

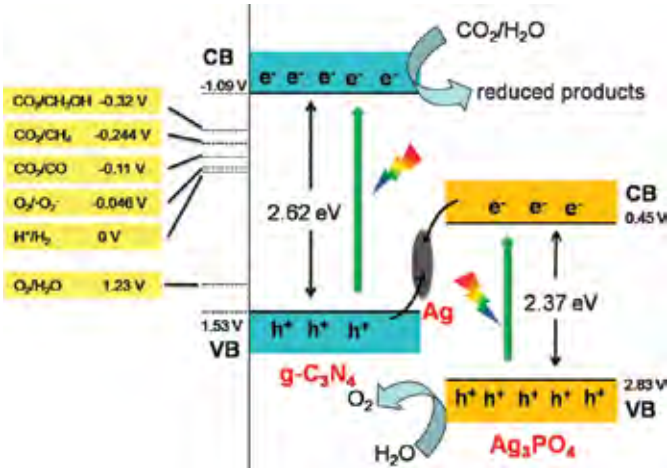
Michael Eisenstein is a contributing editor on this C&EN Supplement, and a freelance science writer based in Philadelphia, PA ■

TOP TEN SUSTAINABLE CHEMISTRY PAPERS

THESE ARE the most-read papers in sustainable or 'green' chemistry from *Environmental Science & Technology*, *Environmental Science & Technology Letters* and *ACS Sustainable Chemistry & Engineering* over the past 12 months.

New Application of Z-Scheme Ag_3PO_4/g-C_3N_4 Composite in Converting CO_2 to Fuel

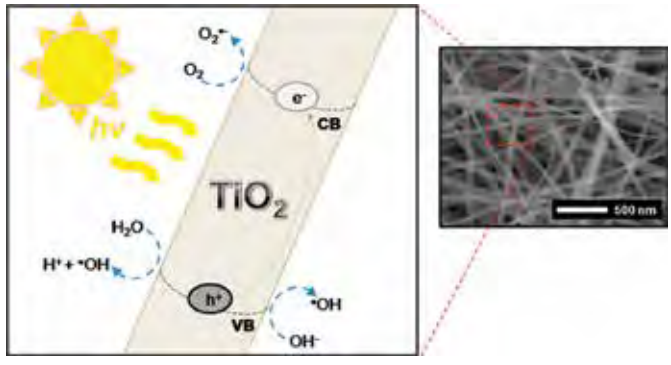
Yiming He[†‡], Lihong Zhang[‡], Botao Teng[†‡], and Maohong Fan[*†]
[†] University of Wyoming, Laramie, Wyoming, USA [‡] Zhejiang Normal University, Jinhua, Zhejiang, China
Environ. Sci. Technol., **2015,** *49* (1), pp 649–656
DOI: 10.1021/es5046309



This research was designed for the first time to investigate the activities of photocatalytic composite, Ag_3PO_4/g-C_3N_4, in converting CO_2 to fuels under simulated sunlight irradiation. The composite was synthesized using a simple in situ deposition method and characterized by various techniques including Brunauer–Emmett–Teller method (BET), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (DRS), photoluminescence spectroscopy (PL), and an electrochemical method. Thorough investigation indicated that the composite consisted of Ag_3PO_4, Ag, and g-C_3N_4. The introduction of Ag_3PO_4 on g-C_3N_4 promoted its light absorption performance. However, more significant was the formation of heterojunction structure between Ag_3PO_4 and g-C_3N_4, which efficiently promoted the separation of electron–hole pairs by a Z-scheme mechanism and ultimately enhanced the photocatalytic CO_2 reduction performance of the Ag_3PO_4/g-C_3N_4. The optimal Ag_3PO_4/g-C_3N_4 photocatalyst showed a CO_2 conversion rate of 57.5 μmol $h^{-1} \cdot g_{cat}^{-1}$, which was 6.1 and 10.4 times higher than those of g-C_3N_4 and P25, respectively, under simulated sunlight irradiation. The work found a new application of the photocatalyst, Ag_3PO_4/g-C_3N_4, in simultaneous environmental protection and energy production. ■

Tailored Synthesis of Photoactive TiO_2 Nanofibers and Au/TiO_2 Nanofiber Composites: Structure and Reactivity Optimization for Water Treatment Applications

Michael J. Nalbandian[†], Katherine E. Greenstein[‡], Danmeng Shuai[‡], Miluo Zhang[†], Yong-Ho Choa[§], Gene F. Parkin[‡], Nosang V. Myung[*†], and David M. Cwiertny[*‡]
[†] University of California—Riverside, California, USA [‡] University of Iowa, Iowa City, Iowa, USA [§] Hanyang University, Ansan, Kyeonggi-do, Korea
Environ. Sci. Technol., **2015,** *49* (3), pp 1654–1663
DOI: 10.1021/es502963t



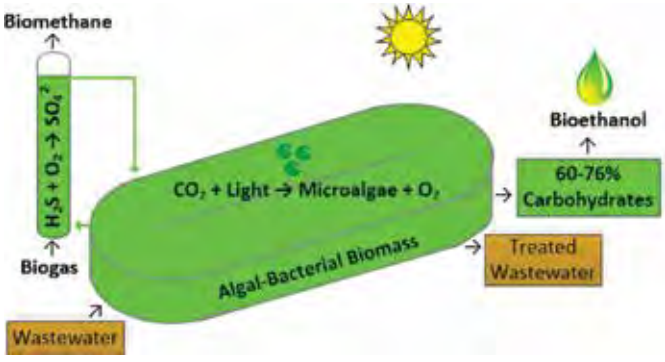
Titanium dioxide (TiO_2) nanofibers with tailored structure and composition were synthesized by electrospinning to optimize photocatalytic treatment efficiency. Nanofibers of controlled

diameter (30–210 nm), crystal structure (anatase, rutile, mixed phases), and grain size (20–50 nm) were developed along with composite nanofibers with either surface-deposited or bulk-integrated Au nanoparticle cocatalysts. Their reactivity was then examined in batch suspensions toward model (phenol) and emerging (pharmaceuticals, personal care products) pollutants across various water qualities. Optimized TiO_2 nanofibers meet or exceed the performance of traditional nanoparticulate photocatalysts (e.g., Aeroxide P25) with the greatest reactivity enhancements arising from (i) decreasing diameter (i.e., increasing surface area), (ii) mixed phase composition [74/26 (±0.5) % anatase/rutile], and (iii) small amounts (1.5 wt %) of surface-deposited, more so than bulk-integrated, Au nanoparticles. Surface Au deposition consistently enhanced photoactivity by 5- to 10-fold across our micropollutant suite independent of their solution concentration, behavior that we attribute to higher photocatalytic efficiency from improved charge separation. However, the practical value of Au/TiO_2 nanofibers was limited by their greater degree of inhibition by solution-phase radical scavengers and higher rate of reactivity loss from surface fouling in nonidealized matrixes (e.g., partially treated surface water). Ultimately, unmodified TiO_2 nanofibers appear most promising for use as reactive filtration materials because their performance was less influenced by water quality, although future efforts must increase the strength of TiO_2 nanofiber mats to realize such applications. ■

Influence of Biogas Flow Rate on Biomass Composition During the Optimization of Biogas Upgrading in Microalgal-Bacterial Processes

Mayara L. Serejo[†‡], Esther Posadas[†], Marc A. Boncz[‡], Saúl Blanco[§], Pedro García-Encina[†], and Raúl Muñoz[*†]
[†] University of Valladolid, Spain [‡] Federal University of Mato Grosso do Sul, Campo Grande, Brazil [§] University of León, Spain
Environ. Sci. Technol., **2015**, *49* (5), pp 3228–3236
DOI: 10.1021/es5056116

The influence of biogas flow rate (0, 0.3, 0.6, and 1.2 $m^3\ m^{-2}\ h^{-1}$) on the elemental and macromolecular composition of the algal-bacterial biomass produced from biogas upgrading in a 180 L photobioreactor interconnected to a 2.5 L external bubbled absorption column was investigated using diluted anaerobically digested vinasse as cultivation medium. The influence of the external liquid recirculation/biogas ratio ($0.5 < L/G < 67$) on the removal of CO_2 and H_2S, and on the concentrations of O_2 and N_2 in the upgraded biogas, was also evaluated. A *L/G* ratio of 10 was considered optimum to support CO_2 and H_2S removals of 80% and 100%, respectively, at all biogas flow rates tested. Biomass productivity increased at increasing biogas flow rate, with a maximum of $12 \pm 1\ g\ m^{-2}\ d^{-1}$ at $1.2\ m^3\ m^{-2}\ h^{-1}$, while the C, N, and P



biomass content remained constant at 49 ± 2%, 9 ± 0%, and 1 ± 0%, respectively, over the 175 days of experimentation. The high carbohydrate contents (60–76%), inversely correlated to biogas flow rates, would allow the production of ≈100 L of ethanol per 1000 m^3 of biogas upgraded under a biorefinery process approach. ■

Re-Designing of Existing Pharmaceuticals for Environmental Biodegradability: A Tiered Approach with β-Blocker Propranolol as an Example

Tushar Rastogi, Christoph Leder, and Klaus Kümmerer*
Leuphana University Lüneburg, Germany
Environ. Sci. Technol., **2015,** *49* (19), pp 11756–11763
DOI: 10.1021/acs.estlett.6b00046

Worldwide, contamination of aquatic systems with micropollutants, including pharmaceuticals, is one of the challenges for sustainable management of water resources. Although micropollutants are present at low concentrations, many of them raise considerable toxicological concerns, particularly when present as components of complex mixtures. Recent research has shown that this problem cannot be sustainably solved with advanced effluent treatment. Therefore, an alternative that might overcome these environmental problems is the design of new pharmaceutical molecules or the redesign of existing pharmaceutical molecules that present the functionality needed for their application and have improved environmental biodegradability. Such redesigning can be performed by small molecular changes in the drug molecule with intact drug moiety which could incorporate the additional attribute such as biodegradability while retaining its pharmacological potency. This proof of concept study provides an approach for the rational redesign of a given pharmaceutical (Propranolol as an example). New derivatives with small molecular changes as compared to

propranolol molecule were generated by a nontargeted photolysis process. Generated derivatives with intact drug moieties (an aromatic ring and a β-ethanolamine moiety) were further screened for aerobic biodegradability and pharmacological potency. The feasibility of the approach of redesigning an existing pharmaceutical through nontargeted generation of new derivatives with intact drug moiety and through subsequent screening was demonstrated in this study. Application of such approaches in turn might contribute to the protection of water resources in a truly sustainable manner. ■

Toward Microcapsule-Embedded Self-Healing Membranes

Sang-Ryoung Kim[†], Bezawit A. Getachew[†], Seon-Joo Park[†], Oh-Seok Kwon[†], Won-Hee Ryu[†], André D. Taylor[†], Joonwon Bae[‡], and Jae-Hong Kim[*†]

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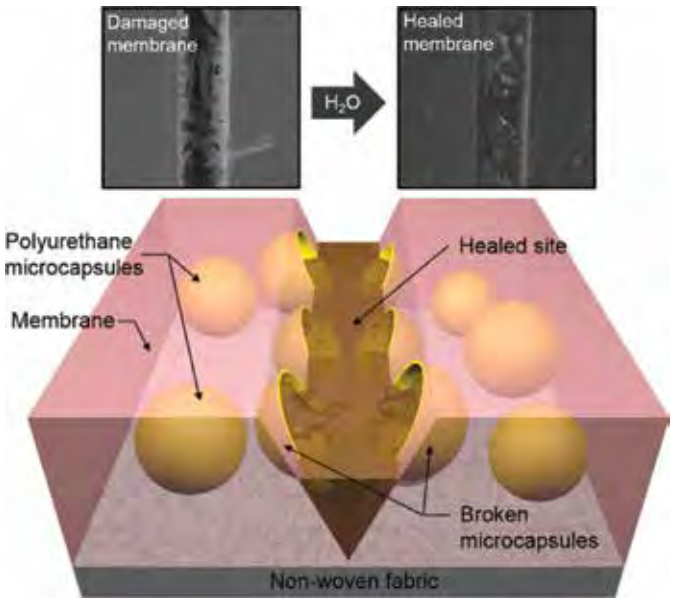
Environ. Sci. Technol. Lett., **2016,** *3* (5), pp 216–221
DOI: 10.1021/acs.estlett.6b00046

We herein report the first instance of a self-healing water treatment membrane that restores its water flux and particle rejection properties autonomously. The self-healing membrane is fabricated by embedding microcapsules with a polyurethane shell and an isophorone diisocyanate core within a conventional poly(ether sulfone) membrane. A dual-surfactant system and polydopamine coating were used to control the size of these microcapsules and avoid capsule buckling. When the membrane structure is physically damaged, the microcapsules release a reactive isocyanate healing agent that reacts with the surrounding water to form a polyurea matrix that plugs the damage. The self-healing was found to recover the water flux and particle rejection of the membrane to 103 and 90% of the original membrane's performance, respectively. The results of this study show that microcapsule-embedded membranes are a promising approach to fabricating versatile, next-generation membranes that can self-heal. ■



Toward Resource Recovery from Textile Wastewater: Dye Extraction, Water and Base/Acid Regeneration Using a Hybrid NF-BMED Process

Jiuyang Lin[†], Wenyuan Ye[*†], Jie Huang[‡], Borrego Ricard[§], Marian-Cornel Baltaru[∥], Benjamin Greydanus[⊥], Stefan Balta[∥], Jiangnan Shen[*‡], Maria Vlad[∥], Arcadio Sotto[#], Patricia Luis[⊗], and Bart Van der Bruggen[†]

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ACS Sustainable Chem. Eng., **2015,** *3* (9), pp 1993–2001
DOI: 10.1021/acssuschemeng.5b00234

In this work, textile wastewater is explored for resource recovery in a hybrid loose nanofiltration (NF)-bipolar membrane electrodialysis (BMED) process for fractionation of dyes and salt, in view of dye purification and water and salt reuse. A loose nanofiltration membrane, i.e., Sepro NF 6 (Ultura), found to have a low salt rejection (0.27% in 120 $g \cdot L^{-1}$ NaCl solution) and high rejection for direct dyes and reactive dyes (≥99.93%), was used for fractionation of dye/salt mixtures through diafiltration. In diafiltration, the addition of pure water with a volume factor of 5.0 can effectively remove the NaCl salt by using Sepro NF 6 with an invariable dye concentration, in view of the recovery of high purity dyes. The overall salt rejections in diafiltration for the dye/salt mixtures with 40, 50 and 60 $g \cdot L^{-1}$ NaCl are 2.2%, 1.8% and 1.1%, respectively, enabling a further treatment by BMED. Subsequently, application of BMED for reuse of salt-containing NF permeate demonstrates that desalinated water with ~100 ppm of NaCl can be obtained, and base/acid can be produced from the salts without any membrane fouling by dyes. Therefore, the hybrid loose NF-BMED process allows for resource (i.e., dye, salt and pure water) extraction from textile wastewater, which closes the salt and water cycle, in view of process intensification. ■

Fruit Peels as Efficient Renewable Adsorbents for Removal of Dissolved Heavy Metals and Dyes from Water

Ramakrishna Mallampati, Li Xuanjun, Avner Adin, and Suresh Valiyaveettil*
National University of Singapore, Singapore
ACS Sustainable Chem. Eng., **2015***, 3* (6), pp 1117–1124
DOI: 10.1021/acssuschemeng.5b00207

Removal of heavy metal ions and dissolved organic compounds present in wastewater is a challenge for many countries owing to high cost of existing technologies and continued increase in water consumption. In this study, three natural materials, avocado, hamimelon and dragon fruit peels, were selected and used as simple and renewable adsorbents for water purification. The presence of surface functional groups such as $-CO_2H$, $-OH$ and morphologies of the peels were characterized using spectroscopic and electron microscopic techniques, respectively. All peels were effective toward removing dyes and toxic metal ions from water. The extraction capacity of peels increased with extraction time and a plateau was reached at equilibrium. Dragon fruit peels showed highest extraction efficiency toward alcian blue (71.85 mg/g) and methylene blue (62.58 mg/g). Hamimelon peels and avocado peels showed moderate extraction capacity for Pb^{2+} (7.89 mg/g, 9.82 mg/g) and Ni^{2+} (9.45 mg/g, 4.93 mg/g) cations. The Langmuir isotherm model was useful to explain the adsorption process, dominated by electrostatic interaction between adsorbent and adsorbates, indicating a monolayer adsorption at the binding sites on the surface of the peels. However, the adsorption model for methylene blue and neutral red is still a matter of conjecture. The adsorbents can be regenerated at acidic pH and could reuse for a few cycles. ■

Constructing Three-Dimensional Hierarchical Architectures by Integrating Carbon Nanofibers into Graphite Felts for Water Purification

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† South China University of Technology, Guangzhou,China ‡ Tsinghua University, Shenzhen, China
ACS Sustainable Chem. Eng., **2016,** *4* (4), pp 2351–2358
DOI: 10.1021/acssuschemeng.6b00030

Developing high-performance nanostructured sorbents for water treatment is of great importance. Herein, we report a facile strategy to fabricate three-dimensional hierarchical architectures by integrating carbon nanofibers (CNFs) into macroscopic graphite felt (GF) supports. The physicochemical properties of CNF@GF monoliths including surface areas, densities, porosities, and pore structures could be conveniently tuned by varying reaction time. The CNF@GF monoliths were utilized as advanced sorbents for the removal of Pb^{2+}, Congo red, organic solvents, and oils from aqueous solutions. The characteristics of adsorption processes including kinetics, isotherms, and regeneration were investigated. It is demonstrated that the CNF@GF exhibits outstanding performance for water treatment in terms of adsorption capacities, recovering, and recyclability. As such, the versatile CNS@GF monoliths show great application potential for water treatment. ■

Facile Synthesis of Silver Nanoparticles Decorated Magnetic-Chitosan Microsphere for Efficient Removal of Dyes and Microbial Contaminants

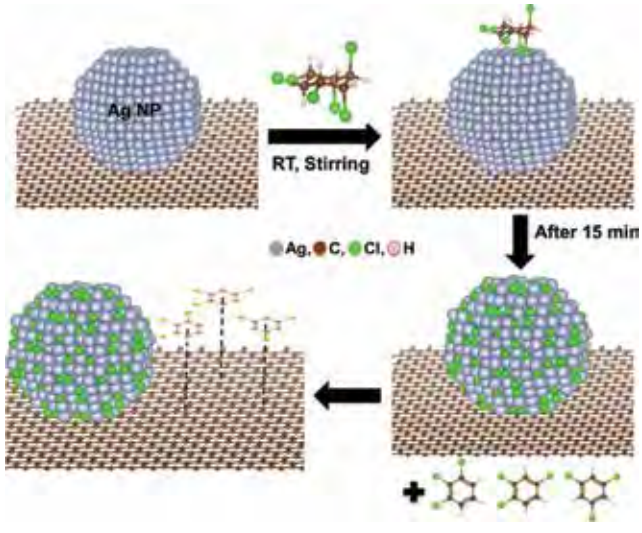
Baskaran Ramalingam[†], Md. Motiar R. Khan[‡], Bholanath Mondal[§], Asit Baran Mandal[*‖⊥], and Sujoy K. Das[*†⊥]
Chinese Academy of Sciences, Dalian, China ‡ The First Affiliated Hospital of Zhejiang Chinese Medical University, Hangzhou, China § University Hospital Tuebingen, Germany ‖ Institute for Diabetes Research and Metabolic Diseases of the Helmholtz Centre Munich at the University of Tuebingen, Germany ⊥ German Center for Diabetes Research, Tuebingen, Germany
ACS Sustainable Chem. Eng., **2015,** *3* (9), pp 2291–2302
DOI: 10.1021/acssuschemeng.5b00577

A facile and rapid synthesis of core–shell type magnetite-chitosan microsphere decorated with silver nanoparticles (MCSM) is described. The composition and structure of the as-synthesized microsphere characterized by various spectroscopic and microscopic techniques demonstrated formation of 3.63 ± 0.76 μm MCSM with decoration of silver nanoparticles (AgNPs) having 16 ± 2.5 nm size. The thermogravimetric analysis (TGA) data showed good thermal stability, whereas vibrating sample magnetometry (VSM) analysis indicated the superparamagnetic behavior of the as-synthesized microsphere. The adsorptive removal and antimicrobial property of MCSM was explored for eco-friendly and cost-effective water purification. The MCSM removed 99.99% microbial contaminants and 99.5% of dyes from single as well as multicomponent systems from water bodies efficiently. Furthermore, the dye removal capacity of MCSM (q_e = 271.2 ± 14.5 mg/g) was found to be higher compared to the other nanoadsorbents attributing to the high effective surface area of the microsphere and plenty of functional groups of shell structure of chitosan favored binding of dyes on MCSM. Moreover, the adsorbed dyes were desorbed from MCSM at higher pH values and regenerated MCSM was used for next cycle of dye removal. The magnetic behavior of MCSM facilitated easy separation using external magnetic field leading to recycling and reuse, whereas decoration of AgNPs on the microsphere inhibited the bacterial growth. The long-term antibacterial activity of MCSM significantly improved the antifouling property to inhibit the biofilm formation on MCSM. The proposed core–shell type MCSM thus provides a promising opportunity for cost-effective water purification. ■

Simultaneous Dehalogenation and Removal of Persistent Halocarbon Pesticides from Water Using Graphene Nanocomposites: A Case Study of Lindane

Soujit Sen Gupta[†], Indranath Chakraborty[†], Shihabudheen Mundampra Maliyekkal[‡], Tuhina Adit Mark[†], Dheeraj Kumar Pandey[†], Sarit Kumar Das[§], and Thalappil Pradeep[*†]
† Seoul National University, Republic of Korea ‡ Konkuk University, Seoul, Republic of Korea § Soonchunhyang University Bucheon Hospital, Bucheon, Republic of Korea
ACS Sustainable Chem. Eng., **2015**, *3* (6), pp 1155–1163
DOI: 10.1021/acssuschemeng.5b00080

This paper describes an unusual chemical reaction that takes place on a graphene composite in a concerted fashion. The reaction shows the conversion of a persistent organochlorine pesticide, lindane ($C_6H_6Cl_6$), present in water, to different isomers of trichlorobenzenes (TCBs, $C_6H_3Cl_3$) on the surface of reduced graphene oxide–silver composites (RGO@Ag). The reaction is unique to the composite and does not occur on RGO and nanoparticles of Ag separately. The products of the reaction were isolated and extensively characterized using analytical techniques such as gas chromatography–mass spectrometry, electrospray ionization mass spectrometry, infrared and NMR, which unequivocally confirmed their identity. The as-formed TCBs were removed from the aqueous medium by adsorption on the same composite. Adsorption of



lindane is physical in nature, but that of TCBs is through π–π interactions. The study reveals the unusual chemical reactivity of graphene–metal composites and their potential for water treatment. The uniqueness of the reaction on RGO@Ag is due to the simultaneous removal of three HCl molecules, leading to the formation of aromatic compounds and concomitant formation of silver chloride. Recycling capacity and effect of diverse species present in natural waters were tested for potential applications in sustainable water treatment. ■

3

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DYESTUFF ANALYSIS OF TEXTILES: DIRECT ANALYSIS ON A COMPACT MASS SPECTROMETER

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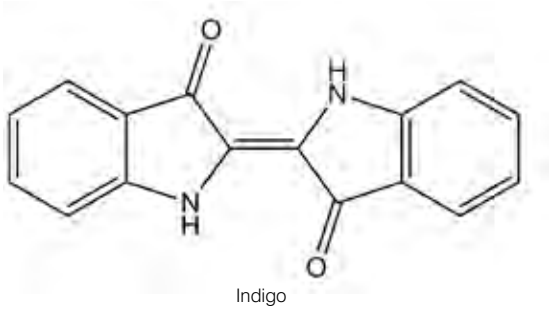
Introduction

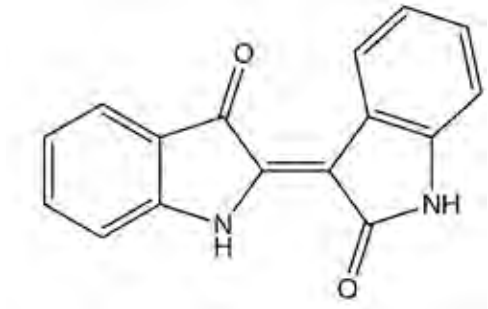
The scientific investigation of cultural heritage objects is the only access to knowledge about long-gone, ancient societies and their cultural, technological and social stage of development. In addition, the materials used by our ancestors—e.g. their textiles and the organic dyestuff employed to color these materials—allow researchers to draw some conclusions about cultural exchanges and trading routes. But in-depth knowledge about materials and dyestuff is also of highest importance for proper conservation and restoration of these materials. Specimens are rare, however, and available only in minute amounts. For their investigation, it is preferable to employ non destructive or at least minimally invasive methods.

Direct analysis by compact mass spectrometry (CMS) offers such a minimally invasive technique, allowing for rapid and direct sampling without any sample preparation prior to analysis.

Figure 1
Isomeric compounds indigo and indirubin.



Indigo



Indirubin

Molecular Formula: $C_{16}H_{10}N_2O_2$
Nomial Mass: 262 amu

Table 1
Summary of the investigated cultural heritage objects.

Culture/Region of Origin	Object ID and description	Fiber/colour
Ancient Peruvian cultures, South America	VA65545 Head ornament, Paracas-culture (800–200 BC)	Wool, blue
	VA31000 Fabric fragment, Chimú-culture (1200–1450 AD)	Wool, green
	VA57042 Fabric fragment, Ixchma (1400–1550 AD)	Cotton, blue
	VA62696 Shirt, Inca culture (1450–1550 AD)	Cotton, blue
	VA66840 Kipu (knot-cord), Inca culture (1450–1550 AD)	Cotton, blue
Cemetery of Niya, Xinjiang Uyghur Autonomous Region, China (probably 2nd century BC – 5th century AD)South America)	VA66840 Kipu (knot-cord), Inca culture (1450–1550 AD)	Cotton, blue
	95MNIM5:8-2 Bag	Wool, blue
	95MNIM3:16:1 Wooden bow and banner	Silk, blue

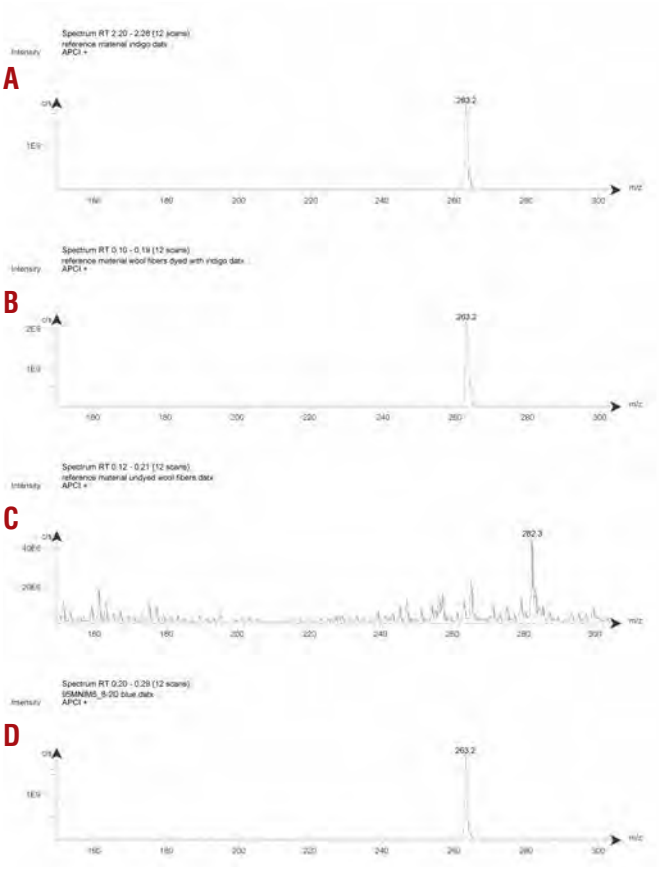
Example

Blue and green hues can be created from different inorganic and organic sources. For generating blue colored textiles, indigo (a vat dye) has widely been used since the very early days of humankind. In this study, a direct analysis probe, Atmospheric Sample Analysis Probe (ASAP®)/CMS, is applied to analyze colorants of blueish and greenish historic textile differing both in material and age (Table 1).

As a first step, the ionization efficiency of the authentic standard compounds indigo and indirubin (Fig. 1) was tested, followed by a thorough investigation of the reference fibers: undyed wool, silk, cotton and linen, followed by fibers that had been treated with synthetic indigo or indirubin or with extracts

Figure 2

ASAP/CMS-spectra for (A) wool fibers dyed with synthetic indigo, (B) wool fibers dyed with the dye plant woad (Isatis tinctoria L.), (C) undyed wool fibers and (D) historic blue wool fibers 95MNIM5:8-2D.



from the dye plant woad (*Isatis tinctoria L.*). Regardless of the kind of fibers, for all blue-colored reference materials, the quasimolecular ion $[M+H]^+$ *m/z* 263 was detected as a base peak (scan range *m/z* 150–550), while in colorless samples this peak was not seen (Fig. 2). Investigation of the blue- and green-shaded historical samples revealed the presence of indigoid dyes; in all of these samples, the quasimolecular ion m/z 263 was detected (scan range m/z 150–550 or 150–1050) regardless of the kind of fiber, the age of the sample, its appearance or its workmanship

Summary

- ASAP/CMS is a minimally invasive method - in this case study, single fragments of the yarns or a couple of fibers are sufficient for the detection of indigoid-like dyes.
- ASAP/CMS is a very rapid and reliable method, without the need for any sample preparation prior to measurements.
- ASAP/CMS allows the analysis of both solid and liquid samples.
- ASAP/CMS was shown in this case study to successfully detect indigoid dyes, independent of the type of fiber, sample age, workmanship or the state of its preservation.

Additional information: http://www.advion.com/applications/expression-applications/direct-mass-analysis-from-solid-and-liquid-samples/

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