Zeitschrift: Bulletin / Vereinigung der Schweizerischen Hochschuldozierenden = Association Suisse des Enseignant-e-s d'Université

Herausgeber: Vereinigung der Schweizerischen Hochschuldozierenden

Band: 37 (2011)

Heft: 1

Artikel: Nature-Copy-Chemistry-Paste

Autor: Zumbühl, Andreas

DOI: https://doi.org/10.5169/seals-893913

Nature-Copy-Chemistry-Paste

Andreas Zumbühl*

A few decades ago, the world of natural sciences was a world with clear, fixed boundaries where inner- and interdisciplinary collaboration was hard to find and frowned upon. This picture has changed dramatically over the past decade with a surge of new disciplines populating the space between the classical disciplines.

A third revolution is now taking place: convergence, true collaboration between chemists, biologists, physicists, engineers, and medical doctors. Helped by physical proximity, e.g., within the same institute, each team member is providing the specialties of his field with the goal to tackle problems that cannot be solved by one research group alone. The results can be solutions of unprecedented creativity and this short article highlights a few recent examples from the world of convergence.

The text is focussing on solutions that have been inspired by nature, that copy nature and, sometimes, even enhance it. Most of the presented research is still at the concept stage but it might serve as a glimpse into the future of chemistry.

Superhydrophobic Surfaces

Spring draws nearer and brings with it the Sundays spent watching raindrops sliding down the windows. It is times like these that can be very inspiring; sliding raindrops, e.g., leave behind traces and make it necessary to clean a window from time to time. While this is no big deal at home, it can be dangerous and very expensive when the windows of skyscrapers have to be cleaned. The dream, of course, would be self-cleaning surfaces. And here, nature is already offering a solution ready to be copied: superhydrophobic surfaces.

A long time ago, it was noted that the lotus plant never gets dirty. Water rolls off the lotus leaf surface and with the rolling motion, the water droplets drag dust and other dirt particles with them, leaving behind a pristinely clean surface. Contrary to what might be thought, a closer look at a lotus leaf does not reveal a totally flat surface but a very rough surface with thousands of microscopically small pillars made of wax crystals. The water molecules are efficiently rejected from the plant's surface because the wax is a hydrophobic, water-repellent material. Furthermore, air bubbles that fill the valleys between the pillars physically block the water droplets from touching the plant leaf and wetting its surface.

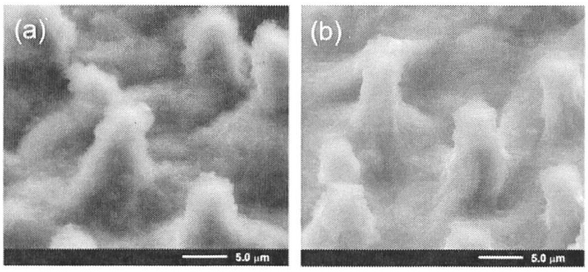

Figure 1. An exact replica (b) of a natural lotus leaf (a). A fresh leaf has been coated with the silicon-based polymer poly(dimethylsiloxane), creating a negative imprint. A second layer of the polymer again created the positive replica showing the same characteristics as the natural leaf surface. Reprinted with permission from Langmuir 2005, 21, 8978–8981. Copyright 2005 American Chemical Society.

The dream of self-cleaning windows, vehicles and clothing led many research groups to look into how natural structures could be replicated. One straightforward technique has recently been reported by the group of Ji and colleagues. A fresh lotus leaf was covered with the widely used silicon-based polymer poly(dimethylsiloxane), an elastic, transparent material. Peeling off the leaf revealed a negative imprint of a lotus-leaf structure. Using a second polymer and a special surface coating preventing a chemical reaction between the two polymers, a positive replica was casted. This polymer now looked identical to the natural lotus leaf but was made by chemical means, a true «copy-paste» from nature.

Gecko-inspired Surgical Tape

Higher magnification images of natural surfaces reveal that nature is using pillars also in other surprising situations.

* Université de Genève, Département de Chimie Organique, 30, Quai Ernest-Ansermet, 1211 Genève 4.

E-mail: *andreas.zumbuehl@unige.ch*

Andreas Zumbühl, Dr. sc. nat. ETH, ist in Interlaken aufgewachsen. Er hat sein Chemiestudium an der ETH Zürich 1999 mit dem Diplom und 2004 mit einem Doktorat in bioorganischer Chemie abgeschlossen. Von 2004–2006 war er Postdoctoral Fellow und Associate in der Gruppe von Professor Robert S. Langer am Massachusetts Institute of Technology in Cambridge, USA. Danach folgte ein Postdoc in der Gruppe von Professor Joachim Seelig am Biozentrum Basel. Seit 2008 ist er als Maître Assistant an der Universität Genf angestellt. Andreas Zumbühl beschäftigt sich mit der Synthese künstlicher Lipide und deren Anwendung in Biologie und Medizin.

Nothing will stop geckos, small reptiles, from gathering food. On the search for small insects a gecko will walk up vertical walls and hang from ceilings without falling down. Since a long time already, this phenomenon fascinated physicists who were searching for the reasons behind the stickiness of a gecko foot. Only recently, microscopy techniques revealed that geckos are not using liquid glue excreted by glands but found a much simpler, dry solution to the problem of walking up smooth surfaces. Each gecko foot contains hundreds of thousands of rigid hairs, setae, that themselves are split into even more hairs, spatulae, at the tip. These millions of hairs maximize the van der Waals contact between a gecko foot and the surface it is walking on. One single van der Waals interaction itself would not be enough to allow a gecko to climb up a wall. But the shear multiplication of these weak forces results in a strong adhesion, based on a fundamental physical property. Capillary forces of monolayers of water that are present between the spatulae and the smooth surface further increase the adhesion of the animal. The hairs of a gecko are oriented in a way that putting the foot down in one direction lets the animal stick to the wall, moving the foot into the other direction breaks the adhesive forces and allows the gecko to move forward instantaneously.

When the basic principle and geometry of a gecko foot was published, several groups immediately grasped the potential of gecko-inspired surfaces. A solution might have been found for an extremely sticky, but reusable Scotch tape with very special properties. A recent example shows a mass of 500 g hanging on a single a 1 × 2 cm large strip of a «Gecko-tape»!

Simple copy-paste from nature was not as easy as in the case of lotus leaves, as the structures of gecko setae were too small and fragile and could not be copied directly. Other replica molding techniques had to be developed. A silicon wafer, known from microchip fabrication, served as a negative template. Using a laser beam, discrete holes were cast into the material. The holes in the silicon wafer were then covered with an elastomeric polymer. After curing, the final polymer was peeled off (see Figure 2).

Surgery is one field of applications where such a material would be highly appreciated. During a minimal-invasive operation closing a wound with needle and thread gets very tedious and the task would be much simpler if a degradable, elastomeric Scotch tape could seal the internal wound. Also, ruptures of the intestine could simply be covered with a sealing tape that would withstand the high forces applied to the tissue (today, needle and thread or stapling techniques are used). Of course, working with degradable polymers would be highly appreciated; after closing a wound, the polymer would slowly degrade into non toxic compounds and it would not be necessary to perform a second surgery in order to remove the implant.

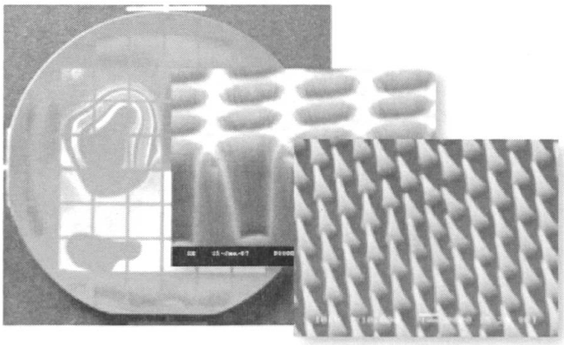

Figure 2. Casting a Gecko-inspired surface. Holes were drilled into a silicon wafer using laser technology. Then the wafer was coated with the elastomeric material poly(glycerol sebacate acrylate). After photocuring, a positive replica could be peeled off. Pictures courtesy of Robert S. Langer and Jeffrey M. Karp.

Shape-memory Polymers

The fact that our body temperature is much higher than the surrounding temperature leads to interesting, temperature-sensitive materials.

As already mentioned above, suturing a wound through an endoscope is a difficult task. If the knots are too tight, the surrounding tissue might show necrosis, if the knots are too weak, scar tissue might form, which has inferior mechanical properties and might even break and lead to a hernia. Using the optimum force might be achieved by letting the thread tie its own knot. This solution would involve shape-memory polymers. If these materials were degradable, only one surgical procedure would be needed, a truly minimal-invasive operation.

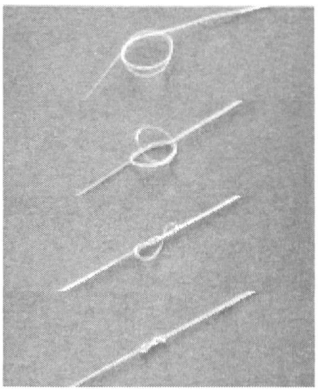

Figure 3. Going beyond what Nature can achieve: shape-shifting polymers allow hand-free tightening of a knot. Such a polymer would be appreciated in minimal-invasive surgery where tying knots through an endoscope is difficult due to the confined space. From Science 2002, 296, 1673-1676. Reprinted with permission from AAAS.

Shape-memory materials come in many forms and we are surrounded by them, probably without us paying too much attention. Frames of modern glasses can be treated roughly without them losing their initial form, shrink-wrap foil tightly holds together bundles of wires after heating with a heat-gun, sunsails of satellites unfold magically, and wrinkle-free shirts need no ironing anymore.

A self-tying knot for sutures would need two physical states; a loosely tied state that would allow easy insertion of the material through an endoscope, and a tightly tied final state. The shape-memory effect would then be provoked by the increase of the temperature (room temperature to body temperature). The materials used are degradable block copolymers, linear polymeric chains that are physically crosslinked in the final shape of the polymer. The material is then forced into a second state and fixed temporarily with a second set of crosslinkers. Heating the material above a specific temperature will revert the geometry of the material to its original state, in our case a tied knot or various other applications such as, e.g., drug encapsulation and release.

DNA Origami

The prototypical long, linear polymer in our body is DNA and it is intriguing what can be done with this molecule.

DNA is the main source of information of our body. The blueprints for our life are contained on two complementary linear polymers that wrap around each other and form the famous double helix. But the double helix is not the only form DNA can adopt and therefore, in the past few years, DNA has been used more and more in ways that were not predicted by nature. DNA is formed from two linear molecules that recognize each other via Watson-Crick pairing of the nucleobases. Other molecules that can undergo the same interactions with the leading strand can replace the second DNA strand. The result could be a single strand that is stapled together into a new form by many small snippets of complementary DNA. This is DNA origami, first reported by the team of Rothemund.

The goal of DNA origami is to staple a long single strand of DNA into a new two- or even three-dimensional form using hundreds of smaller, comple-

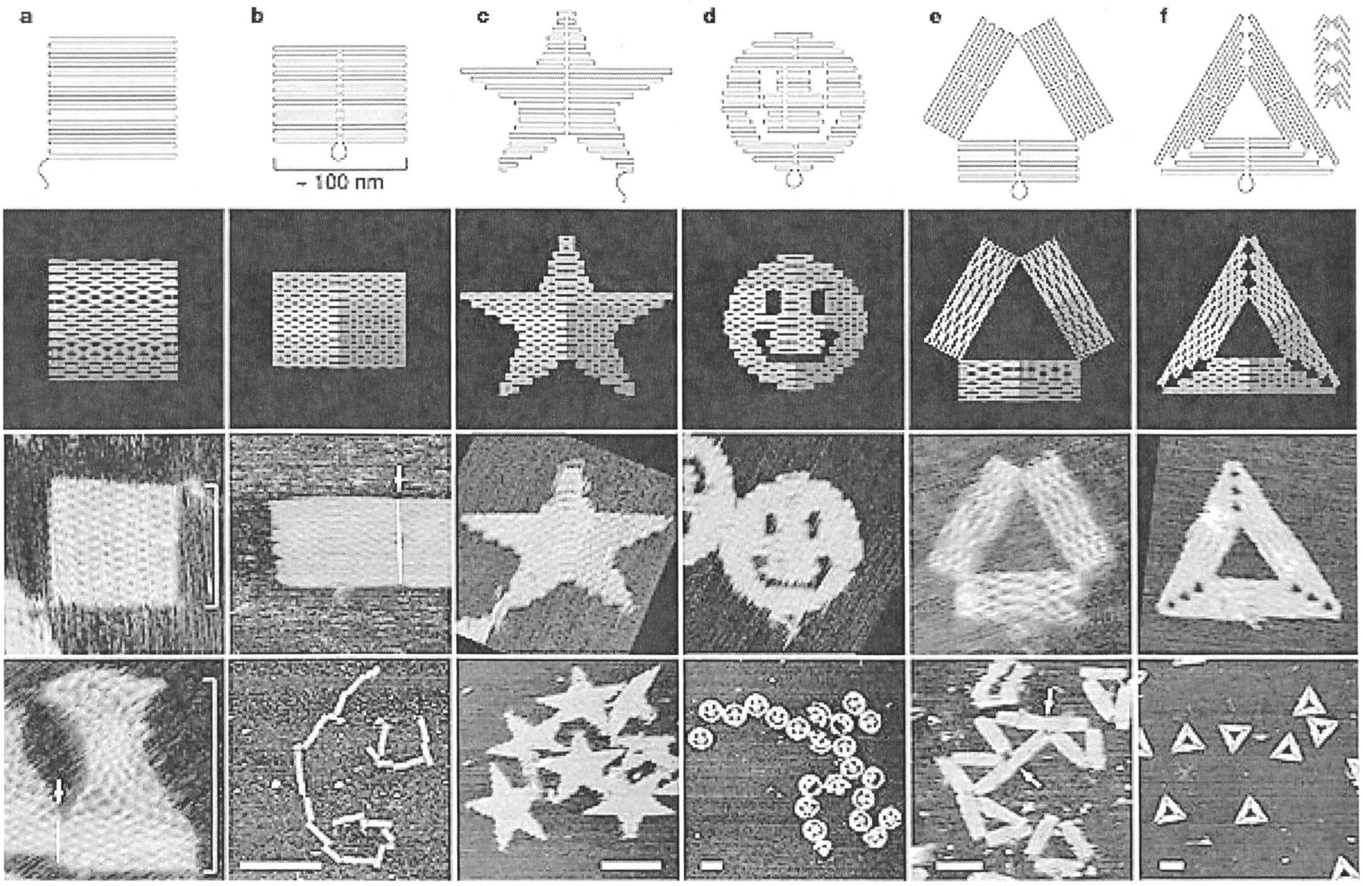

Figure 4. A long single strand of DNA can be stapled together with hundreds of smaller, complementary pieces of DNA. Depending on how the staples are applied, various two- and three-dimensional shapes can be made. Top row, folding paths. a, square; b, rectangle; c, star; d, disk with three holes; e, triangle with rectangular domains; f, sharp triangle with trapezoidal domains and bridges between them. All images and panels without scale bars are the same size, 165 nm by 165 nm. Scale bars for lower AFM images: b, 1 µm; c–f, 100 nm. Reprinted by permission from Macmillan Publishers Ltd: Nature 440, 297-302, Copyright 2006.

mentary pieces of DNA. A computer program helps designing the small staples, complementary snippets to the long DNA strand. When all the molecules are mixed together, only one configuration is possible and adopted.

These DNA-organized devices could end up as drug encapsulating boxes, nano machines that organize different proteins on a very small footprint like an assembly line, or entire production facilities that could synthesize drugs. Also there could be applications in electronics, where DNA could serve as a next generation in the miniaturization of microelectronics.

Soft Robotics

Surprising solutions can also be found in other, unexpected fields.

Ever so often, a lucky scientist discovers a field of research that lies wide open and for a while he or she enjoys the freedom of being able to do research without fearing that another group will be faster in publishing. These fields often lie hidden in plain sight. A recent example is the field of soft robotics.

Many animals have developed fascinating solutions for gripping objects with their flexible extensions. These body parts do not contain a skeletal support but nonetheless are able to exert a surprisingly high force. The trunks of elephants are such an example, also the tongues of lizards or the tentacles of a squid. An elephant's trunk is in essence a fusion of the animal's upper lip and nose. It contains neither nasal nor other bones but tens of thousands of orthogonally organized, interdigitated bundles of muscles. The trunk is a very sensitive organ that can be used to transport heavy loads but also to pick up a single blade of grass.

Human-built robots do not show this combination of sensitivity and force. The instrument are not built from soft materials but typically from rigid parts that are connected by joints to allow the system being flexible. While being extremely useful for handling hard objects, these robots have their limitations for handling fragile objects such as, e.g., eggs or human tissue during surgery. Applying the principles from nature, the team of Whitesides recently proposed an intriguing soft robotic arm: The chemists used a silicon polymer [again poly(dimethylsiloxane)] and fabricated air-filled chambers, each connected to the next one. One side of the chamber is made of a thin wall; the other sides have a thicker membrane. Pushing air into the chamber will inflate it, while the force primarily deforms the thinner wall. The result is a deformation of the material into a curved surface. A star-shaped soft robotic hand of 10 cm diameter was able to lift a mass of 300 grams. At the same time the touch of the robotic «hand» was gentle enough to lift a raw egg without crushing its shell. This soft robot may be a solution for handling soft materials (like fruit) or human organs. Overall, the concept is an intriguing structure, mimicking and enhancing nature.

Switchable Surfaces

The concept of shifting the properties of a material by applying an external trigger can be minimized to the absolute molecular minimum. Several groups are working on surfaces that are coated with long molecules that contain special head groups. Upon application of a trigger such as light or electrons, the long molecules bend upon themselves. As a result it is not anymore the head group that is the highest point of the surface but the bent long part of the molecule. In the simplest case, the surface will switch from being hydrophilic (having carboxylic acids as head groups)

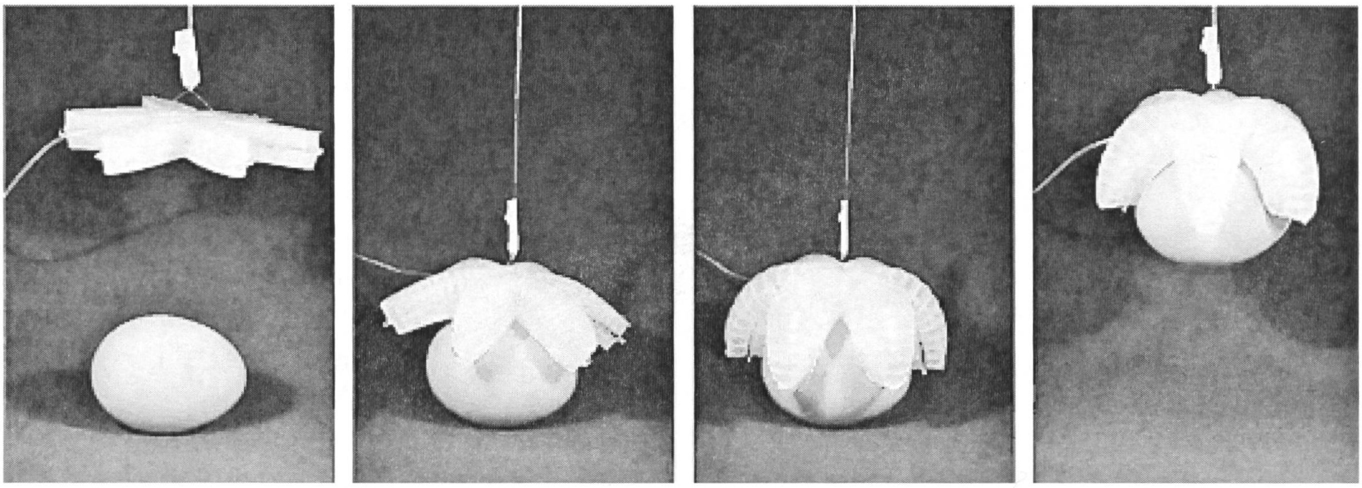

Figure 5. Soft robotics in action. Compartments made from a silicon-based polymer are filled with air. As the sides of the compartments have different wall strengths, the application of air will lead to a reversible deformation of the material. The six-legged star-shaped polymer is forced into a bent conformation and can grip a raw egg without crushing it. Reprinted with permission from Angewandte Chemie International Edition 2011, 50, 1890–1895. Copyright 2011.

to being hydrophobic (displaying only fat-like functionalities).

These switchable surfaces will open new applications in the future. E.g., a futuristic toilet will capture the urine, analyze it and then the surface will switch to being hydrophobic, leaving behind a clean surface.

There are also other medical applications possible. Today, taking a drug basically means swallowing something like 1'000'000'000'000'000'000 molecules. One might call this approach efficient and it certainly helps keeping us healthy. Nonetheless it would be interesting to treat a disease by releasing only a minimal amount of drug from an addressable drug-releasing device placed in the vicinity of the problematic tissue. The team of Ferri has recently reported an interesting concept in this direction. A cyclodextrin «basket»was closed by a surface-anchored iron-molecule lid. The application of a surface potential led to the reversible closing and opening of the molecular lid. If the «basket» would be bigger, e.g., drug molecules might be loaded into the cavity and released at the site where they are needed and at the time they are needed.

Planar Supported Bilayer Membranes

Another intriguing way of copying-pasting from nature is the anchoring of a bilayer membrane onto a solid support.

Our cellular membrane is host to a fascinating mixture of lipids and proteins. Proteins are the factories in our body, constantly producing needed molecules, tightly controlled by feedback loops. Each protein is surrounded by a set of specific lipids that are assisting the protein in assuming the right three-dimensional structure and that are organizing the proteins at the correct location in the membrane.

Malfunctioning proteins lead to overproduction or underproduction of protein-derived molecules and are at the heart of many diseases. Current small-molecule drugs aim at blocking or activating proteins, leveling the negative effects of a malfunctioning system. Gene therapy holds the promise to introduce new proteins into the human body and RNA interference therapy hopes to block the production of specific proteins. The concept of planar supported bilayer membranes might allow to pin proteins onto a surface and to implant such a device to where the protein might be needed.

The cellular membrane is made from a double layer of lipids supported on the cytoskeleton of a cell. This lipid bilayer is virtually impenetrable for most molecules and nature evolved a whole system of proteins dedicated to transporting ions, water, lipids, or

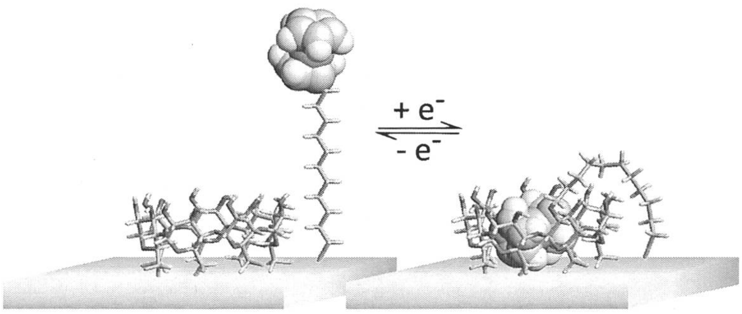

Figure 6. Concept of a switchable surface: A small cyclodextrin-made basket can be closed with an iron-based lid. Theoretically, a slightly longer basket could be synthetized and filled with drug molecules that could be released by an external trigger. Reprinted with permission from Langmuir 2009, 25, 12937–12944. Copyright 2009 American Chemical Society.

foreign material from one side of the membrane to the other side. The proteins are either anchored into one layer of the membrane or they span the entire membrane.
Instead of supporting a membrane on the cellular cytoskeleton, it is also possible to support a membrane on a surface such as glass. Various techniques

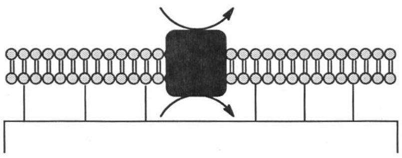

Figure 7. Schematic drawing of a planar supported bilayer membrane. The bilayer of lipids can be supported, e.g., on a glass or gold surface by various techniques. Here, certain lipids are directly anchored to the support, holding up the rest of the membrane. A protein (black) is incorporated into the supported bilayer. The membrane is not touching the support, allowing a flux of adducts to and products towards and away from the protein.

exist for achieving this goal. Probably the most straightforward way is the adsorption of a bilayer membrane onto a hydrophilic, water-rich polymer that is covering the glass slide. The planar supported membrane retains its fluidity and it is also possible to introduce proteins into the mixture. Given the right support, organized sets of proteins, according to the individual needs of a patient, might become implantable and help controling a disease for a long time by copying a protein from nature and pasting the protein into a human-made setting.

Conclusions

This article highlighted several concepts and hopefully enhanced the reader's view of modern-day chemistry. All the presented concepts are based on the interdisciplinary, convergent interplay of chemists with scientists from other fields. Solutions become available that would not have been possible or even dreamed of few decades ago. ■