critical tradeoff between water permeance and solute rejection in conventional desalination membranes."

The combination of high water permeance and salt rejection properties of the membrane could be ideal for transforming salty water sources into potable freshwater. The researchers believe that there are no fundamental limitations to producing large sheets of the material, even up to the meter-scale.

César Moreno of the Catalan Institute of Nanoscience and Nanotechnology (ICN2) believes the work of Yang et al. addresses the Achilles heel of graphene membranes, the porous support.

"The great interest in graphene as membrane stems from the capability to drill pores with exquisite precision, in addition to its atomic thickness," he explains. "The porous support should provide enough mechanical strength to enable one-atom-thick nanoporous graphene withstand the pressure required for filtration while avoiding the generation of cracks or defects. In Yang et al.'s work, this critical role is played by the carbon nanotube-based support, which provides a meritorious equilibrium between selectivity, permeability, and mechanical strength."

The future success of this approach will depend on improving the packing of the carbon nanotubes to enhance the permeance until it is one order of magnitude higher, he adds. This has been reported in atomically thin nanoporous graphene on flat silicon nitride supports but only at micrometer scales [Surwade et al., *Nature Nanotechnology* **10** (2015), 459–464].

Qilei Song of the Barrer Centre at Imperial College London points out that Yang et al. have applied the well-known oxygen plasma etching approach in an elegant new way to tune the porosity of graphene membranes on carbon nanotube membrane supports.

"The resulting hybrid membranes combine the size-exclusion function of nanoporous graphene and high mechanical strength of nanotubes," he says. "This will inspire further work on developing nanoporous graphene membranes or using the graphene membranes as building blocks for fabricating thin film composite membranes."

Song cautions, however, that there are many challenges to overcome before these supported graphene membranes can be used in practical seawater desalination or nanofiltration.

"The salt rejections are still low and need to be improved to a higher level (>99%)," he points out. "In practical nanofiltration applications, selectivity is more important rather than high water flux, so more precise control of pore size distribution and functional groups will be required, which is not an easy task. Furthermore, it remains challenging to scale up these membranes to the meter-square size for industrial applications."

While there is still a long way to go in making real membranes from graphene, Song believes that this study brings the possibility a step closer.

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Gold's atomic structure puts the brakes on carriers

Cordelia Sealy

Gold atoms prefer to take up a particular spatial arrangement, face-centered cubic, in bulk material but can behave differently when limited to tiny nanoclusters. These collections of atoms less than 2 nm in diameter can adopt different packing arrangements including hexagonal close packed and body-centered cubic structures. Now researchers have found that these atomic structures have a profound effect on carrier lifetimes, which could have important implications for the application of metal nanoclusters in solar energy converters, photocatalysis, and optoelectronics [Zhou et al., *Science* **364** (2019) 279, DOI:10.1126/science.aaw8007].

Very small gold nanoclusters (Au NCs) protected by organic ligands have distinct energy levels and multiple absorption peaks in the ultraviolet-visible light spectrum. This presents an attractive option for light-harvesting devices converting absorbed solar light into electron-hole pairs. These electron-hole pairs either recombine unproductively or form free charge carriers. The lifetime of these charge carriers, which is vital to the usefulness of devices, depends upon various factors, such as the band gap and temperature, and can be tailored by varying the size, composition, and structure of the nanoclusters.

It is already well known that in larger nanoclusters reducing the energy gap leads to shorter carrier lifetimes, but in smaller nanoclusters structure-related factors can take over. Now Rongchao Jin of Carnegie Mellon University and De-en Jiang of the University of California, Riverside along with colleagues at Brookhaven National Laboratory have observed huge differences in carrier lifetimes in Au nanoclusters with different crystalline structures.

"We found that new structures of gold nanoclusters led to a difference in photoexcited states by more than three orders of magnitude," says Jin. "Such a drastic difference in carrier lifetime is unprecedented and fundamentally important."

When Au atoms take up a body-centered cubic structure, carriers show an exceptionally long lifetime (of 4.7 microseconds), which is comparable to that of Si. By contrast, the carrier lifetime in hexagonal close-packed Au nanoclusters is just 1 nanosecond (Fig. 1). The researchers believe that differences in the electronic structure of the various arrangements of Au_4 tetrahedral building blocks in the three crystal structures lead to the large variation in carrier lifetime.

"The achieved control over quantum states originates from the different overlap of molecular orbitals of the two nanoclusters," explains Jin.

In hexagonal close-packed Au NCs, the distance between neighboring Au_4 tetrahedral units is zero and the carrier lifetime is, as the researchers show, very short. By contrast, the distance between neighboring Au_4 tetrahedral units in body-centered cubic NCs is

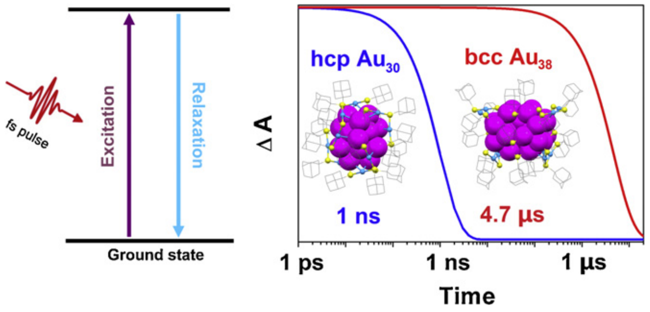

Fig. 1. Structure-enabled exquisite control of quantum states of electrons in gold nanoclusters.

2.86 Å and the carrier lifetime is longer. In the regular face-centered cubic arrangement, the distance between neighboring Au_4 tetrahedral units is 3.0 Å, but they take up a double-helix-like arrangement that allows relatively efficient energy transfer. Consequently, face-centered cubic NCs demonstrate an intermediate carrier lifetime of around 100 ns.

The researchers' findings indicate that structure rather than size is the crucial factor in determining carrier lifetimes in very small Au NCs.

"The strategy of manipulating the excited-state lifetime from very short to very long is exciting," points out Jin. "Our results demonstrate that the atomic packing structure, which houses electrons, can greatly affect their excited-state lifetimes, providing a means for exquisite control. Such results open a new door to quantum manipulation, which is of tremendous importance in exploring new nanoscale phenomena and designing nanodevices."

Now the researchers plan to turn their attention to the effects of doping and alloying on carrier lifetimes and hopes to establish a set of rules for controlling the quantum behavior of electrons.

Jin Ho Bang of Hanyang University in Korea believes that the work represents a very important breakthrough, which will help to advance metal nanoclusters as an active material for optoelectronic applications.

"Metal nanoclusters with discrete electronic structures are a relatively new class of photoactive materials that provide exciting new opportunities for light energy conversion applications," he comments. "One of the important aspects of these applications is the excited state lifetime of a photoactive material. Usually, however, the excited state lifetime of metal nanoclusters tends to decrease with the decrease in the HL gap. Zhou et al. have now shown that may not always be the case."

As well as demonstrating that body-centered cubic NCs have three orders of magnitude longer excited state lifetimes than hexagonal close-packed NCs with a similar HL gap, the researchers have also identified the origin of the dramatic difference, he points out.

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Inorganic nanosheets make food packaging recyclable

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Researchers from the University of Oxford have developed a nanotoxic food packaging film that effectively keeps out air and moisture but is easier to recycle than currently used materials [Yu et al., *Nature Communications* (2019) 10:2398, https://doi.org/10.1038/s41467-019-10362-2]. Packaging materials for food such as crisps and coffee are made from several layers bonded together, usually polyethylene terephthalate or PET and thin metallized layers of aluminum, to preserve freshness.

"The main problem is recyclability," points out Dermot O'Hare, who led the research. "To recycle [the material], the different layers need to be separated, so while technically it can be recycled at the industrial level, it is not yet economically viable to do so."

Moreover, the fusing together of the polymer and metal layers requires long baking times, which adds up to a large carbon footprint.

In the search for an easier to recycle alternative, the team from Oxford turned to a class of synthetic inorganic clay-like materials called layered double hydroxides (LDHs). These layered metal hydroxides can be exfoliated into dispersions of nanosheets, which can in turn be deposited in thin films onto flexible polymer substrates.

"Because the LDHs we are using are entirely synthetic, unlike some clays that have been used previously for barrier applications, we can tailor them to be entirely nontoxic, free of any heavy metal traces," says O'Hare. "In terms of the chemistry, this is a breakthrough."

The process starts with Mg_2Al LDH, which is heated to create a layered double oxide. The oxide is then exfoliated in an amino acid solution to make a translucent gel. Diluting the gel creates a liquid dispersion of Mg_2Al LDH nanosheets, which can be added to polyvinyl alcohol (PVA) and coated onto a desired substrate such as PET (Fig. 1).

"Our low-energy alternative barrier coating for food packaging eliminates the metallic layers from the polymer film so not only is it much easier to recycle, completely nontoxic, and mechanically stronger than metallized films, it is also transparent and has a lower carbon footprint," explains O'Hare.

The LDH nanosheet layer can be as thin as 100 nm or as thick as 1.8 μm, without affecting the transparency of the substrate film, which could be of significant benefit in food packaging. Most importantly, however, the nanosheets line up parallel to the substrate and form an impenetrable maze – or what is known as a 'tortuous pathway' – for oxygen and water molecules to pass through. This reduces the oxygen and water transmission rate of the LDH-coated PET film to below measurable or very low levels, respectively.