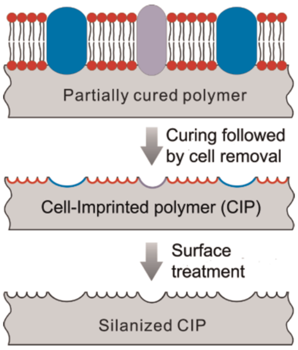
Chemical Recognition Key for Cell Sorting

Molecular imprinting is a useful way to sort molecules and other entities. The basic protocol involves allowing molecules of interest to form complexes with polymers, which are then cured. Once the template molecules are removed, the polymer retains recognition sites complementary to the analytes' sizes and shapes. Recent work has expanded beyond molecules to larger objects with more varied surface areas, such as viruses, bacteria, and cells. Although researchers have repeatedly confirmed the usefulness of this technique, the relative importance of physical shape and chemical recognition remains unknown.

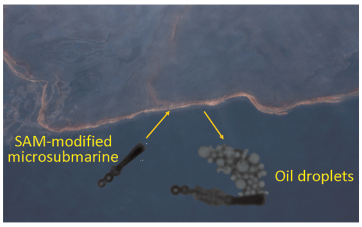
To investigate, Ren and Zare (DOI: 10.1021/nn300901z) ran imprinting experiments with four bacterial species that represent the two different Gram-staining groups: *Staphylococcus epidermis* and *Staphylococcus aureus*, which are both Gram-positive, and *Escherichia coli* and *Klebsiella pneumoniae*, which are both Gram-negative. The researchers created cell-imprinted polymers (CIPs) for each of these species on polydimethylsiloxane (PDMS), then used each sample to test cell-sorting abilities in a microfluidic stream of many bacterial types. Their experiments showed that unmodified PDMS CIPs were successful at preferentially capturing the templated bacterial species. However, when the researchers coated these CIPs with a thin layer of methylsilane, they lost much of their ability to capture the bacteria of interest, even though atomic force microscopy showed that the shape of the imprints had barely changed. These findings suggest that chemical recognition is the dominant force for PDMS CIPs, the authors say, which resolves the mystery for this particular type of CIP.



Tiniest of Submarines Cleans up Oil Spills

Oil spills continue to be a major source of ocean pollution and groundwater contamination. In large spills, such as the 1989 *Exxon Valdez* and 2010 *Deepwater Horizon* accidents, millions of gallons of crude oil seeped into the ocean, harming numerous species of sea and coastal wildlife as well as the livelihoods of people whose income relies on ocean resources. Currently, there are few cost-effective and environmentally friendly methods for the remediation and cleanup of oil spills, making the development of new ways to solve these environmental disasters a high priority. Recent studies suggest that superhydrophobic surfaces, particularly those formed by self-assembled monolayers (SAMs) of alkanethiols on Au or Ag surfaces, could hold promise in attracting oil while repelling water.

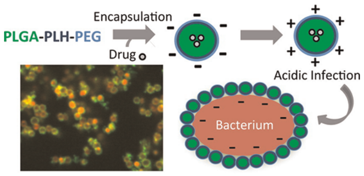
Testing these surfaces in a new way, Guix *et al.* (DOI: 10.1021/nn301175b) developed SAM-modified microtubular engine prototypes capable of capturing and subsequently transporting oil droplets. The researchers prepared these microsubmarines through a template-based electrodeposition of a PEDOT/Pt bilayer microtube, then used electron-beam vapor deposition to add Ni and Au outer layers for magnetic navigation and surface functionalization. Lastly, the resulting microtubes were immersed in dodecanethiol to form a long-chain SAM on its surface, making it superhydrophobic. Experiments showed that these microsubmarines, propelled by bubbles from H_2O_2, interact with fixed oil droplets on slides as well as free-floating olive and motor oil, carting some of the free-floating oil away from bulk samples. The authors suggest that these microsubmarines hold promise for future oil remediation efforts, where similar micro- or nanomotors could be propelled by their own environment in order to remove oily contaminants.



Fighting Bacteria with Charge-Switching Drug Carriers

Nanoparticles have become promising candidates for drug carriers for a variety of disease-fighting applications in the past several years, with recent gains in the ability to design precise biological interactions that increase drug potency or properties *in vivo*. For example, researchers have designed interaction features for molecular targeting, environmental switching that leads to drug release, optimized physicochemical properties, and sustained drug release. However, a significant challenge that remains is developing antibacterial nanoparticles that are suitable for systemic administration. Most antibacterial nanoparticles developed to date have strong cationic surface charges, which can adversely affect circulation and lead to toxicity.

To solve this problem, Radovic-Moreno *et al.* (DOI: 10.1021/nn3008383) developed nanoparticle drug carriers that take advantage of the low pH that characterizes many bacterial infections to switch from anionic surface charge to cationic, allowing them to attach more effectively to the bacterial wall. These novel carriers are layered, with biologically friendly polyethylene glycol (PEG) on the outside and poly(D,L-lactic-*co*-glycolic acid) (PLGA) as the inner drug depot, with a layer of poly-L-histidine (PLH) sandwiched between. This PLH layer has the capability of becoming positively charged under acidic conditions, yielding an overall positive zeta-potential on the nanoparticle surface. Before loading, the nanoparticles successfully bound to both Gram-positive and Gram-negative bacteria, with enhanced binding capabilities at lower pH. When loaded with the antibiotic vancomycin, which tends to lose efficacy at lower pH, these drug carriers were significantly more bacteriocidal than the free drug. The authors suggest that similar charge-switching drug carriers could be used in a variety of infection-fighting scenarios in which systemic delivery is preferable.

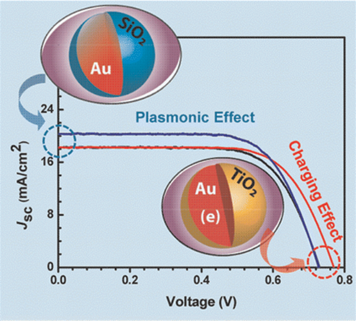


10.1021/nn302035d

Friendly Nano-Neighbors Help Solar Cells in Different Ways

Next-generation solar cells often incorporate semiconductor nanoparticles into their designs in conjunction with metal-semiconductor nanoparticles that have core–shell geometries. These latter materials can boost a solar cell's overall performance by enhancing their photocatalytic or photovoltaic behavior. However, the reasons behind the increased photoconversion efficiency are not known. Researchers have suggested a variety of explanations, including better light absorption due to surface plasmons and light trapping effects, better charge separation from a localized electromagnetic field, encouraging electron transfer to adsorbed species, and electron storage that drives the Fermi level to more negative potentials.

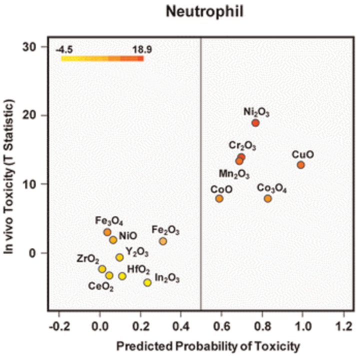
To gain insight into the potential mechanisms behind this phenomenon, Choi *et al.* (DOI: 10.1021/nn301137r) examined dye-sensitized solar cells (DSSC) that incorporate two commonly used core–shell nanoparticles: Au@SiO_2 and Au@TiO_2. Results from absorption spectra for each of these core–shell nanoparticles suspended in solution show changes in the plasmon absorption band upon UV irradiation of Au@TiO_2, suggesting that this core–shell nanoparticle generates electron–hole pairs within its shell, transferring electrons to its core while holes are scavenged. Alternatively, results from Au@SiO_2 show a stable plasmon absorption band. Since this material is an insulator and incapable of electron storage, Au@SiO_2's enhancement likely results from plasmonic effects. In DSSCs, both nanoparticles significantly enhanced efficiency, with Au@TiO_2 nanoparticles boosting efficiency from 9.3 to 9.8%, and Au@SiO_2 nanoparticles increasing efficiency further to 10.2%. However, those DSSCs with Au@SiO_2 produced higher photocurrents, and those with Au@TiO_2 produced higher photovoltages. The authors suggest that combining these paradigms might further enhance DSSC performance.



Band Gap Predicts Nanomaterial Toxicity

Engineered nanomaterials (ENM) have had substantial impact on a variety of technologies. However, many of these materials are potentially hazardous to human and animal health. Previous research has suggested that one of the principle inducers of ENM's health dangers is their ability to generate oxygen radicals and, consequently, oxidative stress. For metal oxide (MO_x) nanoparticles, this effect could be caused by electron exchange between semiconductors in these materials and redox-active substances in cell interiors. If this mechanism holds true, the toxicity of various ENMs could be predicted by whether their band gaps fall within the cellular redox potential (−4.12 to −4.84 eV).

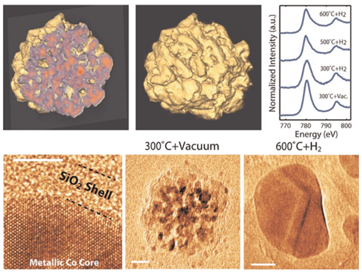
Putting this idea to the test, Zhang *et al.* (DOI: 10.1021/nn3010087) examined the toxicity of 24 different MO_x nanoparticle compositions, covering representative oxides from across the periodic table. Using common single-parameter assays, along with multiparameter toxicity testing developed in their lab and *in vivo* toxicity testing, the researchers found that Co_3O_4, Cr_2O_3, Ni_2O_3, Mn_2O_3, CoO, CuO, and ZnO generated severe toxicity in each type of testing. When the researchers determined the conduction band energy (E_c) levels of each type of ENM sampled, Co_3O_4, Cr_2O_3, Ni_2O_3, Mn_2O_3, and CoO overlapped with cellular redox potentials, showing good agreement with theory. However, the E_c for neither CuO nor ZnO was in this range. Further investigations using inductively coupled plasma mass spectrometry suggest that the toxicity of these two ENMs can be explained by their solubility. The authors suggest that combining E_c with solubility can effectively predict MO_x nanoparticle toxicity, which could in turn guide regulatory decisions about these materials.



Valence State and Nanoporous Structure: Reducing the Mystery

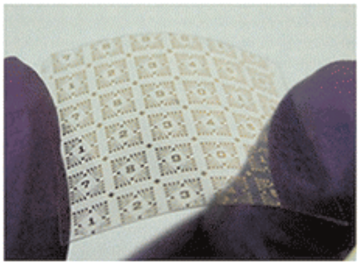
Fischer–Tropsch (F–T) synthesis, an industrial reaction that converts a mixture of hydrogen and carbon monoxide to liquid fuels, relies on iron or cobalt catalysts. The initial reduction of oxide nanoparticles into these metallic catalysts is a critical step in this process. Consequently, preparing and conditioning the catalyst's microstructure and valence state is important for achieving the necessary durability and effective catalytic activity. While understanding how the microstructure changes that occur with oxidation correlate with valence state could help optimize catalyst production, there have been few studies thus far that examined the reduction process simultaneously with *in situ* imaging and spectroscopy.

To accomplish this goal for an important F–T catalyst, Xin *et al.* (DOI: 10.1021/nn3007652) correlated the changes in nanoporous structure and valence state in porous CoO_x/SiO_2 nanoparticles as this material becomes reduced in H_2 gas under high heat. The researchers placed nanoparticle samples into an enclosed gas cell in an environmental transmission electron microscope, then pumped in gas while gradually increasing the temperature. While imaging, they simultaneously performed electron energy loss spectroscopy (EELS). Their investigations show that as the temperature increased from 300 to 600 °C, the sample underwent structural changes, markedly coarsening and decreasing in porosity. *In situ* EELS measurements showed that the electronic structure of Co paralleled these structural changes, reducing with increasing temperature, and suggesting an optimum reduction temperature of 410 °C. The authors suggest that correlating the valence state and structural changes for other materials could lead to those with better catalytic activity and selectivity.



Graphene Field-Effect Transistor, Heal Thyself

Using plastic as a substrate, graphene holds particular potential as a high-speed platform for flexible and transparent field-effect transistors (FETs). However, the electron mobility of graphene FETs manufactured using chemical vapor deposition (CVD) has been relatively low, presumably because of long access lengths in the ungated channel region between the drain/source contacts and gate, which lead to high access resistance. Self-aligned top gates applied using the hydrophobic characteristics of exfoliated graphene can help mitigate this problem, but transferring CVD-produced graphene typically leaves a thin layer of polymer residue, which harms the quality of subsequently deposited dielectrics.

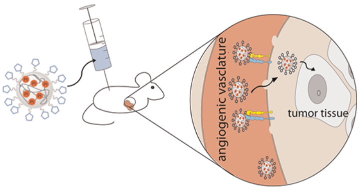


To get around these difficulties, Lu *et al.* (DOI: 10.1021/nn301199j) looked to naturally formed aluminum oxide as a gate dielectric and spacer for self-alignment. The researchers first crafted graphene FETs on Si substrates with dual gates. After exposing the device to air for at least 6 h, which enables the formation of a thin dielectric layer of AlO_x, they deposited a layer of Cr/Au that became automatically aligned by the Al/AlO_x gate edges into the source and drain electrodes. This process reduced the access length to about 20 nm. The researchers were able to replicate this fabrication method on flexible poly(ethylene terephthalate), with resulting devices showing high on/off ratios, low operation voltages, and high mobilities compared to other reported flexible FETs. Additionally, the AlO_x showed a unique capability for self-healing upon electrical breakdown. After increasing the gate-source voltage above the breakdown field, the investigators found that the damaged oxide repaired automatically through more exposure to air. The authors suggest that this protocol could significantly advance device performance and stability in flexible FETs.

Going Platinum with Better Efficacy, Less Toxicity

Cisplatin, a Pt(II) compound, is widely used to treat ovarian and testicular cancer. However, its beneficial effects come with a host of limitations. This drug is known to cause severe nephrotoxicity, limiting the dose that can be safely delivered. It is also difficult to deliver to other types of cancers for which it might be useful, such as breast cancers. Additionally, only a small fraction of the delivered drug enters cells and binds to nuclear DNA, where it exerts its effects.

Troubleshooting each of these problems, Graf *et al.* (DOI: 10.1021/nn301148e) combined several strategies to target more Pt(II) to cancer cells. First, the researchers relied on a Pt(IV) compound, a more inert precursor to Pt(II), rather than Pt(II) itself. They further improved retention by encapsulating this compound in the polyester poly(D,L-lactic-*co*-glycolic acid) (PLGA), surrounded by the biologically friendly polymer polyethylene glycol (PEG), packaged into nanoparticles of approximately 100 nm in diameter. To the PEG, they attached the cyclic pentapeptide c(RGDfK), which targets $\alpha_v\beta_3$ integrin, a receptor overexpressed in many cancer types and commonly expressed in tumor vasculature. Testing the resulting product on prostate and breast cancer cell lines *in vitro*, the researchers found that these targeted nanoparticles were significantly more cytotoxic than cisplatin and other delivery systems that packaged Pt(IV) in different ways. In a xenograft animal model of breast cancer, the novel targeted nanoparticles were more efficacious than cisplatin and better tolerated, with significantly less Pt accumulation in the kidneys. The authors suggest that these targeted, Pt(IV)-loaded polymer nanoparticles could be optimized for even better efficacy with future dose response studies.



Conserving Indium with Novel ITO Films

Indium tin oxide (ITO) electrodes are widely used as components in devices in which an optically transparent electrode is necessary. Films for these electrodes have traditionally been prepared using vapor phase deposition. However, a global shortage of indium has triggered a need for novel ways to conserve this material, such as preparing electrodes from ITO nanoparticle inks. Because the resulting electrodes tend to suffer from low conductivity, further improvements are needed to synthesize more effective ITO electrodes in materials-conscious ways.

In a step toward this goal, Yarema *et al.* (DOI: 10.1021/nn3005558) developed self-assembled ITO nanoelectrodes using monodisperse solutions of colloidal nanocrystals. The researchers first prepared colloidal indium nanocrystals through a novel method that involved two subsequent injections into a coordinating hot solvent. The first contained a mixture of indium(III) tris[bis(trimethylsilyl)-amide] and lithium bis(trimethylsilyl)amide, and the second contained a solution of lithium triethylborohydride, a strong reducing agent known as a superhydride. By adding tin(II) bis[bis(trimethylsilyl)amide], the researchers used the same method to create $In_{1-x}Sn_x$ nanocrystals. Both types of resulting nanocrystals were nearly perfectly spherical, with uniform sizes and shapes. Drop-casting these nanocrystals onto silicon substrates showcased their ability to self-assemble into highly ordered superlattices. By spin-casting nanoparticle solutions onto patterned substrates, then treating these films with oxygen plasma and heat, the researchers produced ITO electrodes that performed as well as the best values for ITO electrodes from nanoparticle inks but allowed the formation of electronics with lateral dimensions as small as 25 nm. The authors suggest these nanoscale electrodes could eventually be integrated with traditional silicon electronics to improve performance.