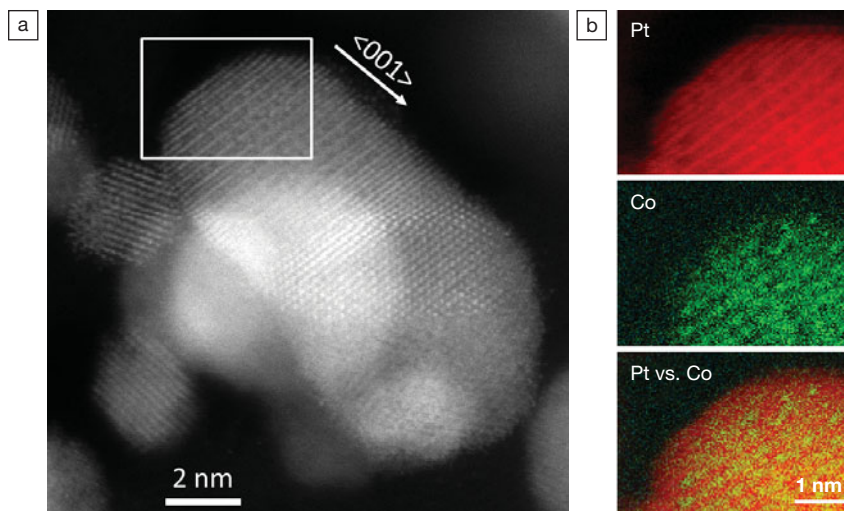


Energy Focus
Atomic ordering in Pt-Co alloy core-shell nanoparticles boosts electrocatalytic activity and stability

One of the primary limitations to the realization of efficient fuel cells is the lack of effective and chemically stable electrocatalysts. Specifically, the slow oxidation–reduction reaction occurring at the cathode limits the practical utility of exchange membrane fuel cells. As a step toward finding a solution to this problem, researchers at Cornell University have observed an increase in activity and enhanced chemical stability of electrocatalysts made of atomically ordered platinum-cobalt alloy nanoparticles with a platinum shell.

As reported in the October 28, 2012 online edition of *Nature Materials* (DOI: 10.1038/NMAT3458), D. Wang, H.L. Xin, and collaborators found that structurally ordered nanoparticles have the highest reported activity for Pt-Co nanoparticle systems, and that they display a threefold increase in specific activity over both disordered Pt₃Co alloy and carbon-supported platinum nanoparticles. In the study, nanoparticles were created using an impregnation-reduction method and then heated to 400°C or 700°C in a hydrogen atmosphere. While the 400°C annealed nanoparticles remained disordered, x-ray diffraction, together with atomic-resolution imaging



Annular dark-field scanning transmission electron microscopy image shows structural stability of Pt₃Co/C-700 nanoparticles after 5,000 electrochemical cycles. Reproduced with permission from *Nature Mater.* DOI: 10.1038/NMAT3458. © 2012 Macmillan Publishers Ltd.

and chemical mapping techniques, revealed the 700°C annealed nanoparticle structure to be that of an ordered alloy with a 2–3 atomic layer platinum shell.

The advantage of using the higher temperature protocol to order the Pt-Co alloy is clearly seen by using the nanoparticles as electrocatalysts in the form of thin films on a rotating disk electrode to test their activity. This demonstrated that ordered alloy nanoparticles exhibit triple the mass activity of the disordered alloy nanoparticles. In addition to the enhancement in activity, cyclic voltammetry revealed that the 700°C-annealed

Pt₃Co nanoparticles suffer minimal loss after 5000 cycles while the core-shell structure is preserved. The researchers attribute the increased durability and activity of these carbon-supported core-shell nanoparticles (Pt₃Co@Pt/C) to the resilience of the shell and stable atomic arrangement of the intermetallic alloy.

This work presents a new approach to electrocatalyst design for applications in fuel cells, and is an important step toward a clean energy future.

Charles M. Brooks

Nano Focus
Porous graphene sieve selectively passes molecules

Many applications rely on porous membranes to pass specific molecules while excluding others, such as industrial-scale chemical and gas purification. As reported in the October 7, 2012 online issue of *Nature Nanotechnology* (DOI: 10.1038/NNANO.2012.162), S.P. Koenig and co-workers at the University of Colorado have fabricated molecular sieves by etching pores in bilayer graphene

membranes, where the graphene membranes provide atomic thickness, mechanical robustness, chemical inertness and impermeability to standard gases.

The researchers defined an array of 5- μ m-diameter microcavities in silicon oxide using standard photolithographic techniques, and then mechanically exfoliated graphene over these wells to form suspended membranes. The as-deposited graphene flakes cling to the oxide substrate through surface forces in a gas-tight manner, although gases are able to enter/exit the microcavity through very slow diffusion through the oxide.

The graphene-sealed microcavities are then loaded with a desired gas species by placing them in a high-pressure (200 kPa above ambient) environment containing the charging gas and allowing the system to equilibrate for 4–12 days. When the samples are brought out to ambient conditions, the membrane bulges outward due to the pressure differential. Slow leak rates were demonstrated through the pristine membranes (on the order of minutes to hours) by using an atomic force microscope to measure the deflection δ of the swollen blister with time.



Finally, pores were generated in the graphene membranes by oxidative etching on exposure to ultraviolet light. The molecular selectivity of these membranes was then demonstrated by the observation that δ decreases two orders of magnitude more rapidly as compared with nonporous graphene for small gas molecules such as H_2 and CO_2 , while the rate

remains largely unchanged for Ar and gas molecules with a larger kinetic diameter.

In graphene membranes that have larger pores, faster leak rates were measured using a mechanical resonance method which again demonstrated size-selective leak rates, but this time for molecules above and below the size of SF_6 .

“Our results are consistent with theo-

retical models based on effusion through Ångstrom-sized pores,” stated group leader J. Scott Bunch, “and represent an important step toward the realization of macroscopic, size-selective porous graphene barriers.”

Rich Louie

Energy Focus

Energy harvesting in electronic displays enabled by fluorescent-dye-cascade linear polarizer

As anyone with a smart phone or tablet knows, battery life is the key to a useful mobile device. Recently, luminescent solar concentrators (LSCs) have gained attention as a possible energy-harvesting technique to extend mobile battery life. When integrated into a display, LSCs steer incoming light that would otherwise be wasted (sunlight, room lights, or the internal backlight) to small photovoltaics placed inside the device perimeter. However, current LSCs reduce display quality and therefore remain impractical. Now, A.M. Velázquez and colleagues at the Massachusetts Institute of Technology have demonstrated an LSC based on cascading fluorescence that may eliminate this problem by shifting reemitted light into the infrared. They reported their findings in the October 25, 2012 online edition of *Energy & Environmental Science* (DOI: 10.1039/c2ee23265k).

LSCs studied to date have been based on luminescent dye molecules placed

in a glass sandwich waveguide. These molecules can be aligned within a liquid crystal host, making the system into a linear polarizer, which could potentially replace the standard linear polarizers used in display technology. However, photons that result from the dye fluorescence can escape from the waveguide and be reemitted from the surface, contaminating the display image. The researchers hypothesized that they could overcome this problem by combining four different fluorescent dyes, with emission and absorption spectra that overlap to cover the optical spectrum all the way to the infrared. The final emission of this cascade could therefore be filtered out by a standard infrared filter.

The researchers prepared the device by first dissolving four dyes in chloroform, mixing them with a nematic liquid-crystal host at 60°C for five minutes and desiccating the mixture for 12 hours. Next, they used capillary action to fill a 5- μ m-gap liquid-crystal cell with the mixture, heating the materials to 70°C and slow-cooling them to ensure good alignment on the rubbed polyamide surfaces of the cell. The dyes chosen were (in wt% in the final device) coumarin 6

(0.3%), DCM2 (0.3%), Nile Red (0.6%), and a squaraine dye (0.2%).

Using an integrating sphere to make optical measurements, the researchers found that the final device exhibits good optical quantum efficiency: approximately 20% of incident photons at the peak absorption wavelengths are steered to the perimeter, which is in good agreement with theory. This suggests that the cascade of multiple dyes undergoes Förster resonant energy transfer with approximately unity efficiency. The combination of dyes selected also ensured that the photoluminescence of the dye cascade peaks in the near-infrared, meaning that light escaping the waveguide could be easily filtered without affecting display quality. If used in a standard crossed-polarizer display, the researchers estimate that the device could generate over 10 μ W/cm² indoors and as much as 1–10 mW/cm² outdoors.

These results suggest that displays on mobile devices may someday do double duty, providing information for the user while also generating electrical power for the device.

Colin McCormick

Bio Focus

Bioinspired polymeric carbon nitride nanospheres dramatically improve photoredox catalysis

Many attempts have been made to create synthetic analogues of the natural photosynthesis system. However, the ability to mimic the spatial

organization of this system, where the thylakoid membrane acts as a photosynthetic scaffold that captures and distributes light, and separates the oxidative from reductive species, remains a significant challenge. As reported in the October 16, 2012 online edition of *Nature Communications* (DOI: 10.1038/ncomms2152), X. Wang and co-researchers at Fuzhou University, China,

and M. Antonietti at the Max Planck Institute of Colloids and Interfaces, Potsdam, Germany, have addressed this challenge by employing polymerized hollow nanospheres as analogues of the thylakoid membrane of a chloroplast. These hollow carbon nitride nanospheres (HCNSs) were used as a light-harvesting platform for catalyzing hydrogen evolution under visible light