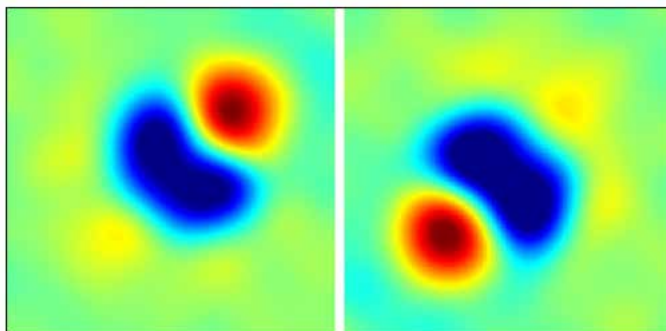


August 10, 2015

Gold cations make atomic rocker switches. The potential uses for atomic switches in data storage and processing are well known, but these switches also might be used to control the formation of chemical bonds. G. Meyer and colleagues at IBM Research-Zurich (Switzerland) and the University of Liverpool (UK) made atomic “rocker switches” from individual gold(I) cations (Au^+) adsorbed on a NaCl film. Each Au^+ forms a tilted linear complex with the two nearest chloride ions, creating an anisotropic electrostatic field. The tilt can be toggled repeatedly and reversibly by using a probe tip (see figure).



Gold cation toggles between two mirror-image electrostatic fields

The authors deposited neutral gold atoms onto a NaCl film that had been coated on a single-crystal copper substrate. Cations were made one at a time by using the probe tip to apply a voltage. Scanning tunneling microscope (STM) images show small round protrusions, which appear as bright spots, adjacent to larger oblong depressions, which appear as dark areas. The protrusions and depressions appear to switch places, accompanied by a sudden frequency shift, as the STM tip (with voltage set to zero) scans the surface.

Atomic force microscopy scans show that the field can be switched back and forth repeatedly when the fast scan direction is perpendicular to the switching axis. Only one switching event is observed when the fast scan direction is parallel to this axis.

The authors replicated this effect with density functional theory calculations. When the gold atom is centered in the linear Cl-Au-Cl complex, the complex is parallel to the surface. When it is shifted off-center, the complex tilts by $\approx 10^\circ$. The observed negative electrical charge and interatomic distances support the identification of the bright protrusions in the experimental images as chlorine atoms lifted from the surface in the tilted complexes.

The observed switch always occurs at the position of the lower-lying chloride ion in the tilted complex. The authors conclude that the probe tip exerts an attractive force that pulls this anion up, forcing the other Cl^- down. The local contact potential difference changes by several hundredths of an electron volt during switching, depending on the tip height.

This potential shift could be used to manipulate reactions of nearby molecules, for example, intramolecular hydrogen transfers in porphycene. Because the Au^+ is embedded in the NaCl film, the switch remains stable while it influences its surroundings. (Nano Lett. DOI: 10.1021/acs.nanolett.5b02145; Nancy McGuire)

August 3, 2015

Biofuel cultivation affects more than greenhouse gases.

Biogenic volatile organic compounds (VOCs) account for >90% of non-methane hydrocarbon emissions in the atmosphere. Isoprene is emitted in the largest amounts and has the greatest effect on atmospheric composition. Photochemical oxidation of isoprene in the presence of nitrogen oxides governs the production rate of ground-level ozone. It also forms aerosol-phase reaction products that damage plant and animal health.

O. Wild and coauthors at Lancaster University (UK) and the University of Colorado, Boulder, produced a lower-bound estimate of increases in ground-level ozone that would occur by planting poplar trees, a high-isoprene emitting species, to use as a biofuel feedstock.



Some types of poplar trees emit isoprene (Pixabay photo)

Few grasses and conventional food crops emit detectable amounts of isoprene. Various types of poplars emit different levels of isoprene, but they also produce different biomass yields. Genetically modified poplars that do not emit isoprene have been developed but are not commercially available.

The researchers studied relationships between biomass yield and isoprene emissions by using experimental data for 29 commercially available poplar hybrids. They predict that increases in poplar plantings across Europe will increase ground-level ozone enough to cause substantial wheat and maize crop losses (3–9 Mt/year) and increase the annual number of premature human deaths that are attributable to ozone pollution by as much as 6%.

The impact of poplar plantings depends on their location, which determines the prevailing weather, population density, and dominant crop type. To meet EU biomass targets, medium-yielding poplar cultivars would require 33 Mha of land. Planting this area in commercially available poplar trees would increase isoprene emissions from 12 to 36%. The highest increase in emissions would occur in hot, sunny Mediterranean regions; the lowest would occur in northwestern Europe.

Because isoprene has an atmospheric lifetime of ≈ 90 min, increases in its atmospheric concentration would be confined to near its origin. Boundary-layer nitrogen oxide concentrations, however, are moderately high across Europe, but VOC emissions are relatively low. Thus, even a small increase in VOC emissions could have a significant effect on ozone production. Background levels of ground-level ozone are rising across Europe, so a small increase could raise levels above the threshold of observable health effects. (Environ. Sci. Technol. DOI: 10.1021/acs.est.5b00266; Nancy McGuire)

August 3, 2015

Thin, flexible device generates electricity from waves. Converting water-wave kinetic energy to electricity could provide power for corrosion protection devices, pollution degradation, water desalination, and wireless sensing for marine surveillance. Triboelectrification, electricity generated from two surfaces in contact, has been used on a small scale to harvest wave energy, but scale-up has proven difficult.



Thin-film triboelectric generator interacting with a water wave

G. Zhu and coauthors at the Chinese Academy of Sciences (Beijing) and Georgia Tech (Atlanta) developed a flexible thin-film triboelectric generator. As water waves hit the device, they generate a triboelectric charge at the nanostructured solid-liquid interface that induces a flow of free electrons in an external circuit. The thin, flexible device can be applied to the surfaces of objects placed in rivers, lakes, or oceans without adding much in the way of size and weight. The figure shows a wave splashing on the device (scale bar = 25 mm).

The device uses an array of surface-mounted bridge rectifiers to link an array of electrodes together in parallel. The authors linked 11 electrodes to create a 100 mm x 60 mm device with optimum output power of 1.1 mW, an order of magnitude higher than a previously reported device. The generated electricity can power small electronic devices or LED arrays, or it can provide cathodic protection for carbon steel.

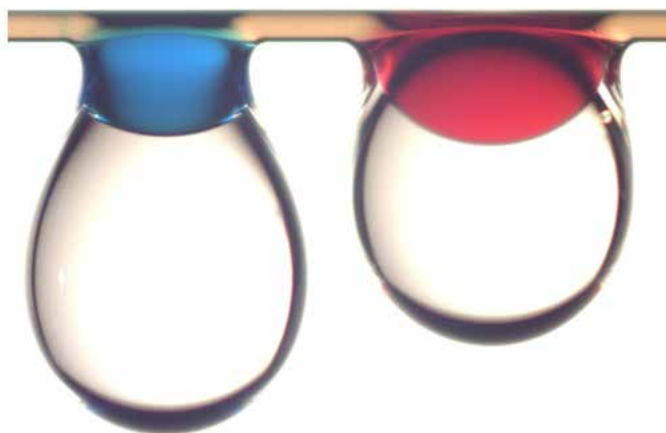
The device consists of a polyimide film substrate that supports a parallel array of strip-shaped copper electrodes. A thin top film consists of a dense uniform array of 200-nm diameter poly(tetrafluoroethylene) spheres. This hydrophobic surface protects the electrodes beneath it and provides a rough surface for greater contact area with the water waves. The bridge rectifiers ensure that the current in the external circuit always flows in one direction to produce a single current peak for all the linked electrodes.

The authors measured up to 230 V for a pulsed current of 13 μA . The maximum power of 1.1 mW was reached at an optimal load of 25 M Ω . The charge carried by a single current peak scales linearly with the number of electrodes. If more than six electrodes are linked, however, the voltage amplitude starts to saturate, possibly because the diodes begin to break down.

Faster-propagating waves induce a larger current amplitude and a faster charge flow. Salt water, with its higher conductivity, generates less triboelectric charge than fresh water, but even a saturated salt solution produces 40% of the current that fresh water does. (ACS Nano DOI: 10.1021/acs.nano.5b03093; Nancy McGuire)

July 27, 2015

Compound droplets form four-phase linear junctions. The equilibrium shapes of simple droplets hanging from horizontal fibers are well established, but the situation becomes more complex for compound fluidic systems. Thermodynamic laws suggest that three phases meet along a line, whereas four phases should join at a single point. A recent study of compound droplets demonstrated what may be the first observation of a linear junction of four phases.



Left, oil–pure water droplet;
Right, oil–soapy water droplet

Compound droplet systems can be used to understand and develop a variety of microfluidic devices in which water droplets are encased in oil coatings to prevent evaporation and contamination. Such devices include “open digital microfluidic” systems that allow sample transfers, biochemical reactions, and analyte detection on a microliter scale. These systems use programmable sequences of dispensing, moving, splitting, and merging droplets on an open surface. Optofluidics combines microfluidic and nanophotonic technologies to produce lab-on-a-chip and biophotonic devices.

F. Weyer and coauthors at the University of Liège (Belgium), Karlsruhe Institute of Technology (Germany), and the University of Applied Sciences (Karlsruhe) show that compound droplets on horizontal fibers adopt specific geometries. Depending on the surface tensions, the air–oil–fiber triple contact line can remain separate from the oil–water–fiber triple contact line; or the lines can merge to form air–oil–water–fiber quadruple lines.

The authors used droplets of colored water, with and without a soap solution, encased in silicone oil and suspended from nylon fibers. Pure water droplets form spherical caps, with well-defined contact angles, surrounded by oil. Soapy water droplets spread inside the oil droplet, and the inner contact line moves toward the outer contact line. For some volume ratios of soapy water to oil, the contact lines merge to form a quadruple contact. The authors used numerical modeling to replicate this effect.

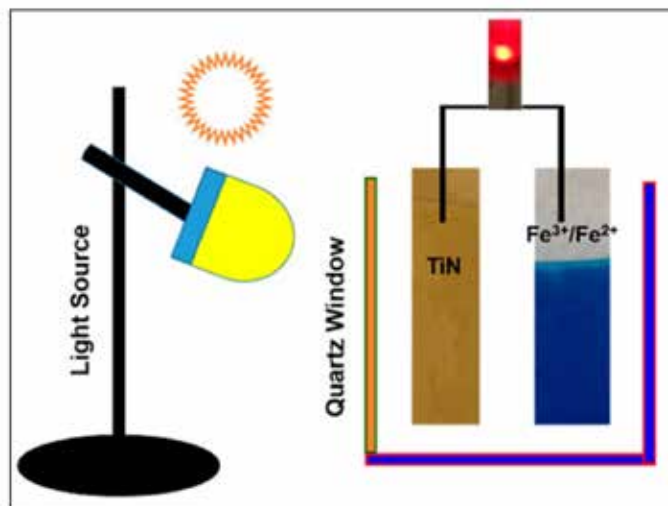
For pure water encased in oil, the oil droplet hangs from the water droplet, which adheres to the fiber (left in the figure). Detachment depends only on the diameter of the water droplet. For soapy water, the oil and water move together along the fiber (right); the detachment process is controlled by the diameter of the fiber. (Langmuir DOI: 10.1021/acs.langmuir.5b01391; Nancy McGuire)

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July 13, 2015

Photochemical battery keeps going and going. Anode degradation and dissolution are especially problematic in aqueous rechargeable batteries (ARBs). These difficulties cause safety concerns and capacity fading (a decrease in the amount of charge a battery can deliver).

M. O. Thotiyl and coauthors at the Indian Institute of Science Education and Research (Pune), Acharya Institute of Technology (Bangalore, India), and the National Chemical Laboratory (Pune) developed an ARB (see schematic) that uses light to trigger electrochemical reactions. This battery avoids several problems with anode materials, and it can be recharged in ≈ 30 s with a chemical charging agent.



Aqueous rechargeable battery uses sunlight to trigger electrochemical reactions

The titanium nitride photoanode has a native oxynitride surface layer that absorbs UV–visible light. The cathode is iron(III) hexacyanoferrate(II) $\{KFe[Fe(CN)_6]\}$ supported on carbon, and the electrolyte solution, which contains the sodium persulfate ($Na_2S_2O_8$) charging agent, is 3 M potassium chloride.

The open-circuit voltage of a single cell is ≈ 0.74 V in the dark, 1.2 V under artificial visible light, and 1.1 V under ambient light. Light generates electron–hole pairs in the anode material. The electrons reduce the iron(III) in $KFe[Fe(CN)_6]$ to iron(II) $\{K_2Fe[Fe(CN)_6]\}$ in the cathode.

The holes oxidize water to molecular oxygen, as shown by oxygen bubble formation after the first discharge. After the first cycle, $SO_4^{\bullet-}$ hole scavenging replaces water oxidation as the balancing reaction.

The battery's discharge capacity is negligible in the dark; but it delivers 77.8 mA•h/g under artificial visible light, 55.5 mA•h/g in ambient light, and just over 80 mA•h/g for UV–visible light. After the battery is discharged, the system is left in the open-circuit state for 30 s, during which the $Na_2S_2O_8$ reoxidizes the $K_2Fe[Fe(CN)_6]$.

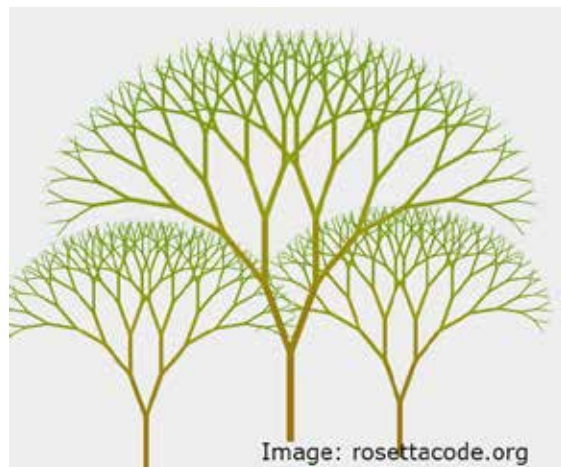
The battery was used to power a light-emitting diode under ambient light; it retained 97.9% of its initial capacity after 100 cycles. The titanium nitride photoanode showed no degradation, producing almost identical X-ray diffraction patterns before and after 100 cycles. $Na_2S_2O_8$ is consumed irreversibly during battery recharging and must be replaced when it is exhausted; this chemical, however, is inexpensive and readily available. (J. Phys. Chem. C DOI: 10.1021/acs.jpcc.5b02871; Nancy McGuire)

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July 6, 2015

A forest of decision trees “elects” materials candidates. Structural building blocks can be combined in many ways to produce nanoporous materials for gas storage, separation, and sensing, among many other applications. The structural possibilities are so numerous that the Materials Genome Initiative took on the task of developing and using computational tools to produce manageable lists of viable candidates for specific applications.

M. Haranczyk and coauthors at the University of California, Berkeley, the Norwegian University of Science and Technology (Trondheim), the Swiss Federal Institute of Technology in Lausanne (Sion, Switzerland), and Lawrence Berkeley National Laboratory screened the Nanoporous Materials Genome, a database of more than 670,000 structures, for candidate adsorbents for separating mixtures of xenon and krypton at room temperature. The current cryogenic separation methods are expensive and require a large expenditure of energy, which is reflected in the price of about \$5,000/kg of high-purity xenon.



The Materials Genome Initiative uses decision trees to parse large databases

The computational resources required for a brute-force screening that uses grand-canonical Monte Carlo simulations of Xe–Kr adsorption are prohibitive. Thus, the authors combined machine learning algorithms with molecular simulations to examine the relationships between pore size and selectivity.

The authors created an ensemble of decision trees that they call a “random forest”. A decision tree is “grown” by using a training set of materials with known selectivities. Test materials are vetted for selectivity by running their vector descriptors through the decision tree. Using the entire training set to train a single decision tree can lead to overfitting errors, so many decision trees (1000 in this study) are trained by using randomly selected subsets of the training set. The resulting selectivity prediction is a product of the average “vote” of each tree in the forest.

This screening study predicts that the two most selective materials in the database are an aluminophosphate zeolite analogue and a calcium-based coordination network. Both have been synthesized but not yet tested for separating xenon and krypton. (Chem. Mater. DOI: 10.1021/acs.chemmater.5b01475; Nancy McGuire)

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