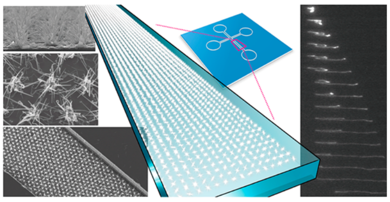
Getting Your DNA in a Row

Researchers have recently developed a bevy of new devices and techniques for examining biomolecules with ultrahigh resolution, including electrokinetic manipulation of biomolecules through the use of artificial nanostructures within microfluidic channels. Thus far, this technique has included a variety of different nanostructures, including nanopillar arrays, nanowall arrays, nanofilter arrays, nanofence arrays, nanochannels, and nanoparticles. Although these nanostructures have grown progressively smaller over the years, their size is limited by lithography. To develop microfluidic technology toward manipulating and analyzing single molecules, researchers must develop novel, small, and inexpensive nanostructures within microchannels.

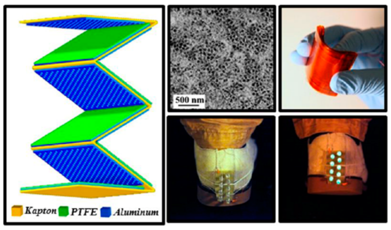
In a new study, Yasui *et al.* (DOI: 10.1021/nn4002424) demonstrate the feasibility of using nanowires for this task. Within a microchannel 25 μm across, the researchers constructed arrays of SnO_2 nanowires by precisely positioning Au catalysts on a fused silica substrate. These nanowire arrays successfully elongated T4-DNA strands under an applied electrical field, stretching the molecules at each end. Further examination showed that the relaxation within these functionalized microchannels had dynamics akin to DNA in free solution. Using this tool, the researchers were also able to separate DNA molecules by size. The authors suggest that their nanowire spot-array structures are superior to conventional gel matrices in spatial control over biomolecules within microchannels. They add that this platform could eventually be used in conjunction with other nanostructures for sensing and sequencing DNA, such as nanopores.



A Step Forward for Harvesting Biomechanical Energy

Ambient mechanical energy, including the biomechanical energy of human walking, generally goes wasted. However, this energy offers an opportunity to offset or to replace traditional power supplies for portable electronic devices, such as batteries. Numerous efforts have focused on developing ways to harvest the energy of human motions, with techniques based on piezoelectric, electrostatic, and electromagnetic mechanisms. An attractive alternative that is gathering increasing interest is triboelectric nanogenerators (TENGs), which generate electrical charge through friction between two materials. Thus far, demonstrated TENGs have had only a single layer, substantially limiting the output power.

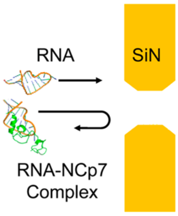
Taking a different tack, Bai *et al.* (DOI: 10.1021/nn4007708) developed a new type of TENG with layers integrated into a single flexible substrate, significantly ramping up energy harvesting without substantially increasing the device's size. The researchers started with a base of Kapton thin film shaped into a zigzag structure, which allowed both sides of the device to serve as substrates for TENG units. Each layer of the device incorporated an aluminum-coated polytetrafluoroethylene (PTFE) thin film and an aluminum foil pitted with nanopores, which substantially increased the surface area, as the contact electrode. A thin layer of aluminum on the back of PTFE acted as a back electrode. When these materials were brought into contact with mechanical compression, surface triboelectric charges were generated through electron transfer from aluminum to PTFE. The researchers demonstrate this concept by incorporating this device in a shoe equipped with light-emitting diodes, showing that normal walking lit up nine bulbs simultaneously. The authors suggest that a multilayered TENG holds promise for providing supplementary power for portable electronics.



Nanopores as Biodetectors

For more than a decade, researchers have explored the idea of using nanopores to probe a variety of biological molecules, including DNA, RNA, and proteins. By placing the nanopore into a conducting fluid and applying a voltage across it, small changes in current can provide information about molecules passing through the pore. This technique is particularly appealing because it does not require the probed molecules to be chemically modified or labeled, can take place in physiological conditions, and can examine single molecules at a time. Recently, this technique has been exploited to examine interactions between biomolecules in real time. Additionally, DNA and RNA aptamers have also been adapted for use with nanopores.

Bringing these concepts together, Niedzwiecki *et al.* (DOI: 10.1021/nn400125c) demonstrate a scheme to detect the nucleocapsid protein (NCp7), a biomarker of the human immunodeficiency virus 1, at the single-molecule level. The researchers created nanopores in a variety of sizes in silicon nitride membranes using electron-beam ablation. Using three RNA aptamers of varying binding affinity, the team tested the interactions between these aptamers and NCp7. Results showed that complexes of aptamer and protein were prevented from passing through the pore when pore size was smaller than 6 nm, although aptamers alone could pass through pores unrestricted. Through titration experiments, the researchers showed that it was possible to detect the presence of NCp7 reliably because this protein bound free aptamers, preventing them from passing through nanopores. A drug that prevented this interaction allowed more aptamers to pass through the nanopore. The authors suggest that this technique could be expanded for detection of a variety of important biomolecules.

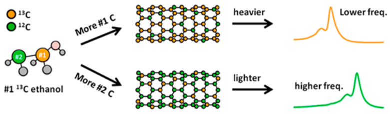


Published online April 23, 2013
10.1021/nn401795t

Not All Carbon Nanotube Atoms Are Created Equally

Chemical vapor deposition for the formation of carbon nanotubes (CNTs) requires several ingredients, including catalyst particles or films, catalysts supports or substrates, and a carbon source. Each of these components has an extensive variety of possibilities, which can be combined into many different combinations that, in turn, affect the quality and quantity of the resulting CNTs. For example, transition metal catalysts, such as Fe, Ni, Co, and their combinations have been shown to produce the highest CNT yield. Similarly, experiments with Al oxide as a substrate show that this material produces single-walled carbon nanotubes (SWNTs) with high selectivity and yield. Although the end product is known, exactly how varying these parameters leads to the resulting outcomes is not.

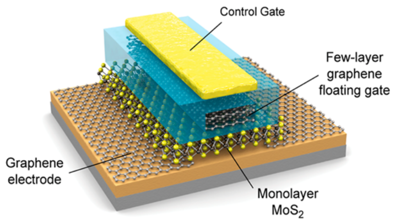
In a new study, Xiang *et al.* (DOI: 10.1021/nn305180g) examine exactly how ethanol as a carbon source contributes to building SWNTs. Unlike other carbon sources, such as methane, ethylene, or acetylene, ethanol contains two inequivalent carbon atoms. By using isotopically labeled ethanol, in which one carbon atom was ^{13}C and the other was ^{12}C, the researchers tracked the proportion of each isotope in the resulting SWNTs. Results showed that the carbon farthest from the hydroxyl group was preferentially incorporated into a SWNT structure. Further examination showed that this preference could be altered by growth temperature, the presence of a secondary catalyst species, and even by the substrate material. The authors suggest that this novel experimental technique provides evidence that the two carbons in ethanol are not treated equally during SWNT formation.



Memory Goes Skinny

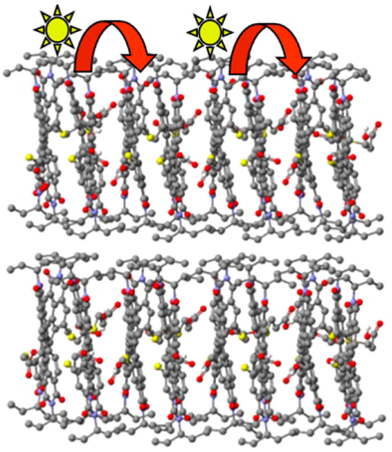
Contemporary flash memory has several roadblocks that must be overcome before devices that use this technology can be further miniaturized. For example, vertical scaling, which leads to a reduction of the program/erase voltages, is limited by charge retention requirements of about 5 nm thickness for a minimum tunneling oxide at the floating gate. Similarly, lateral scaling, which increases data storage capability, is limited by capacitive coupling between the drain electrode and floating gate at increasing electrode thicknesses. Developing two-dimensional materials for use in flash memory could effectively solve both problems, replacing traditional materials for semiconducting channels, interconnects, and charge-trapping layers. Consequently, researchers have investigated constructing novel memory cells using single layers of BN, MoS_2, and/or graphene, the thinnest known materials with electronic properties useful for nanotechnology applications.

In a move toward advancing this technology, Bertolazzi *et al.* (DOI: 10.1021/nn3059136) developed memory cells that combine MoS_2 with graphene in a field effect transistor geometry. In their design, monolayer MoS_2 acts as a channel, with graphene composing electrodes and a charge-trapping layer. Tests show that this device has a difference of 10^4 between memory program and erase states, with memory estimated to decrease a little over a decade. The authors suggest that this memory cell's two-dimensional nature could open it up to large-scale fabrication and integration into a variety of flexible nanoelectronic devices.



Nanosheets See the Light

A variety of recent studies suggest that water can bring simple building blocks into ordered and complex nanoscale arrays. For example, dendritic amphiphiles in water can come together into the far more complex and diverse structures known as dendrimerosomes. Similarly, polyalcohol-based amphiphiles, including glycerol mono-olein and phytantriol, can self-assemble in water into cubosomes. Controlling molecular interactions in water to produce assemblies with crystalline order, particularly crystalline aromatic arrays, could prove useful for a variety of applications, including photonic and electronic devices. These materials are capable of fast exciton transfer over long distances, a property useful for solar cells and artificial photosynthesis. However, rationally designing such materials to self-assemble in water purposefully has proven challenging.

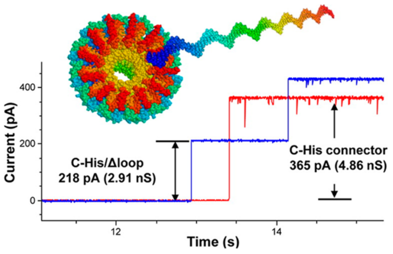


In a new study, Shahar *et al.* (DOI: 10.1021/nn400484y) achieved this goal by designing two-dimensional crystalline sheets several nanometers thick that self-assemble in water from well-defined perylene diimide (PDI) amphiphiles. The researchers created three different assemblies, all having an amphiphile with a large aromatic core decorated by two alkyls and two hydrophilic groups. The as-assembled structures ranged in thickness from 1.5 to 4.3 nm. Tests showed that two of these assemblies are excellent light harvesters, with broad solar spectrum coverage and fast exciton transfer. The authors note that this example of rationally designing and efficiently assembling aromatic crystalline assemblies in aqueous media could lead to photonic and electronic materials with simple, economical, and environmentally friendly fabrication and processing.

Paring Down the Pore

Nanopores, both those borrowed from nature and those of synthetic origins, have become a heavy focus for research due to their role in detecting the conformation and dynamics of polymers including DNA and RNA. The channel of the phi29 bacteriophage DNA-packaging motor is one well-studied biological nanopore. This connector, 3.6 nm in diameter at its narrow end and 6 nm in diameter at its wide end, is composed of 12 copies of the gene protein gp10. When this nanopore has been inserted into a lipid bilayer, the resulting system has displayed reliable, precise, and sensitive changes in conductance when ions or double-stranded DNA passes through the channel. However, in its native form, this channel cannot detect single-stranded DNA, and DNA traffic through the pore is only unidirectional.

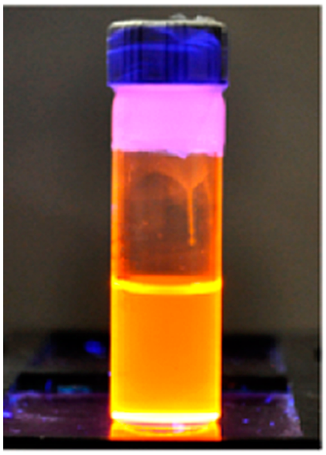
Seeking a new type of pore to get around these constraints, Geng *et al.* (DOI: 10.1021/nn400020z) re-engineered the phi29 pore. The researchers mutated this channel, removing an internal loop segment from the gp10 subunit. This created two distinct subpopulations of phi29 pores: one the same size as the wild-type channel and the other about 60% smaller. When placed into a bilayer lipid membrane, tests showed that this smaller channel could not only translocate single-stranded DNA but could do it bidirectionally. The authors suggest that this newly engineered pore might be used in conjunction with the wild-type pore to detect both double-stranded and single-stranded DNA simultaneously.



The Good Seed

Quantum dots (QDs), nanosized semiconductor particles that trap excitons in all dimensions, have become a significant focus for research due to their interesting size-dependent optical and electronic properties. Besides modulating size, another way to tune these materials' magneto-optical properties is to add guest impurities into their crystal lattices. However, each of these methods produces QDs that differ in the number of guest ions with a Poisson distribution across the same population.

In a recent study, Jawaid *et al.* (DOI: 10.1021/nn305697q) developed a new way to produce QDs that have the same exact number of guest ions per particle. This novel synthesis method is an offshoot of the cluster-seed method, in which a quantity of organometallic clusters is added to a solvent with additional semiconductor precursors, then slowly heated, allowing the clusters to function as QD nucleation sites. The researchers prepared Cu-doped CdSe QDs by using $[Na(H_2O)_3]_2[Cu_4(Sph)_6]$ as nuclei. When a precise quantity of these particles was used as starting materials, QD nanocrystal growth occurred rapidly. A variety of tests showed that not only was Cu incorporated into the resulting QDs, but each QD had exactly four Cu ions. Further examination showed that, when these dopants were oxidized, QD photoluminescence was quenched and the Cu ions translocated within the nanoparticle matrix, resulting in a slow return to the emissive state. The authors suggest that this method could be used to produce a variety of differently doped QDs that do not follow Poisson statistics for dopant levels.



Doped Graphene Sounds Off

With their high electrical conductivity and excellent optical transparency, indium tin oxide (ITO) thin films have been widely used in transparent electrodes for various electronic applications. However, this material comes with some drawbacks. Indium tin oxide films are brittle, and for many applications, this material often requires an extra annealing step with temperatures above the melting point of conventional plastic films. This property severely limits ITO films' applications in lightweight and flexible devices, including acoustic actuators and nanogenerators. Graphene's high electrical properties, optical transparency, and mechanical strength suggest that it could be a suitable replacement for ITO films, but its conductivity lags behind ITO's. Recent studies show that graphene's conductivity can be improved by using $Pb(Zr_xTi_{1-x})O_3$ as a substrate, the new material is no longer as flexible or transparent as unmodified graphene.

In search of a new film, Bae *et al.* (DOI: 10.1021/nn400848j) investigated sandwiching the polymer piezoelectric material poly(vinylidene fluoride-*co*-trifluoroethylene) (P(Vdf-TrFE)) between two layers of graphene. The resulting film displayed only slightly reduced transparency compared to monolayer graphene and showed enhanced conductivity. A variety of tests suggested that this material had piezoelectric properties. Demonstrating this multilayer film's potential in devices, the researchers incorporated it into a transparent acoustic actuator and a nanogenerator. The actuator produced acoustic pressure or mechanical vibrations in response to an electrical signal, and the nanogenerator produced enough output voltage to power an LED. The authors suggest that this film could play a role in a new generation of flexible, transparent electronics.