

in the development of semi-analytical models for investigating cavity-assisted processes (for example, spontaneous decay, nonlinear effects and lasing). The most intriguing questions are those regarding the fundamental limits of a resonator. What is the smallest possible structure that yields the desired enhancement of light–matter interaction? Are there scaling laws that apply to resonators when their size reaches nanoscale dimensions?

These questions may now be more easily tackled by combining the result of Sauvan *et al.* with the theory of electrically small antennas applied to nanoresonators<sup>9</sup>. The latter states that the available space in which one can build an antenna system imposes fundamental restrictions on its radiative properties. More precisely, the *Q*-factor turns out to be inversely proportional to the antenna volume. Moreover, because field confinement increases with decreasing nanoresonator dimensions, the *Q*-factor and mode volume are not independent of each other; their dependence has to be accounted for when designing nanoresonators. As a result, the Purcell factor scales as the inverse square of the resonator volume, giving rise to extreme enhancement of spontaneous decay.

Incidentally, this is precisely the case Purcell discussed in his seminal work<sup>3</sup>. He considered metallic spheres with a radius of the order of one millionth of the wavelength of radio waves. By assuming a nonresonant system and setting the *Q*-factor equal to one, he seems to have calculated the enhancement to be inversely proportional to the volume of a sphere. However, for the dimensions he considered, the *Q*-factor could be inversely proportional to the microsphere volume. Consequently, his estimation would be a few orders of magnitude off, meaning that the same enhancement ( $10^{19}$ !) could have been obtained with a much larger resonator.

This example demonstrates how an accurate formulation of the Purcell factor for deep-subwavelength systems is a powerful tool for exploring the limits of light–matter interaction at the nanoscale on a sound basis. It is also a unique way to identify scaling laws that could shed new light on the modification of spontaneous decay and other processes. Making very small resonators to realize cavity-enhanced processes at the nanoscale is very important for a wide range of applications<sup>10</sup>. However, we should not overlook the fact that we are just beginning

to explore the extreme regimes Purcell suggested at optical frequencies. It looks probable that we will soon be able to extend light–matter interaction to these unexplored regions, spawning innovation in optical nanomaterials and nano-optics. There is plenty of room at the nanoscale for the Purcell factor. □

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## OPTOELECTRONICS

# Plasmon-enhanced plastic devices

The abundance of unique effects found at the nanoscale offers advantages for electronics. Now, complex heterostructures of metal clusters grown on a carbon-dot support exhibit interactive plasmonic activity that enhances the performances of LEDs and solar cells.

Joseph M. Luther and Jeffrey L. Blackburn

The use of nanostructures in optoelectronics is alluring because it has the potential to realize more efficient and faster devices, as electron transport distances can be reduced. Furthermore, bottom-up nanostructures allow researchers to exploit a wide range of new light–matter interactions. Efforts are now underway to understand and harness energy flow in nanoscale systems and to use this knowledge to produce efficient electronics. For example, inorganic nanostructures and carbon-based nanomaterials (such as those made from organic polymers, fullerenes, carbon nanotubes or graphene) allow the realization of components that are processed and deposited by inexpensive solution-based methods onto flexible substrates. This enables lightweight,

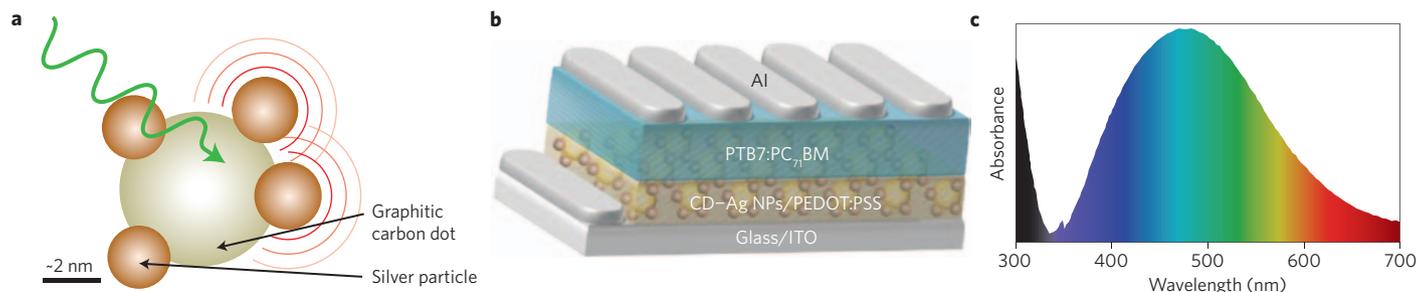
convenient and portable large-area devices to be fabricated, including photovoltaic devices and light-emitting diodes (LEDs).

Now, writing in *Nature Photonics*, Hyosung Choi and co-workers<sup>1</sup> demonstrate plasmon-enhanced organic devices that use heterostructured nanoparticles. In brief, the researchers show that polymer photovoltaic devices with near-record efficiencies may be improved by incorporating heterostructures consisting of carbon nanodots and silver nanoparticles. Furthermore, they demonstrate that such structures can enhance an LED's luminous efficiency (the number of photons emitted per electron–hole pair injected into the LED) by a factor of up to three in select operating regimes.

Heterostructured nanoparticles (that is, nanoparticles consisting of multiple

phases that are joined together) exhibit the size-specific properties of the individual nanostructures from which they are made. They can also exploit a synergy resulting from the interfaces or interactions between substructures. This synergy can be used to improve the functionality of a heterostructure for specific goals. They offer seemingly limitless tunability for separating charge, channelling energy towards a reaction site, and enhancing (or otherwise modifying) the local density of states and/or the photocatalytic properties. These attributes are especially important when nanomaterials are used in devices for which energy efficiency is crucial.

Varying the atomic arrangement or the material shape provides additional means to modify their material properties. The best example of this may be  $sp^2$ -hybridized



**Figure 1** | Plasmon-enhanced optical properties achieved using nanoheterostructures. **a**, Carbon dots are decorated with silver nanoparticles. **b**, They are then embedded in a conductive polymer. **c**, The resulting functional composite material exhibits broadband plasmonic resonance across much of the visible spectrum. Choi *et al.*<sup>1</sup> use this contact electrode in efficient polymer LEDs and polymer photovoltaic cells, both of which display improved overall performance resulting from plasmonic enhancement of the optical properties.

carbon, which exists in a variety of allotropes that differ in the degree to which quantum confinement effects occur. The confinement, in turn, dramatically alters the optical and electrical properties, which range from molecular-like for fullerenes (three-dimensional confinement) to semiconducting or semi-metallic for carbon nanotubes (two-dimensional confinement), and to semi-metallic for graphene (one-dimensional confinement).

A relative newcomer in the field of carbon nanomaterials is the ‘carbon (quantum) dot’. Typically described as “tiny fragments of graphite” and having dimensions smaller than 10 nm (ref. 2), carbon dots possess properties that are more difficult to characterize succinctly than those of fullerenes, nanotubes or graphene. This is because the rigorously defined structural specifications of fullerenes, nanotubes and graphene can be more easily handled by theory. However, it has been suggested that some properties of carbon dots may make them useful for optoelectronic devices; such properties include broadband luminescence ranging from the ultraviolet to the near-infrared region, the ability to donate or accept electrons in hybrid systems, photocatalytic properties, and high surface area and edge functionality for catalyst immobilization<sup>2</sup>.

The advantages of using carbon as a tunable support for other nanoscale species are well recognized<sup>3,4</sup>, especially in catalytic applications such as fuel cells<sup>5</sup> for which carbons are typically used to immobilize highly active noble metal catalysts. Broadly speaking, such applications are based on the excellent charge transport in conjugated carbon and the potential ability to create specific binding sites for nanoparticles that prevent diffusion and agglomeration from occurring during device operation<sup>6</sup>. A holy grail for carbon-based nanoparticle supports is the direct and rational creation of binding sites at desired locations on

the carbon support, which would permit the size, location, density and stability of bound nanoparticles to be controlled precisely. Such control would enable the realization of hybrid systems with widely tunable properties arising from the tailored properties of semiconducting or metallic nanoparticles, which may act in an isolated or collective fashion depending on their spatial organization.

The potential synergy between these phenomena may allow scientists to develop fully functional electronic devices with extremely high figures of merit. However, the challenge lies in optimizing multiple nanoscale processes in a single complex system. For example, in a polymer photovoltaic device, a high external quantum efficiency (the spectrally resolved ratio of collected electrons to the number of incident photons) requires an active layer that is thick enough to absorb ample incident light, yet thin enough and possessing sufficient intermixing of hole- and electron-conducting phases such that light absorption, exciton dissociation and near-lossless charge transport can be realized simultaneously. In addition, charge-extracting contacts suitably matched to the composite must selectively extract holes on one side and electrons on the other. If these criteria cannot be met at an optimal thickness for solar capture, then the incorporation of metallic-like nanostructures with localized surface plasmons may effectively increase the absorption coefficient through coupling of the electronic transition dipole to the electric field of the plasmon, which would permit thinner layers to be used<sup>7</sup>. Conversely, in LEDs, the emitter layer must enable efficient and balanced charge carrier injection from both electrodes and promote quantitative radiative recombination without the reabsorption of light<sup>8,9</sup>. For plasmon-enhanced LEDs, coupling to the plasmonic field can increase the

spontaneous emission rate, leading to an enhanced luminous efficiency.

Choi *et al.*<sup>1</sup> fabricated hole-conducting poly(3,4-ethylenedioxythiophene):poly(styrene sulphonic acid) (PEDOT:PSS) layers ‘doped’ with silver-decorated carbon dots (deposited in separate steps). They demonstrated that devices containing these nanoheterostructures in the PEDOT:PSS layers exhibit enhanced optical-to-electrical conversion in solar cells and greater electrical-to-optical conversion in LEDs. The ~5-nm-diameter carbon nanodots provide a support for the nucleation and growth of clustered silver particles that form in solution and are cast onto the device substrate before spin casting the polymers. Although it is often nontrivial to isolate the direct enhancement from plasmonic structures in polymer devices<sup>10–12</sup>, Choi *et al.*<sup>1</sup> found that near-record-efficiency devices using state-of-the-art polymers are improved by employing their carbon nanodot–silver nanoparticle heterostructures.

The use of the plasmonic heterostructures made by Choi *et al.*<sup>1</sup> in organic electronic devices is depicted in Fig. 1. The photovoltaic cell with embedded plasmonic structures exhibited increased quantum efficiencies for photons with wavelengths in the range 400–750 nm, which covers almost the whole visible region of the spectrum. Furthermore, the quantum efficiency peaks near the green region of the spectrum, where solar photons are most abundant. This translates to the enhanced cell having an improved short-circuit current.

Control experiments suggest that this broad plasmonic enhancement arises from the unique heterostructure obtained when the particles are grown directly on the carbon nanodots. The researchers suggest that the carbon dots play two important roles in generating this enhancement. First, the photoexcited carbon dots serve to reduce silver ions in solution and template

appropriately sized silver nanoparticles onto the carbon-nanodot surface. Second, electric-field simulations presented by the researchers suggest that the optical fields of closely assembled silver particles on a carbon dot interact and exhibit broad plasmonic activity over a wide spectrum of visible wavelengths, as indicated in Fig. 1.

There are many exciting future directions for plasmon-enhanced solar cells and LEDs. Absorption enhancement within the active layer by surface-plasmon effects can be realized through either direct near-field interactions or by optical-field enhancements arising from forward-scattering processes. These mechanisms depend sensitively on the size, form factor and chemical identity of the metal, as well as the proximity of the metal nanostructures

to the active layer<sup>13</sup>. Also critical are the micro- and mesoscopic morphologies, which, if engineered rationally, can influence interparticle interactions, regulate constructive and destructive interference, and ultimately control the spatial optical-field distribution over many length scales<sup>14</sup>. Complex heterostructures may be useful for addressing these issues by providing a platform for realizing bottom-up control of the properties of plasmonic nanostructures. □

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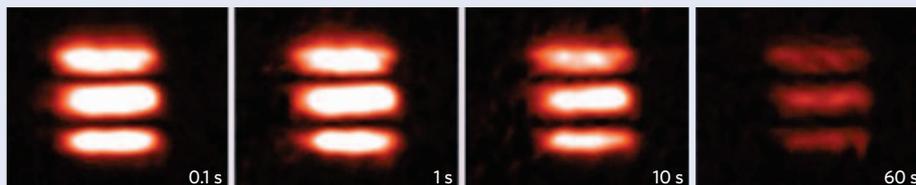
## QUANTUM MEMORY

# Extended storage times

The most promising approach for achieving long-distance quantum communication is to employ quantum repeaters, but they require high-fidelity quantum memories with much longer storage times than the current state-of-the-art memories. The long-term goal of the quantum-communication community is to develop a reliable solid-state optical quantum memory that has a high efficiency, a high storage capacity and long storage times for single or few photons. To realize this goal it is critical to determine the most appropriate medium, the best coherent quantum storage protocol and the most effective control techniques.

Now, Georg Heinze, Christian Hubrich and Thomas Halfmann report light-storage experiments based on electromagnetically induced transparency (EIT) in crystals doped with rare-earth ions (*Phys. Rev. Lett.* **111**, 033601; 2013) and realize storage times close to one minute.

In principle, ion-doped crystals are ideal for use in photon memories because they combine the advantages of solids and isolated atoms with very long hyperfine lifetimes. However, stochastic magnetic interactions with the host material substantially reduce the lifetime of the coherence between the two relevant atomic spin states, which, in turn, reduces photon storage times.



Heinze *et al.* achieved high storage capacities by imprinting two-dimensional image data onto the optical data pulse. In addition, they applied a combination of static and high-frequency magnetic fields to make the medium, a  $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$  crystal, less sensitive to external fluctuations, leading to longer storage durations. The applied magnetic fields made the energy level spectrum of the medium very complicated. Consequently, they used feedback-controlled pulse shaping in combination with a self-learning evolutionary algorithm to determine an optical preparation sequence for their medium. According to them, this is the first time that this combined approach has been applied to EIT, quantum memory and the complex level schemes of doped solids in strong magnetic fields. It can also be used to support other storage protocols.

“The most important achievement of our work is the prolongation of the storage time of an EIT-driven memory up to the regime of 1 min. This is very close to the fundamental limit of the population lifetime in our

medium, which is 100 s,” said Heinze. They also demonstrated the ability to store images in the solid medium for up to 1 min, which is six orders of magnitude longer than the image storage times obtained using hot atomic gases.

“If our approach could be transferred to the single-photon level, it would lead to important applications in the fields of spatially multiplexed optical quantum memory, quantum communications, quantum repeaters and deterministic single-photon sources,” Heinze envisaged.

However, their approach has a storage efficiency of only about 1%. The team is planning to overcome this limitation by either optimizing their technique or applying completely different storage protocols. They are also looking at using different media such as  $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ , which would naturally provide longer storage durations because of its smaller decoherence effects. They also intend to extend the scheme to the single-photon level.

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