

Combinatorial materials synthesis

by Ichiro Takeuchi^{1*}, Jochen Lauterbach², and Michael J. Fasolka³

The pace at which major technological changes take place is often dictated by the rate at which new materials are discovered, and the timely arrival of new materials has always played a key role in bringing advances to our society. It is no wonder then that the so-called combinatorial or high-throughput strategy has been embraced by practitioners of materials science in virtually every field. High-throughput experimentation allows simultaneous synthesis and screening of large arrays of different materials. Pioneered by the pharmaceutical industry, the combinatorial method is now widely considered to be a watershed in accelerating the discovery and optimization of new materials¹⁻⁵.

The last century saw an explosion in activity in every avenue of materials science. As the understanding and applications of materials developed, attention shifted away from simple materials formed from just one or two elements of the periodic table to compounds consisting of multiple elements. In particular, chance discoveries of complex compounds with extraordinary properties, such as high-temperature superconductivity, have begun to attract attention to multicomponent materials with complicated structures. However, the number of known compounds is miniscule compared to the almost infinite phase space of previously unexplored materials.

It is now more than ten years since the first report of 'integrated combinatorial materials chips' by Xiang and Schultz⁶, and the field of combinatorial materials science still appears to be rapidly expanding in various directions. However, topics being pursued via the high-throughput approach can be classified approximately into three general areas: catalysts, electronic materials, and polymers. One trend that has emerged across the board in all applications is that researchers are increasingly using the combinatorial technique, not just for identifying new compositions, but also for the rapid optimization and mapping of processing parameters that influence the properties of materials. The rapid mapping of composition-structure-property relationships in compositional phase diagrams and parameter space has become an integral part of all applications of high-throughput experimentation.

¹Department of Materials Science and Engineering and Center for Superconductivity Research, University of Maryland, College Park, MD 20742-4111, USA
*E-mail: takeuchi@umd.edu

²Department of Chemical Engineering, University of Delaware, 150 Academy Street, Newark, DE 19716, USA

³NIST Combinatorial Methods Center, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8500, Gaithersburg, MD 20899-8500, USA

Materials discovery for electronics

Evolution and advances in the electronics industry are driven by continuing cycles of development and insertion of novel solid-state materials into electronic devices and circuits. Most functional electronic materials are inorganic, and range from semiconductors for transistors and luminescent materials for display devices to ferroelectric and ferromagnetic materials for memory devices. Their combinatorial investigation is best performed in the form of thin-film libraries. A variety of physical vapor deposition techniques (as well as some chemical vapor deposition techniques) have been implemented for the quick synthesis of libraries where diverse compositional variation is generated⁵⁻¹². Spatially selective deposition can be performed easily using shadow deposition or photolithographic techniques. Fig. 1 shows a photographic picture of a library of luminescent materials after a series of deposition and lift-off steps were performed to arrange 1024 different compositions on a 1" Si substrate¹³. The variation in color reflects the diversity one can achieve in a single library.

In some materials systems, atomically controlled layer-by-layer construction of functional materials has been incorporated into combinatorial synthesis using laser molecular beam epitaxy¹⁴. Because electronic materials are often used as device components, it is natural to characterize their performance directly in the form of device arrays, and commonly available microfabrication and metrology tools can lend themselves to the synthesis and characterization of thin-film library chips. Some of the more sophisticated forms

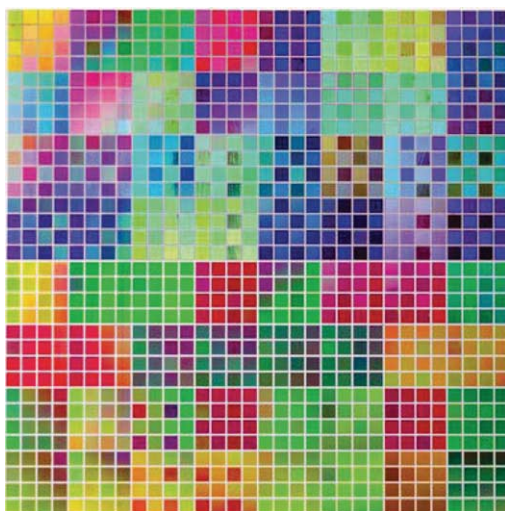


Fig. 1 Photograph of a 1024 member combinatorial library of luminescent materials on a 1" x 1" Si chip following thin-film deposition. Color variation arises from various precursor materials of different thicknesses deposited at different sites. (Reprinted with permission from¹³. © 1998 AAAS.)

of device libraries involve microelectromechanical systems device arrays such as cantilevers and microhotplates^{15,16}. Fig. 2 is a photograph of a micromachined array of cantilevers used to screen shape memory alloy compounds via visual inspection^{17,18}. Shear diversity and the wide range of functionalities that different electronic materials display for a variety of applications present a tremendous challenge for the task of rapid and accurate screening. Scanning probe techniques have provided some of the most elegant noncontact rapid characterization methods for the screening of different properties, such as magnetic and electrical impedance properties^{5,19}.

To date, the combinatorial approach has led to the discovery of a number of new materials in technologically important fields. A new blue-light-emitting photoluminescent composite material, $\text{Gd}_3\text{Ga}_5\text{O}_{12}/\text{SiO}_2$, was identified from the library shown in Fig. 1¹³. Also, van Dover *et al.*²⁰ used the reactive codeposition technique extensively and found that $\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.6}\text{O}_2$ exhibits the optimum dielectric properties required for capacitors in next-generation dynamic random access memory devices. In the search for ideal high- k (dielectric constant) microwave materials, pulsed laser deposition of precursors was performed, together with microwave microscopy, to zoom into different composition regions in the pseudo-ternary phase diagram of $(\text{Ba},\text{Sr},\text{Ca})\text{TiO}_3$. $\text{Ba}_{0.12-0.25}\text{Sr}_{0.35-0.47}\text{Ca}_{0.32-0.53}\text{TiO}_3$ was isolated as the region that shows low microwave dielectric loss while simultaneously exhibiting sufficient dielectric constant²¹.

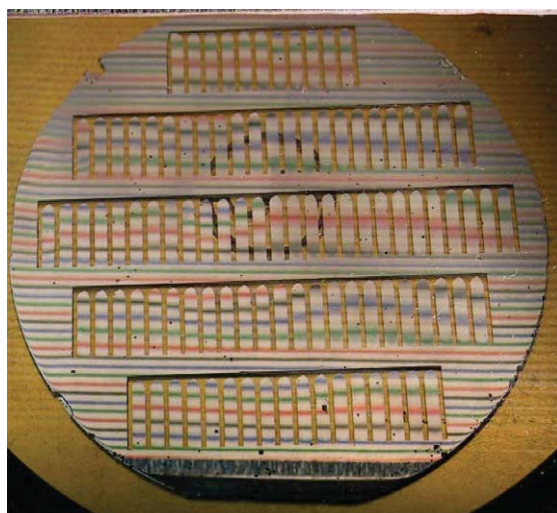


Fig. 2 Micromachined cantilever library on a 3" Si wafer used to detect shape memory alloys from a deposited ternary composition spread. Colored lines are reflections of an image used to visually identify cantilevers undergoing actuation induced by martensitic transformation. (Reprinted with permission from¹⁷. © 2003 Nature Publishing Group.)

Novel magnetic materials

Magnetism continues to be one of the most active fields in condensed matter physics, and magnetic materials are used in a broad spectrum of applications, ranging from permanent magnets for motors to soft magnets for recording media. There are various techniques for mapping magnetic properties from the field emanating from combinatorial samples. These include scanning superconducting quantum interference detector (SQUID) microscopy^{17,18,22}, the scanning Hall probe technique²³, and magneto-optical techniques^{23–25}. The magneto-optical Kerr effect is particularly useful because, by sweeping an applied magnetic field, one can map the magnetic hysteresis loop. From this, one can obtain the saturation magnetization (through calibration) and coercive field values²⁵. The scanning Hall probe technique has also been used to map saturation magnetization²¹. To obtain absolute values of magnetization without calibration, an inversion technique was developed that can be applied to any field distribution data^{26,27}. This uses a computation algorithm that performs inverse Fourier transforms to calculate magnetic pole densities, which are then integrated to obtain magnetization values. This algorithm was applied to room-temperature scanning SQUID microscopy data of a variety of magnetic materials libraries^{17,18,28}.

Room-temperature ferromagnetic semiconductors are of great interest because of their potential 'spintronics' applications, where the charge and spin degrees of freedom of electrons are used simultaneously for novel memory and optical device applications^{29,30}. The prediction of room-temperature ferromagnetism in Mn-doped ZnO and GaN³¹, along with the discovery of ferromagnetism above room temperature in Co-doped TiO₂ anatase by Matsumoto and coworkers³² using the combinatorial technique, have triggered a worldwide search for new dilute magnetic semiconductor materials. A recent combinatorial discovery in this field is ferromagnetic (In_{1-x}Fe_x)₂O_{3-δ}, which is an *n*-type semiconductor^{33,34}. Unlike other doped magnetic semiconductor materials, Fe is found to exhibit solubility of up to 20% in this compound, as revealed by X-ray diffraction (XRD). Fig. 3 shows the result of X-ray microdiffraction of a (In_{1-x}Fe_x)₂O_{3-δ} (*x* = 0–0.4) composition spread, which shows a continuous shift in lattice constant for up to 20% Fe. Subsequent individual bulk and thin-film studies have shown robust room-temperature ferromagnetism in this compound, with strong evidence of transport carriers interacting with

magnetism. Because In₂O₃-based compounds have been widely used as transparent conductors, these materials are attractive to the semiconductor industry, where a wealth of knowledge is already available regarding their integration with conventional semiconductors. In another experiment, Tsui *et al.*³⁵ discovered new Ge-based magnetic semiconductors from the Co–Mn–Ge ternary compositional phase diagram using combinatorial molecular beam epitaxy. In particular, the compound Co_{0.1}Mn_{0.02}Ge_{0.88} was found to have a Curie temperature as high as 280 K and large magnetoresistance effects. The mapping of ternary metallic alloys has also led to the discovery of new composition regions of ferromagnetic shape memory alloys¹⁷.

High-throughput catalysis

Catalysis is a ubiquitous process in the modern world, and there is a perennial need to improve and discover new catalysts. Heterogeneous catalysts are multifunctional materials composed of several active components, promoters, and a high-surface-area support material. The compositional parameter space associated with them is therefore very large. In addition, one also needs to consider a wide variety of parameters related to the method of preparation, as well as reaction conditions to which a given catalyst could be subjected, which increases the total number of possible

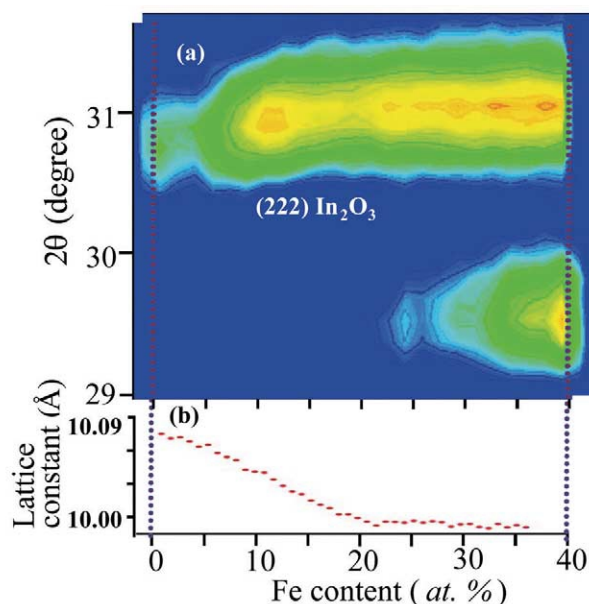


Fig. 3 (a) XRD intensity mapping of a dilute magnetic oxide thin film (In_{1-x}Fe_x)₂O_{3-δ} (*x* = 0–0.4) composition spread. (b) Plot of Vegard's law (lattice constant versus Fe concentration). The continuous change in lattice constant up to ~20% Fe indicates very high solubility. (Reprinted with permission from³⁴. © 2005 American Institute of Physics.)

experimental combinations even more. The screening of catalytic materials via high-throughput techniques started in the 1980s³⁶. In the past decade, the field has experienced significant growth, with multimillion dollar investments by almost all major chemical and petrochemical companies. High-throughput studies of heterogeneous catalysts consist of three components – rapid catalyst synthesis, high-throughput testing of catalyst materials, and appropriate data processing and information mining techniques – which feed back into the synthesis.

For primary screening experiments, libraries are typically synthesized via radio frequency sputtering, pulsed laser deposition, molecular beam epitaxy, or chemical vapor deposition^{37,38}. However, it can be difficult to extrapolate the catalytic properties derived from such model thin-film libraries to much more realistic supported catalyst materials, where a typical synthesis requires phase chemistry and solutions of high-surface-area support materials. Therefore, most work in high-throughput catalysis is now performed on high-surface-area materials, which allow much easier scale-up. To this end, liquid precursors can be dispensed with automated robots to synthesize libraries of more realistic catalytic materials. However, the synthesis of supported catalysts (powders) has a multitude of variables, including precursor materials, support materials, temperature, and drying and calcination parameters. All these variables must be screened and optimized for the particular system under study.

One of the first approaches in high-throughput screening of supported catalysis (powders) used an infrared camera to analyze the temperature of catalyst pellets under reaction conditions^{39–41}. Resonance-enhanced multiphoton ionization (REMPI) was developed to rank various catalysts for the conversion of cyclohexane to benzene^{42,43}. One of the most popular analytical tools is mass spectrometry because of its speed of analysis, maturity of technology, and versatility. Various approaches have been developed to transport the reaction products corresponding to different catalysts to the mass spectrometer in order to facilitate high-throughput operation, ranging from switching valves^{44–46} to *x,y,z* motion control devices^{47–52}. Various other analytical methods have been used, including gas chromatography^{53–65}, gas sensors⁶⁶, and others^{46,67–72}. Fourier transform infrared (FTIR) imaging, which incorporates a focal plane array (FPA) detector into a standard FTIR instrument, allows the collection of spatially

resolved IR spectra and is a chemically sensitive, quantitative, and parallel analytical technique applied to high-throughput experimentation^{46,73–75}. Recently, this analytical approach has been extended to the analysis of multiple transient reactions in parallel⁷⁶.

Advanced experimental design in catalysis

Even with the development of sophisticated high-throughput techniques, it is frequently unfeasible to collect data for all experimental combinations. Experimental design strategies can reduce the number of experiments required to sample the parameter space^{37,77–80}. Approaches include standard statistical design techniques, such as response surface methodology^{44,81} and D-optimal designs⁸². Other approaches used to guide high-throughput experimentation include the use of artificial neural networks^{83,84}, a holographic strategy⁸⁵, and factor-based methods from chemometrics^{86,87}. Caruthers *et al.*⁸⁸ have investigated the process of analyzing high-throughput data to extract chemical understanding using a process termed 'knowledge extraction'.

A good example of the application of statistical design to high-throughput experimentation is recent work on the optimization of nitrous oxide (NO_x) storage and reduction (NSR) catalysts^{81,89}. It is difficult to reduce NO_x under the oxidizing conditions present in the exhaust of lean-burn gasoline and diesel engines. NSR catalysts are designed to store NO_x during fuel-lean cycles and reduce the stored NO_x during a subsequent fuel-rich cycle. Fig. 4 shows the concentration profiles for NO₂ and CO in the effluent of one reactor, when switching from simulated fuel-lean to fuel-rich exhaust conditions, as measured by FTIR imaging^{90,91}. Concentrations are calculated directly from the IR spectra using chemometric methods. The NO₂ band (around 1600 cm⁻¹) decreases with time, while the CO band (around 2143 cm⁻¹) becomes much stronger. Using this approach, 16 catalysts were tested in parallel. Fig. 5 shows spectral images for all 16 catalysts, as seen by the FPA detector, for CO and NO₂ for the same switch in exhaust conditions. The intensity, as seen in the IR images, for the corresponding infrared (IR) band allows rapid analysis of the effluent composition in different reactors.

Generally, it is difficult to develop microkinetic models for such complex catalytic systems, but one can tackle the

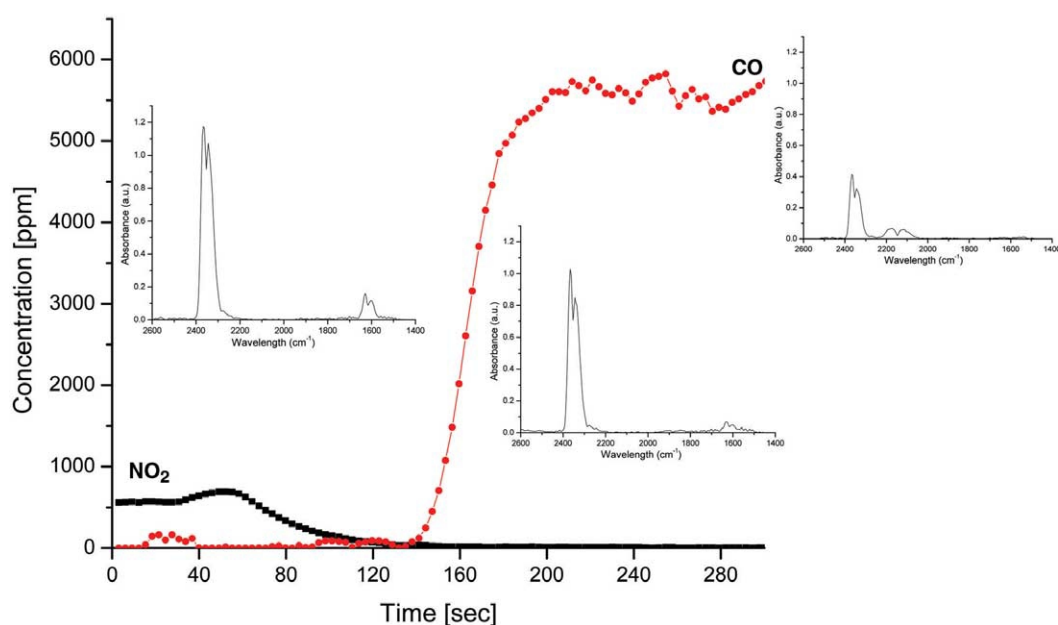


Fig. 4 Concentration profile for NO_2 and CO during a switch from fuel-lean to fuel-rich conditions for a typical NSR catalyst. NO_2 decreases and CO increases with time.

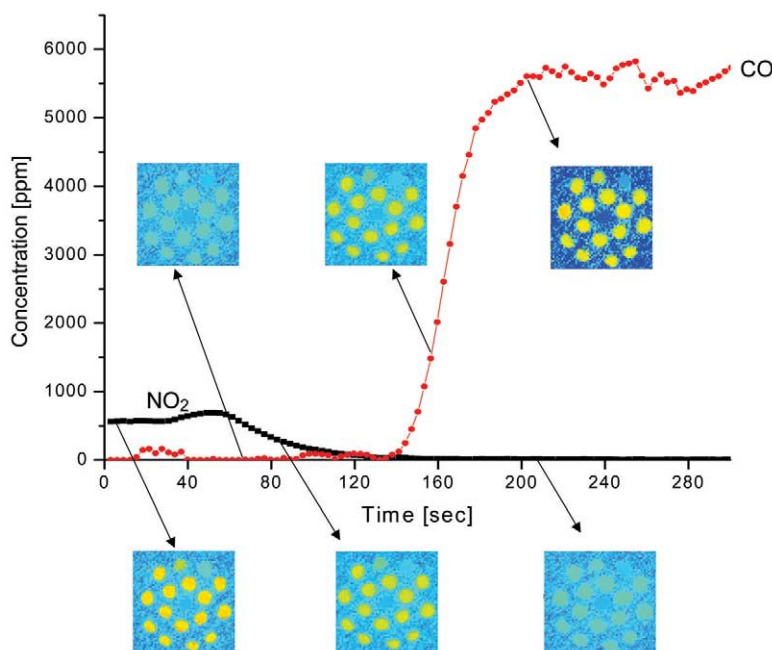


Fig. 5 Concentration profiles for CO and NO_2 with actual images of catalyst effluent in the gas-phase array. Catalyst performance can be judged easily from the spectral images: red implies highly active; yellow means moderately active; and blue means not active at all.

problem using empirical models developed via the statistical design of experiments. Fig. 6 shows a slice through one such general response surface model, developed for Pt/Ba/Fe-based NSR catalysts using high-throughput data from IR imaging. The statistical model describes the performance of the catalyst (e.g. NO_x storage) as a function of the following variables: the amount of active metals

(Pt, Ba, and Fe) and the reaction conditions. This statistical methodology is used to optimize catalyst formulation for a given set of reaction conditions, or vice versa. Experimental design techniques are beneficial for all stages of the high-throughput experimentation process and can assist in maximizing the information that is obtained from the experiments performed.

$$\begin{aligned}\text{NO}_x \text{ Storage } (\pm 13.4) &= 121(\pm 21) * Pt - 96(\pm 19) * Pt^2 + 2.7(\pm 1.4) * Ba - 0.15(\pm 0.09) * Ba^2 \\ \text{N}_2\text{O Prod. } (\pm 3.1) &= 2.6(\pm 1.6) + 26.6(\pm 5.0) * Pt - 22.2(\pm 4.5) * Pt^2 + 0.7(\pm 0.3) * Ba \\ &\quad - 0.05(\pm 0.02) * Ba^2 + 0.07(\pm 0.03) * Ba * Fe\end{aligned}$$

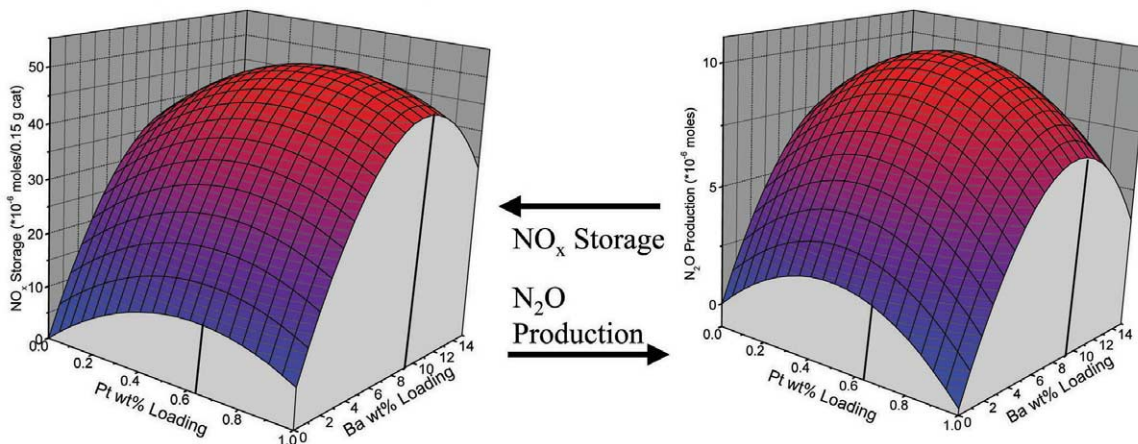


Fig. 6 Prediction of the general response surface model, incorporating the effect of reaction conditions and catalyst composition, for $T = 598 \text{ K}$, $\text{NO} = 0.2\%$, $\text{CO} = 1.0\%$, and $\text{O}_2 = 8\%$ as a function of catalyst composition.

High-throughput techniques also speed the discovery of new catalyst formulations. For example, Lauterbach and coworkers^{92,93} recently disclosed a noble-metal-free formulation for NSR catalysts developed entirely using a high-throughput approach. It was found that an Al_2O_3 -supported catalyst containing 5% w/w Co and 15% w/w Ba is just as effective as conventional NSR catalyst formulations that contained 1% Pt. In addition, adding 1% Pt to Co-Ba catalysts produced a material with twice the NO_x storage capacity of traditional Pt-based NSR catalysts.

The softer side of combinatorial methods: polymers and organic materials

The early adoption of combinatorial methods by the pharmaceutical industry resulted in a strong foundation of parallel organic synthetic routes and techniques for the rapid screening of organic molecules for drug activity. Accordingly, researchers developing new polymers and organic materials took notice of the potential that combinatorial and high-throughput methods hold for accelerating the advance of complex systems such as coatings, structural plastics, personal-care products, biomaterials, and nanostructured materials. However, the combinatorial techniques devised for drug discovery are rarely geared for direct use in organic materials applications. Consequently, organic materials scientists and engineers have

undertaken research aimed at adapting high-throughput methods for their needs.

Combinatorial polymer synthesis provides libraries of new polymers for the high-throughput screening of materials properties. Moreover, combinatorial approaches can also be used for the rapid optimization of reaction parameters (temperature, catalysts, etc.) for the polymerization of specific products. Hence, researchers at the Dutch Polymer Institute (DPI) have adapted and tested commercially available automated parallel reactors for polymerization, and illustrated their use in laboratory-scale combinatorial workflows⁹⁴. DPI research has extended the use of automated reactors to controlled radical polymerization (CRP) and emulsion polymerization⁹⁵, and, recently, to the rapid optimization of cationic polymerization⁹⁶. A different strategy, developed at the National Institute of Standards and Technology (NIST) Combinatorial Methods Center, uses microfluidic technology for polymer library synthesis⁹⁷. For example, the so-called CRP chip (Fig. 7, top)⁹⁸ produces continuous polymer streams that systematically vary in their molecular weight, composition, and architecture. Another fluidic design produces organic droplet 'reactors' (Fig. 7, bottom)⁹⁹, which can produce arrays of polymer microdroplets. Continuous gradient methods can also be used to synthesize libraries of surface-grafted polymers and graded polymer films. Following the lead of Genzer¹⁰⁰ and others, recent developments in gradient surface-polymerization exploit the

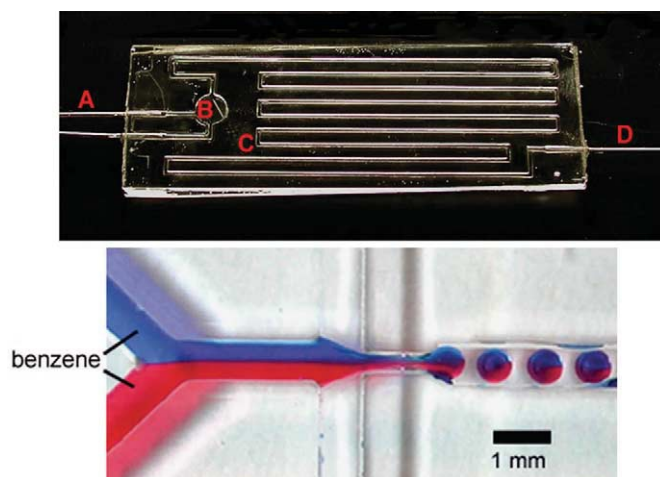


Fig. 7 Microfluidic devices for the combinatorial synthesis of polymer libraries. (Top) Controlled radical polymerization chip, capable of producing continuous gradient streams of homopolymer and block copolymers: (A) Monomer solution inputs; (B) mixing chamber; (C) Polymerization channel; and (D) output. (Reprinted with permission from⁹⁸, © 2004 American Chemical Society). (Bottom) Microfluidic device for creating organic microdrop reactors, here creating mixed droplets of benzene in a water matrix. (Reprinted with permission from⁹⁹, © 2005 American Chemical Society.)

precise flow control that is inherent to microfluidics¹⁰¹. Another strategy, which combines the deposition of continuous composition gradient films of polymer precursors and graded photopolymerization, shows promise for the discovery and optimization of new dental resins¹⁰².

High-throughput measurements of mechanical properties

Historically, mechanical testing has been slow and oriented toward single specimens. Also, rapid mechanical measurement methods, such as nanoindentation¹⁰³, that show promise for libraries of harder materials are often not suitable for polymers. Recent research has produced notable progress, and highlights include a parallel impact tester developed by Meredith and coworkers^{104,105} suitable for rapid testing of polymer film libraries, and used recently to map structure-property-processing relationships in polyurethane ureas. In addition, NIST has developed a suite of high-throughput techniques for polymer films and adhesives. This includes a rapid modulus measurement technique that exploits a wrinkling instability inherent to thin-film laminates¹⁰⁶. A probe tack test¹⁰⁷ and a modified peel test¹⁰⁸ – each geared toward the assessment of gradient adhesive libraries – have also been developed, as well as a 'multilens' adhesion tester capable of up to 1600 simultaneous Johnson-Kendall-Roberts type measurements¹⁰⁹.



Fig. 8 A 24 channel acoustic wave sensor array for the parallel measurement of coatings performance properties. (Reprinted with permission from¹¹², © 2004 Wiley-VCH.)

Coating formulations and performance testing

Manufacturers of organic coatings, such as Bayer¹¹⁰ and BASF¹¹¹, were among the first to adapt combinatorial methods to materials discovery. Today, industrial coatings research continues to be at the forefront of combinatorial technology. A prime example is GE Global Research, which has produced groundbreaking approaches for the combinatorial formulation of coatings materials and high-throughput coatings performance testing. For instance, GE has developed 24-channel acoustic wave sensor arrays (see Fig. 8) for coatings measurements¹¹². Capable of sensing minute mass changes in coatings formulations deposited on them, these multifunctional devices can perform 24 parallel measurements of properties such as vapor absorption, solvent resistance, and abrasion resistance.

A good example of the growth in programs focusing on high-throughput coatings development is at North Dakota State University¹¹³. The key thrust of their research is to develop a single nontoxic coating system for ship hulls that will resist attachment of a huge number of different marine organisms, such as barnacles, tubeworms, algae, diatoms, and mussels. This is an ambitious aim, but combinatorial approaches are allowing them to develop promising leads in siloxane-urethane and other coating materials.

Organic electronic materials

The drive toward lighter, flexible, and/or printable electronic devices has sparked interest in polymer and organic materials for these applications. While candidate organic electronic

(OE) materials for organic light emitting diodes (OLEDs), transistors, and other device components are being developed with increasing regularity, so too are technical barriers to their robust application. A promising route for accelerating the development of OE materials lies in the use of ink-jet technology. Indeed, ink jets are already widely used for printing OE devices¹¹⁴. When properly engineered, ink jets are also well suited to creating combinatorial libraries of OE materials, including spot or line arrays, multilayers, and collections of device prototypes. DPI researchers have worked to adapt ink-jet techniques to the deposition of polymer arrays⁹⁵, including libraries of organic donor/acceptor heterojunctions that could form new polymer-based solar cells¹¹⁵. As part of their US Army-Funded Flexible Display Center, Arizona State University researchers are also employing combinatorial ink-jet techniques, most recently toward the development of polymer OLED devices¹¹⁶. Continuous gradient techniques also play a role in combinatorial studies of OE materials. For example, Meredith and coworkers¹¹⁷ used orthogonal thickness gradients to map film stability in bilayers of conductive and insulating polymers, resulting in the discovery of a previously unknown film dewetting phenomenon. Mirsky and coworkers¹¹⁸ have also used continuous-gradient techniques to deposit libraries of conducting polymers along microfabricated arrays of interdigitated metal electrodes. Rapid serial electrical measurements that use an automated dual 2/4 point probe allow the swift mapping of contact resistance in metal/polymer/metal systems.

Concluding remarks

Combinatorial methodology is quickly finding its way into mainstream materials research and optimization techniques

in a diverse range of fields. Massive arrays of materials are now being produced as libraries in order to swiftly survey a large and complex landscape of composition and other parameter spaces. The goal is not just to discover new compounds, but often to quickly extract 'knowledge' in the form of composition-structure-property relationships. The examples shown here provide snapshots of how the basic idea of high-throughput experimentation has unfolded in recent years in the three areas in which it is most commonly applied: electronic materials, catalysis, and polymeric materials. Our discussion underscores the highly instrumentation-intensive nature of the field, especially in the form of various rapid screening tools. The basic notion of high-throughput experimentation, however, is a straightforward one. Its scope is far-reaching and widely applicable to a variety of problems, ranging from gradient synthesis of complex polymer materials to functional phase diagram mapping in ternary compounds. The technique is also being applied to cutting-edge research such as the search for hydrogen storage materials¹¹⁹ and the synthesis of nanoparticles^{120,121}. Combinatorial methodology is often hailed as a paradigm shift, but in many ways it merely reflects innovation and advances in materials synthesis and characterization methods toward achieving the same old goal of speeding up experiments. Although it is by no means a panacea, we expect that the general high-throughput concept will become more prevalent and will be, eventually, a firmly established component of materials science research. **MT**

Acknowledgments

I.T. acknowledges support from NSF through DMR0094265 (CAREER), NSF DMR 0231291, and MRSEC DMR 00-80008, and from ONR through N000140110761 and N000140410085. J.L. acknowledges support from NSF through 0343758-CTS and 0071730-CTS. For more information on the NIST Combinatorial Methods Center, see www.nist.gov/combi.

REFERENCES

1. Xiang, X.-D., and Takeuchi, I., (eds.), *Combinatorial Materials Synthesis*, Marcel Dekker, (2003)
2. Amis, E. J., et al., (eds.), *MRS Bull.* (2002) **27** (4), 295
3. Xiang, X.-D., *Ann. Rev. Mater. Sci.* (1999) **29**, 149
4. Schubert, U. S., and Amis, E. J., (eds.), *Macromol. Rapid Comm., Special issue on Combinatorial Research and High-Throughput Experimentation in Polymer and Materials Research* (2003) **24** (1)
5. Koinuma, H., and Takeuchi, I., *Nat. Mater.* (2004) **3** (7), 429
6. Xiang, X.-D., et al., *Science* (1995) **268**, 1738
7. Christen, H. M., et al., *Meas. Sci. Technol.* (2005) **16** (1), 21
8. Fleischauer, M. D., et al., *Meas. Sci. Technol.* (2005) **16** (1), 212
9. Wang, Q., *Meas. Sci. Technol.* (2005) **16** (1), 162
10. Takahashi, R., et al., *Meas. Sci. Technol.* (2005) **16** (1), 292
11. Tsui, F., and He, L., *Rev. Sci. Instrum.* (2005) **76**, 062206
12. Choo, J. O., et al., *Rev. Sci. Instrum.* (2005) **76**, 062217
13. Wang, J., et al., *Science* (1998) **279**, 1712
14. Koinuma, H., *Solid State Ionics* (1998) **108** (1-4), 1
15. Semancik, S., and Cavicchi, R. E., *Acc. Chem. Res.* (1998) **31** (5), 279
16. Ludwig, A., et al., *Meas. Sci. Technol.* (2005) **16** (1), 111
17. Takeuchi, I., et al., *Nat. Mater.* (2003) **2** (3), 180
18. Famodu, O. O., et al., *Mater. Trans., JIM* (2005) **45** (18), 173
19. Gao, C., et al., *Meas. Sci. Technol.* (2005) **16** (1), 248
20. van Dover, R. B., et al., *Nature* (1998) **392**, 162
21. Chang, H., et al., *Appl. Phys. Lett.* (1999) **74** (8), 1165
22. Fukumura, T., et al., *Appl. Phys. Lett.* (2000) **77** (21), 3426

23. Yoo, Y. K., *et al.*, *Intermetallics* (2001) **9** (7), 541
24. Yoo, Y. K., and Tsui, F., *MRS Bull.* (2002) **27** (4), 316
25. Yu, M., *et al.*, *J. Appl. Phys.*, in press
26. Fleet, E., Design and applications of a cryo-cooled scanning SQUID microscope, *PhD Thesis*, University of Maryland, 2000
27. Aronova, M. A., Combinatorial investigation of magnetic materials, *PhD Thesis*, University of Maryland, 2004
28. Chang, K.-S., *et al.*, *Appl. Phys. Lett.* (2004) **84** (16), 3091
29. Chambers, S. A., and Yoo, Y. K., (eds.), *MRS Bull.* (2003) **28** (10), 706
30. Matsumoto, Y., *et al.*, *MRS Bull.* (2003) **28** (10), 734
31. Dietl, T., *et al.*, *Science* (2000) **287**, 1019
32. Matsumoto Y., *et al.*, *Science* (2001) **291**, 854
33. Yoo, Y. K., *et al.*, *Appl. Phys. Lett.* (2005) **86**, 042506
34. He, J., *et al.*, *Appl. Phys. Lett.* (2005) **86**, 052503
35. Tsui, F., *et al.*, *Phys. Rev. Lett.* (2003) **91** (17), 177203
36. Thomas, R., *et al.*, *J. Mol. Catal.* (1980) **8** (1-3), 161
37. Cavse, J. N., *Experimental Design for Combinatorial and High Throughput Materials Development*, Wiley-VCH, Hoboken, NJ, (2003)
38. Potyrailo, R. A., and Amis, E. J., (eds.), *High Throughput Analysis: A Tool of Combinatorial Materials Science*, Kluwer, New York, (2003)
39. Moates, F. C., *et al.*, *I&EC Res.* (1996) **35** (12), 4801
40. Holzwarth, A., *et al.*, *Angew. Chem. Int. Ed.* (1998) **37** (19) 2644
41. Reetz, M. T., *et al.*, *Angew. Chem. Int. Ed.* (2000) **39** (7), 1236
42. Senkan, S. M., *Nature* (1998) **394**, 350
43. Senkan, S. M., and Ozturk, S., *Angew. Chem. Int. Ed.* (1999) **38** (6), 791
44. Wang, H., *et al.*, *J. Comb. Chem.* (2003) **5** (6), 802
45. Hahndorf, I., *et al.*, *Chem. Eng. J.* (2002) **89** (1-3), 119
46. Snively, C. M., *et al.*, *Catal. Today* (2001) **67** (4), 357
47. Klein, J., *et al.*, *Catal. Today* (2003) **81** (3), 329
48. Scheidtmann, J., *et al.*, *Appl. Catal., A* (2001) **222** (1-2), 79
49. Orschel, M., *et al.*, *Angew. Chem. Int. Ed.* (1999) **38** (18) 2791
50. Cong, P., *et al.*, *Angew. Chem. Int. Ed.* (1999) **38** (4) 484
51. Senkan, S., *et al.*, *Angew. Chem. Int. Ed.* (1999) **38** (18) 2794
52. Claus, P., *et al.*, *Catal. Today* (2001) **67** (4), 319
53. Li, W., *et al.*, *Catal. Today* (2003) **81** (3), 437
54. Corma, A., *et al.*, *Catal. Today* (2003) **81** (3), 495
55. Huybrechts, W., *et al.*, *Appl. Catal., A* (2003) **243** (1), 1-13
56. Serra, J. M., *et al.*, *Catal. Today* (2003) **81** (3), 425
57. Yamada, Y., *et al.*, *Appl. Catal., A* (2003) **254** (1), 45
58. Serra, J. M., *et al.*, *Appl. Catal., A* (2003) **239** (1-2), 35
59. Hagemeyer, A., *et al.*, *Appl. Catal., A* (2002) **227** (1-2), 43
60. Hoffmann, C., *et al.*, *J. Catal.* (2001) **198** (2), 348
61. Desrosiers, P., *et al.*, *Catal. Today* (2001) **67** (4), 397
62. Reetz, M. T., *et al.*, *Catal. Today* (2001) **67** (4), 389
63. Al-Saedi, J. N., and Gulians, V. V., *Appl. Catal., A* (2002) **237** (1-2), 111
64. Gomez, S., *et al.*, *Appl. Catal., A* (2003) **254** (1), 77
65. Desrosiers, P., *et al.*, *Catal. Today* (2003) **81** (3), 319
66. Yamada, Y., *et al.*, *Catal. Today* (2001) **67** (4), 379
67. Su, H., and Yeung, E. S., *J. Am. Chem. Soc.* (2000) **122** (30), 7422
68. Senkan, S., *et al.*, *Appl. Catal., A* (2003) **254** (1), 97
69. Kubanek, P., *et al.*, *J. Comb. Chem.* (2004) **6** (3), 420
70. Johann, T., *et al.*, *Catal. Today* (2003) **81** (3), 449
71. Busch, O. M., *et al.*, *J. Am. Chem. Soc.* (2002) **124** (45), 13527
72. Staiger, C. L., *et al.*, *J. Am. Chem. Soc.* (2003) **125** (33), 9920
73. Snively, C. M., *et al.*, *Optics Lett.* (1999) **24** (24), 1841
74. Snively, C. M., *et al.*, *J. Comb. Chem.* (2000) **2** (3), 243
75. Snively, C. M., *et al.*, *Angew. Chem. Int. Ed.* (2001) **40** (16), 3028
76. Hendershot, R. J., *et al.*, *Angew. Chem. Int. Ed.* (2003) **42** (10), 1152
77. Maxwell, I. E., *et al.*, *Top. Catal.* (2003) **24** (1-4), 125
78. Harmon, L., *J. Mater. Sci.* (2003) **38** (22), 4479
79. Spivack, J. L., *et al.*, *Appl. Catal., A* (2003) **254** (1), 5
80. Bricker, M. L., *et al.*, *Appl. Surf. Sci.* (2004) **223** (1-3), 109
81. Hendershot, R. J., *et al.*, *Catal. Today* (2004) **98** (3), 375
82. Urschey, J., *et al.*, *Appl. Catal., A* (2003) **252** (1), 91
83. Corma, A., *et al.*, *ChemPhysChem* (2002) **3** (11), 939
84. Rodemerck, U., *et al.*, *Appl. Surf. Sci.* (2004) **223** (1-3), 168
85. Végvári, L., *et al.*, *Catal. Today* (2003) **81** (3), 517
86. Kramer, R., *Chemometric Techniques for Quantitative Analysis*, Marcel Dekker, New York, (1998), 203
87. Otto, M., *Chemometrics: Statistics and Computer Application in Analytical Chemistry*, Wiley-VCH, Weinheim, (1999), 314
88. Caruthers, J. M., *et al.*, *J. Catal.* (2003) **216** (1-2), 98
89. Takahashi, N., *et al.*, *Catal. Today* (1996) **27** (1-2), 63
90. Hendershot, R. J., *et al.*, *Appl. Catal., A* (2003) **254** (1), 107
91. Hendershot, R. J., *et al.*, *Meas. Sci. Technol.* (2005) **16** (1), 302
92. Hendershot, R. J., *et al.*, *Appl. Catal., B* (2005), submitted
93. Vijay, R., *et al.*, *Catal. Commun.* (2005) **6** (2), 167
94. Hoogenboom, R., and Schubert, U. S., *Rev. Sci. Instrum.* (2005) **76** (6), 062202
95. Zhang, H., *et al.*, *Meas. Sci. Technol.* (2005) **16** (1) 203
96. Hoogenboom, R., *et al.*, *J. Polym. Sci., Part A: Polym. Chem.* (2005) **43** (7), 1487
97. Cabral, J. T., *et al.*, *Langmuir* (2004) **20** (23), 10020
98. Wu, T., *et al.*, *J. Am. Chem. Soc.* (2004) **126** (32), 9880
99. Cygan, Z. T., *et al.*, *Langmuir* (2005) **21** (8), 3629
100. See, e.g., Genzer, J., *J. Adhesion* (2005) **81** (3-4), 417 and references therein
101. Xu, C., *et al.*, *Macromolecules* (2005) **38** (1), 6
102. Johnson, P. M., *et al.*, *Polymer* (2005) **46** (10), 3300
103. Warren, O. L., *et al.*, *Rev. Sci. Instrum.* (2005) **76**, 062209
104. Sormana, J.-L., *et al.*, *Rev. Sci. Instrum.* (2005) **76**, 062214
105. Sormana, J.-L., and Meredith, J. C., *Macromolecules* (2004) **37** (6), 2186
106. Stafford, C. M., *et al.*, *Nature Mater.* (2004) **3** (8), 545
107. Moon, S.-H., *et al.*, *Rev. Sci. Instrum.* (2005) **76**, 062210
108. Chiche, A., *et al.*, *Meas. Sci. Technol.* (2005) **16** (1), 183
109. Forster, A. M., *et al.*, *Meas. Sci. Technol.* (2005) **16** (1), 81
110. Wicks, D.A., and Bach, H., *Proc. 29th Int. Waterborne, High-Solids, and Powder Coatings Symp.* (2002), 1
111. Iden, R., *et al.*, *Macromol. Rapid Commun.* (2003) **24** (1), 63
112. Potyrailo, R. A., *Macromol. Rapid Commun.* (2004) **25** (1), 78
113. Webster, D. C., *J. Coatings Technol.* (2005) **2** (15), 24
114. Sirringhaus, H., *et al.*, *Science* (2000) **290**, 2123
115. Marin, V., *et al.*, *Macromol. Rapid Commun.* (2005) **26** (4), 319
116. Yoshioka, Y., *et al.*, *Macromol. Rapid Commun.* (2005) **26** (4), 238
117. Chattopadhyay, S., and Meredith, J. C., *Meas. Sci. Technol.* (2005) **16** (1), 128
118. Kulikov, V., *et al.*, *Meas. Sci. Technol.* (2005) **16** (1), 95
119. Olk, C. H., *Meas. Sci. Technol.* (2005) **16** (1), 14
120. Bao, J., *et al.*, *J. Comb. Chem.* (2004) **6** (5), 699
121. Baek, S.-H., *et al.*, *Meas. Sci. Technol.* (2005) **16** (1), 54