

What are the defining discoveries, moments of inspiration, or shifts in understanding that have shaped the dynamic field of materials science we know today? Here's what we think are the most significant.

Jonathan Wood *Editor, Materials Today*

We've assembled a list of the top ten advances in materials science over the last 50 years. We thought long and hard. We sought the advice of our editorial advisory panel and asked leaders in the field to add their own contributions. We hope the results are interesting and thought-provoking.

In making the final selection, we have tried to focus on the advances that have either changed our lives or are in the process of changing them. This is arguable, of course. Should an advance alter all our daily lives, or does fundamentally changing the research arena count? What about discoveries that can be clearly attributed to a certain date and investigator, or those developments that have come about incrementally through the efforts of many? Where does materials science stop and electronics, physics, or chemistry begin? And how do you assess the value of things like plastic bags? Undeniably they are a boon for carrying shopping but now also an item of scorn for energy and waste reasons.

Instead of ruling any of these out, we've tried to come up with a balanced selection. In doing so, we hope to start some debate about the discoveries that most mark out today's materials science. Let us know what we've missed. If you're incredulous that organic electronics or high-temperature superconductors aren't in the top ten, tell us why. Should Kevlar, Post-it notes, float glass, or F1 racing tires be in the list? What will define the next 50 years of materials science?

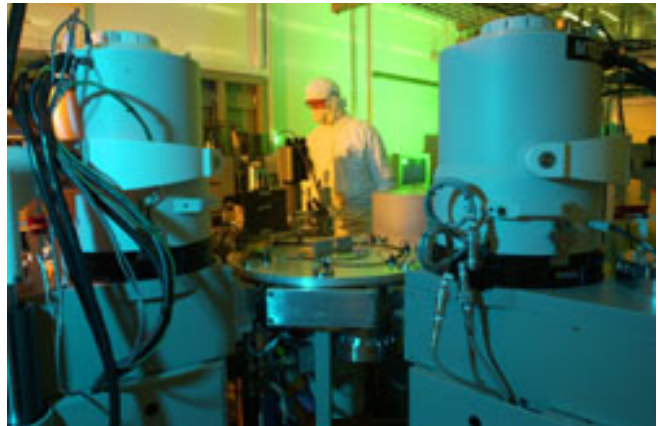
If you believe materials scientists are unsung heroes, that our work goes unnoticed and unheralded, here is your ammunition. With our time limit of 50 years, the list is of immediate relevance. It is about how materials science is affecting our world today, now.

1. International Technology Roadmap for Semiconductors

OK, so it's not a research discovery, solely a way of organizing research priorities and planning R&D. But the International Technology Roadmap for Semiconductors (ITRS) is a remarkable achievement. It sets out goals for innovation, technology needs, and measures for progress that all can sign up to in the fiercely competitive microelectronics industry.

A mixture of science, technology, and economics, it's hard to see how the ITRS could do better in driving forward advances in this area, whether it's in materials, characterization, fabrication, or device design. And it is an appropriate first choice in this list. Not only is electronics absolutely critical to our modern world, progress in semiconductor processing and advances in materials science have gone hand-in-hand for the last 50 years.

Let's just hope the International Panel on Climate Change enjoys similar success in driving innovation and reaching agreed goals.

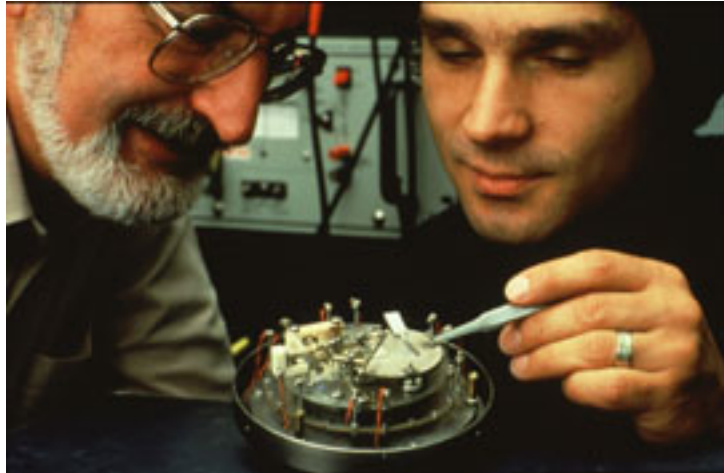


Semiconductor research is guided by the ITRS. (Courtesy of SEMATECH.)

2. Scanning probe microscopes

The invention of the scanning tunneling microscope (STM) by Heinrich Rohrer and Gerd Binnig at IBM's Zurich Research Laboratory was deservedly awarded the Nobel Prize for Physics in 1986.

Not only is this a new microscopy technique – remarkable enough in itself – but it provides a way to probe the local properties of a sample directly with nanometer resolution. Quickly followed by the atomic force microscope (AFM), this new access to the nanoscale world, arguably brought about the current ubiquity of nanotechnology. The invention immeasurably increased our abilities at this scale.



Rohrer (left) and Binnig (right) with a first-generation scanning tunneling microscope. (Courtesy of IBM Zurich Research Laboratory.)

3. Giant magnetoresistive effect

The 2007 Nobel Prize for Physics went jointly to Albert Fert of Université Paris-Sud, France, and Peter Grünberg of Forschungszentrum Jülich, Germany, for independently discovering the giant magnetoresistance (GMR) effect in 1988. So it is no surprise to see this advance on our list.

GMR describes the large change in electrical resistance seen in stacked layers of magnetic and nonmagnetic materials when an external magnetic field is altered. Thanks largely to the subsequent work of Stuart Parkin and coworkers at IBM Research, the phenomenon has been put to great effect in the read heads in hard disk drives. These devices are able to read out the information stored magnetically on a hard disk through changes in electrical current.

The high sensitivity of GMR read heads to tiny magnetic fields means that the magnetic bits on the hard disk can be greatly reduced in size. The phenomenal expansion in our ability to store data that we continue to witness today can be traced back to this discovery.

4. Semiconductor lasers and LEDs

The development of semiconductor lasers and light-emitting diodes (LEDs) in 1962 is a great materials science story. They are now the basis of telecommunications, CD and DVD players, laser printers, barcode readers, you name it. The advent of solid-state lighting is also likely to make a significant contribution to reducing our energy usage.

5. National Nanotechnology Initiative

Bill Clinton gets some of the credit for the fifth materials science development on our list. He was the US president who announced the establishment of the National Nanotechnology Initiative (NNI) in 2000, a US federal, multi-agency research program in nanoscale science and technology.

The NNI has had an immense impact. It cemented the importance and promise of a nascent, emerging field, establishing it immediately as the most exciting area in the whole of the physical sciences. Nanotechnology simultaneously gained an identity, a vision, and a remarkable level of funding through the initiative. It also established a method of funding interdisciplinary science in

such a way that the rest of the world would have to try to match.

Mihail C. Roco of the National Science Foundation was one of those who was involved in the initial NNI vision setting and national organizational efforts. “During 1997 to 1999, I worked with an initially small group including Stan Williams, Paul Alivisatos, James Murday, Dick Siegel, and Evelyn Hu,” recalls Roco. “We envisioned a ‘new industrial revolution’ powered by systematic control of matter at the nanoscale. With this vision, we built a national coalition involving academia, industry, and a group of agencies that become the nucleus of the NNI, launched in 2000.”

The NNI now involves 26 independent agencies and has an estimated budget of ~\$1.5 billion in 2008. It has been the largest single investor in nanotechnology research in the world, providing over \$7 billion in the last seven years. Now 65 countries have national research focus projects on nanotechnology, while industry nanotechnology R&D has exceeded that of governments worldwide. The global nano-related R&D budget was in excess of \$12 billion in 2007.

On behalf of the interagency group, Roco proposed the NNI on March 11, 1999 at the White House Office of Science and Technology Policy (OSTP). The fear of many was that there was little chance of nanotechnology becoming a national priority program. Surely it would be perceived as being of interest just to a small group of researchers? Instead, by defining nanotechnology as a broad platform for scientific advancement, education, medicine, and the economy, the NNI was approved with a budget of \$489 million in 2001. “The NNI was prepared with the same rigor as a science project,” says Roco.

6. Carbon fiber reinforced plastics

The last 50 years have seen advanced composites take off – quite literally, in that many applications of these light but strong materials have been in aviation and aerospace. But modern composite materials have touched just about all industries, including transport, packaging, civil engineering, and sport. They can be found in Formula 1 cars, armor, and wind turbine rotor blades.

Leading the charge are carbon fiber reinforced plastics or, more properly, continuous carbon fiber organic-matrix composites. These materials bond extremely stiff, high-strength carbon fibers into a polymer matrix to give a combined material that is also exceptionally tough and light in weight.

The early 1960s saw the development of carbon fibers produced from rayon, polyacrylonitrile, and pitch-based precursors. The long, oriented aromatic molecular chains give the fibers exceptional strength and stiffness. This was a real gain over the amorphous glass fibers used previously in composite materials.

The development of carbon fibers, together with advances in design, modeling, and manufacturing, has given rise to composite materials with controlled, specific properties. “Rather than an engineer using a constant set of material characteristics, organic-matrix composites and the associated manufacturing methodology now enables the engineer to design the material for a specific application,” says Richard A. Vaia of the Air Force Research Laboratory. “The manufacturing science has opened up new frontiers, effectively



Carbon fiber-reinforced plastics were at the heart of this bike built by Lotus Engineering for the 1992 Barcelona Olympics. It helped Chris Boardman win gold. (Courtesy of Lotus.)

moving component design down to materials design.” The spectacular gain in performance has seen the increasing use of these materials despite the cost and increased difficulty in design, shaping, and recycling, such that the new Boeing 787 uses composites extensively in its wings and fuselage.

7. Materials for Li ion batteries

It is hard to remember how we coped before laptops and cellular phones came along. This revolution would not have been possible without a transition from rechargeable batteries using aqueous electrolytes, where H^+ is the working ion, to the much higher energy densities of Li ion batteries.

Li ion batteries required the development of novel electrode materials that satisfy a number of considerations. In particular, the cathode needs a lightweight framework structure with free volume in between to allow a large amount of Li ions to be inserted and extracted reversibly with high mobility.

The process of materials design and discovery involved a mixture of clever chemical and electrochemical intuition, rational assessment of the technical requirements, and substantial experimental effort, and is dominated by the work of John B. Goodenough and colleagues at the University of Oxford in the 1980s. They came up with the cathode material $LiCoO_2$ that Sony combined with a carbon anode in 1991 to give us the batteries that make possible the portable devices we know today. Work continues to develop cathode materials without the toxic Co and with three-dimensional framework structures like $LiFeO_4$ for environmentally benign, high-energy density batteries.

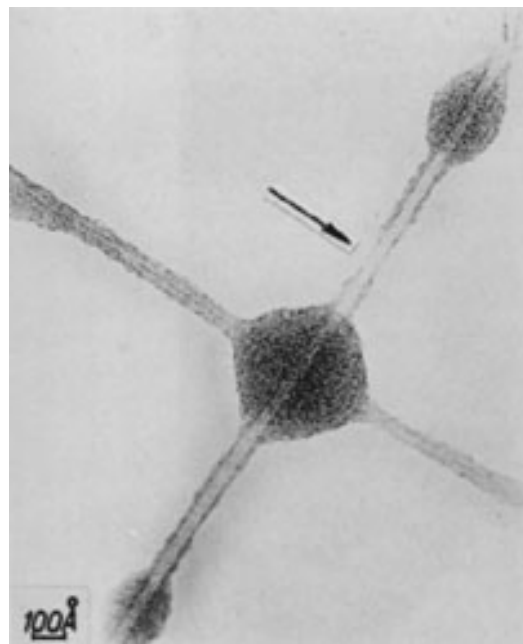
8. Carbon nanotubes

Although a discovery normally attributed to Sumio Iijima of NEC, Japan in 1991, the observation of nanotubes of carbon had actually been made on previous occasions. However, following on from the excitement of the discovery of C_{60} buckyballs in 1985 – a new form of carbon – Iijima’s observations of new fullerene tubes aroused great interest immediately.

Today, the remarkable, unique, and phenomenally promising properties of these nanoscale carbon structures have placed them right among the hottest topics of materials science. So why are they only at number eight in this list? Well, there still remains much to sort out in their synthesis, purification, large-scale production, and assembly into devices. And there’s also the very frustrating inability to manufacture uniform samples of nanotubes with the same properties.

9. Soft lithography

The ability to fabricate functional structures and working devices in different materials is central to the production of microelectronic devices, data-storage systems, and many other products. This process is almost exclusively carried out by highly specialized, complex, and very expensive photolithography equipment confined to the controlled environments of cleanrooms. How valuable, then, is the introduction of an alternative?



Viewgraph showing a single- or double-walled CNT published in 1976. (Reprinted with permission from Oberlin, A., *et al.*, *J. Cryst. Growth* (1976) **32**, 335. © 1976 Elsevier.)

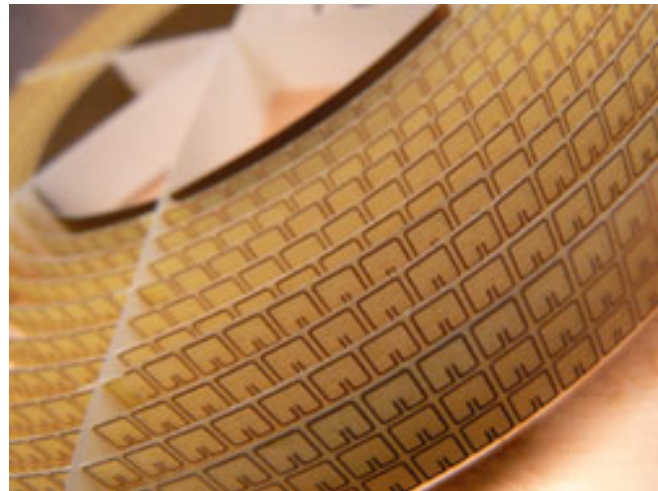
Soft lithography makes use of the simple, ancient concept of using a stamp to produce patterns again and again. It can be used on many different substrates, be they flat, curved, or flexible. What's more, soft lithography is cheap, offers nanoscale resolution, and can be applied to new areas in biotechnology and medicine.

The initial technique of microcontact printing (μ CP) was developed in 1993 at the lab of George Whitesides at Harvard University. "Microcontact printing has revolutionized many aspects of materials research," says Byron Gates of Simon Fraser University, Canada. "Molecules are transferred to a substrate using an elastomeric stamp. This poly(dimethylsiloxane) or PDMS stamp conforms to the substrate, unlike hard masks used in previous lithography techniques." In this way, molecules can be printed over large areas in well-defined patterns with features just 30 nm in size. As well as the transfer of small organic molecules, μ CP has been adapted to print solid materials directly, extending its capabilities into nanofabrication. Since 1993, μ CP has expanded into a suite of printing, molding, and embossing methods known as soft lithography. All of them use an elastomeric stamp to reproduce a pattern from a master template over and over again.

"All these techniques share one thing: the use of organic materials and polymers – 'soft matter' in the language of physicists," says Younan Xia of the University of Washington in St. Louis. "Soft lithography offers an attractive route to microscale structures and systems needed for applications in biotechnology, and most of them exceed the traditional scope defined by classic photolithography."

10. Metamaterials

The beginning of the new millennium brought great excitement when it was conclusively demonstrated that a material with a negative refractive index could exist. Light, or at least microwaves, would bend the 'wrong way' on entering this material, according to a standard understanding of Snell's law of refraction. This ended a long-standing argument over Veselago's prediction in the 1960s that materials simultaneously having a negative permeability and a negative permittivity would have a negative refractive index. At the same time, it opened up a perplexing new optical world full of counterintuitive results that can be explained using 19th century classical electromagnetism.



The metamaterial structure of an invisibility cloak that hides objects from microwave radiation. (Credit: David Schurig, Duke University.)

But the surprising optical properties don't arise from the material's composition as its structure. The first metamaterial was a composite of metal wires and split rings assembled on a lattice of printed circuit boards. It was an example of a metamaterial – an artificial structure of repeated micro-sized elements designed for specific properties.

"Metamaterials derive their properties as much from their internal structure as from their chemical composition," explains John Pendry of Imperial College London, UK. "Adding structure to chemistry as an ingredient greatly increases the range of properties that we can access. There is a new realization that metamaterials can give access to properties not found in nature."

Crucially, if the structure of the material is much smaller than the light's wavelength, then an overall permittivity and permeability of the material can still be used with Maxwell's equations to describe the electric and magnetic response of the material. Thin wire structures can generate a negative electrical response at gigahertz frequencies, while split-ring structures generate a

negative magnetic response. These structures were combined for the first time in 2000 by David Smith, Willie Padilla, and Shelly Schultz at the University of California, San Diego to make a negatively refracting material. “Now many people are going through a process of feverish invention as new possibilities are explored, pushing the concept up in frequency towards the visible and also down wards, even to create novel dc responses,” says Pendry.

“Theorists too have been inspired,” adds Pendry, who pointed out that a negative refractive index could be used to construct a ‘perfect lens’. Such lenses would have a resolution unlimited by fundamental physics of the design, and only limited by quality of manufacture. “A new approach to subwavelength imaging now rides on the back of the metamaterial concept,” he says. Several suggestions for invisibility cloaks to hide objects from electromagnetic radiation have also been made. All of these proposals imply the use of metamaterials to realize their designs.

“The first applications [of metamaterials] will be simple improvements of existing products,” Pendry expects. “For example, lightweight lenses for radar waves have been manufactured using metamaterials. Then entirely novel applications will follow, probably developed by the research students of today’s metamaterials researchers.”

The III-V laser and LED after 45 years

A significant fraction of the Earth’s population has, by now, seen an LED. But few are aware it is not a conventional light source, rather an electronic source related to the transistor.

As John Bardeen’s (one of the inventors of the transistor) first student and then colleague for 40 years, I heard him explain many times that it was not known until the transistor that a current could create a nonequilibrium electron-hole population in a semiconductor. Subsequently, electron-hole recombination could re-establish equilibrium, delivering light.

As we studied recombination for transistor reasons, we were on the path to the laser and LED, especially when we moved to the direct-gap III-V compounds. Studying GaAs for tunnel diodes in 1960–62, I was not happy with its 1.4 eV (infrared) bandgap. I learned how to shift GaAs towards GaP, to $\text{GaAs}_{1-x}\text{P}_x$ and red light wavelengths.

In 1962, a small number of us realized that the GaAs p-n junction might serve as the basis of a laser. But I wanted to work not in the infrared, but with $\text{GaAs}_{1-x}\text{P}_x$ in the visible region where the eye sees. I knew enough about lasers to know I needed a cavity to help my red p-n junctions become lasers.

My astute colleague at General Electric (GE), Bob Hall, was one step ahead of me. He made GaAs diodes with Fabry-Perot resonator edges, with the crystal itself the cavity – very clever! He preferred polishing to make his diode cavities and I preferred cleaving (not so easy).

Then, one early fall day, Hall’s boss called me to tell me that Hall was running a laser, and would I please give up cleaving! I devised at once a simple method to polish my diode Fabry-Perot cavities, and immediately had red III-V alloy lasers and LEDs.

With Hall’s infrared GaAs lasers and incoherent emitters and my visible, red $\text{GaAs}_{1-x}\text{P}_x$ lasers and LEDs, GE announced the availability of these devices for sale late in 1962. The red LED was practical from the beginning, and only got better and cheaper over time.

Now, after 45 years of work by many people, the high-brightness, high-performance LED promises to take over lighting. The scale and variety of what is happening is surprising, totally unbelievable. Since we are talking about an ‘ultimate lamp’, this work won’t stop, will only grow and, of necessity, become cheaper. This will make the universal use of the LED possible – appearing everywhere in lighting and decorating!

Nick Holonyak, Jr., University of Illinois at Urbana-Champaign