Fiber optic SPR sensor for the detection of melamine using molecular Imprinting

Fabrication and characterization of a surface plasmon resonance based fiber optic sensor for the detection of melamine using molecular imprinting are reported by Shrivastav et al. from Physics Department of Indian Institute of Technology in Delhi (February 2015).

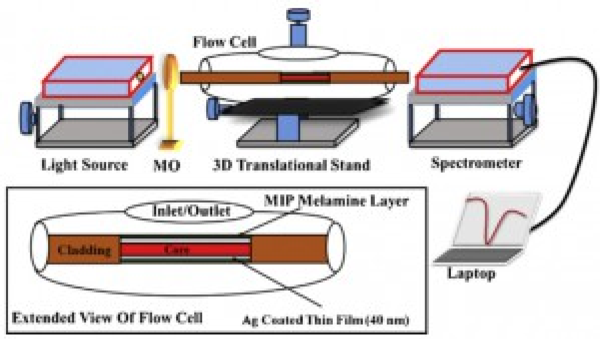


Fig. 1. *Schematic diagram of the experimental setup of surface plasmon resonance based fiber optic sensor for the detection of melamine using molecular imprinting.*

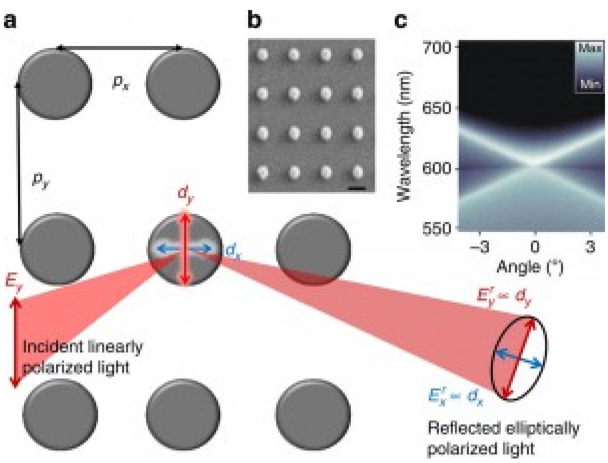
The probe is fabricated by coating a thin film of silver over the unclad core of an optical fiber which is further coated with the molecular imprinted (MIP) polymer using melamine as template molecule. The MIP layer creates binding sites, complementary of the template molecule on the surface. The template molecules have the capability to bind with these active sites. The performance of the sensor is tested for the melamine concentration range from 10−7M to 10−1 M. A shift of 19 nm in resonance wavelength is recorded for this concentration range. The sensitivity is maximized by optimizing melamine concentration in MIP layer formation and the pH of the sample solution. The selectivity of the probe is checked using different analytes and is found to be highly selective for melamine. The sensitivity of the sensor is improved by introducing a thin layer of aluminum between silver and MIP layer. The sensor has advantages of fast response, high selectivity and sensitivity, low cost and can be used for online monitoring and remote sensing applications.

Source: http://www.sciencedirect.com/science/article/pii/S0925400515001902

[Putting a new spin on plasmonics]()

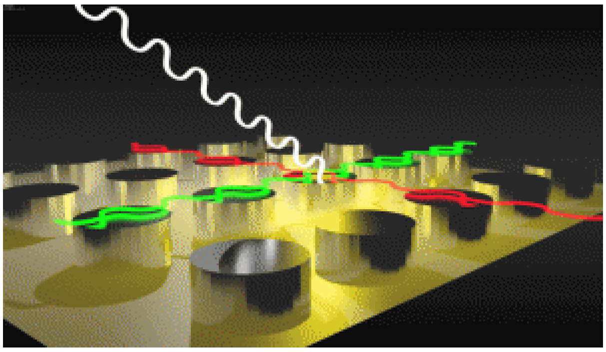
Researchers at Aalto University have discovered a novel way of combining plasmonic and magneto-optical effects.

Magnetic nanoparticles arranged in arrays put a twist on light: depending on the distance between the nanoparticles, one frequency of light (visible to the human eye by its colour) resonates in one direction; in the other direction, light (induced by quantum effects in the magnetic material) is enhanced at a different wavelength.



Researchers experimentally demonstrated that patterning of magnetic materials into arrays of nanoscale dots can lead to a very strong and highly controllable modification of the polarization of light when the beam reflects from the array. This discovery could increase the sensitivity of optical components for telecommunication and biosensing applications. The result was just published in Nature Communications journal.

The coupling between light and magnetization in ferromagnetic materials arises from quantum mechanical interactions. These interactions result in magneto-optical effects that modify the properties, such as the polarization axis or intensity of the light. Interactions between light and matter are enhanced at the nanoscale. This is a key motivation in the field of plasmonics, which studies light interacting with metal nanostructures.



A nano-sized, metallic nanoparticle behaves very much like an antenna for visible wavelengths; such antennas are familiar to us in numerous everyday devices that operate on much longer radio- and micro-waves. The researchers took advantage of a phenomenon known as surface lattice resonances in which all the nanoparticles, the little antennas, radiate in unison in an array. The key to this is to assemble the magnetic nanoantennas on a length scale that matches the wavelength of the incoming light.

In periodic arrays, nanoparticles interact strongly with each other, giving rise to collective oscillations. Such behavior has been previously reported in noble metal nanoparticles and researched extensively at Aalto University in the Quantum Dynamics (QD) research group.

Now, a collaborative effort between QD and the Nanomagnetism and Spintronics (NanoSpin) group shows that such collective oscillations can also be observed in magnetic materials. The surface lattice resonances enhance the light polarization change in ferromagnetic materials, the so-called magneto-optical Kerr effect.

“A key finding of our research was that the frequency, that is the colour of light, for which this happens can be made different from the frequency where the purely optical effect is strongest. The separation of magneto-optical and optical signals was achieved by choosing a different distance between the nanoparticles in the two directions of the array”, explains Professor **Päivi Törmä**.

Using magnetic materials was not an obvious choice. So far, optical activity in ferromagnetic materials has been limited by their high resistance, which makes it impossible to observe the impressive plasmon resonances seen in noble metals.

“However, by ordering the nanoparticles in arrays and taking advantage of collective resonances, this problem was mitigated. Or result opens an important new direction in the research field that focuses on the coupling of light and magnetization at the nanoscale”, says Professor **Sebastiaan van Dijken**.

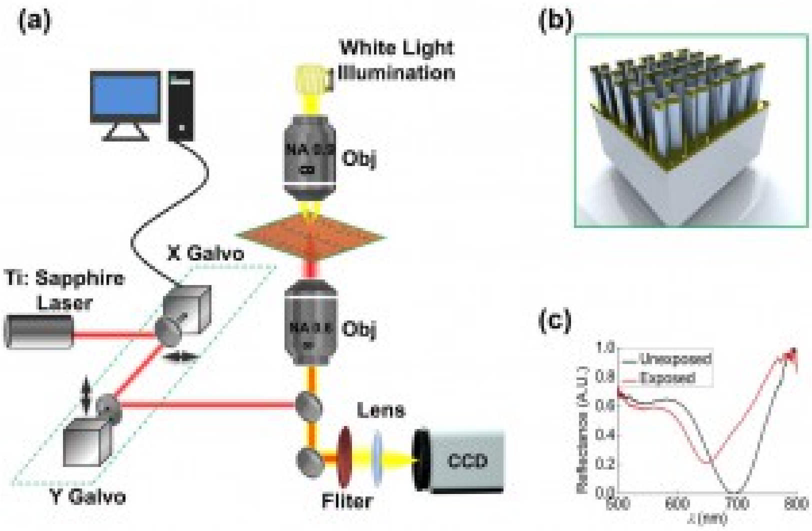
The benefits of collaboration between research groups – those working in different fields – was essential for the success of the project. The authors stress that this kind of project would not have been possible to achieve without extensive knowledge in both optics and magnetism at the nanoscale. Their innovative work has created the groundwork for further explorations and has the potential to advance applications beyond fundamental physics. The joint team used the nanofabrication facilities in the Micronova cleanroom as well as the electron microscopy tools available in the Nanomicroscopy Center.

The results are published this week in the journal Nature Communications. For the article “Surface lattice resonances and magneto-optical response in magnetic nanoparticle arrays” in Nature Communications, please visit http://www.nature.com/ncomms/2015/150507/ncomms8072/full/ncomms8072.html

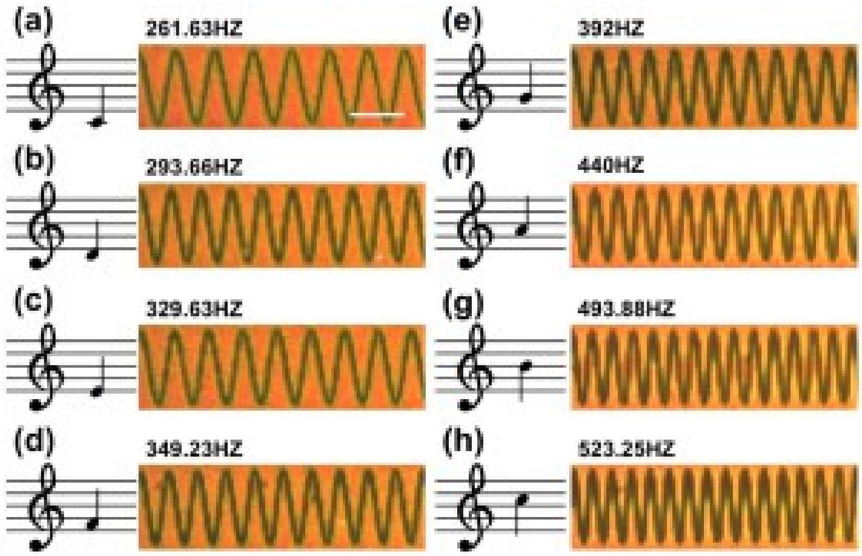
---

Plasmon-Assisted Audio Recording

Researchers at the University of Illinois at Urbana-Champaign have successfully recorded optically encoded audio onto a plasmonic nanostructure that is non-magnetic. This is considered to be the first ever recording of such an audio. This type of recording could be used for archival storage and informational processing.



Toussaint’s group had earlier discovered pillar-supported bowtie nanoantennas (pBNAs) made of gold. An array of gold pBNAs exhibits a specific photographic film property that was utilized for storage of audio and sound files. pBNAs demonstrate a storage capacity that is approximately 5,600 times larger than typical magnetic film that is used for analog data storage. These pBNAs hold promise for a wide array of storage applications.



The research team showed that sound information could be stored by pBNAs in two forms – as a frequency varying intensity waveform or as a temporally varying intensity waveform. They stored the basic eight musical notes along with the middle C, D, and E on a pBNA chip. The team then retrieved these notes and played them in specific order so that a tune was created.

Source: **http://www.nature.com/srep/2015/150316/srep09125/full/srep09125.html**

http://www.nature.com/srep/2015/150316/srep09125/pdf/srep09125.pdf

---

DNA does design: 3D plasmonic photonic crystals are the first devices prepared by DNA-guided colloidal crystallization

Jan 14, 2015 by Stuart Mason Dambrot

(Phys.org)—As biotechnology and nanotechnology continue to merge, DNA-programmable methods have emerged as a way to provide unprecedented control over the assembly of nanoparticles into complex structures, including customizable periodic structures known as superlattices that allow fine tuning the interaction between light and highly organized collections of particles. Lattice structures have historically been two-dimensional because fabricating three-dimensional DNA lattices has been too difficult, while three-dimensional dielectric photonic crystals have well-established enhanced light–matter interactions. However, the dearth of synthetic means of creating plasmonic crystals (those that exploit surface plasmons produced from the interaction of light with metal-dielectric materials) based on arrays of nanoparticles has prevented them from being experimentally studied. At the same time, it has been suggested that polaritonic photonic crystals (PPCs) – plasmonic counterparts of photonic crystals – can prohibit light propagation and open a photonic band gap (also known as a polariton gap) by strong coupling between surface plasmons and photonic modes if the crystal is in a deep subwavelength size regime. (*Polaritons* are quasiparticles resulting from strong coupling of electromagnetic waves with an electric or magnetic dipole-carrying excitation.)

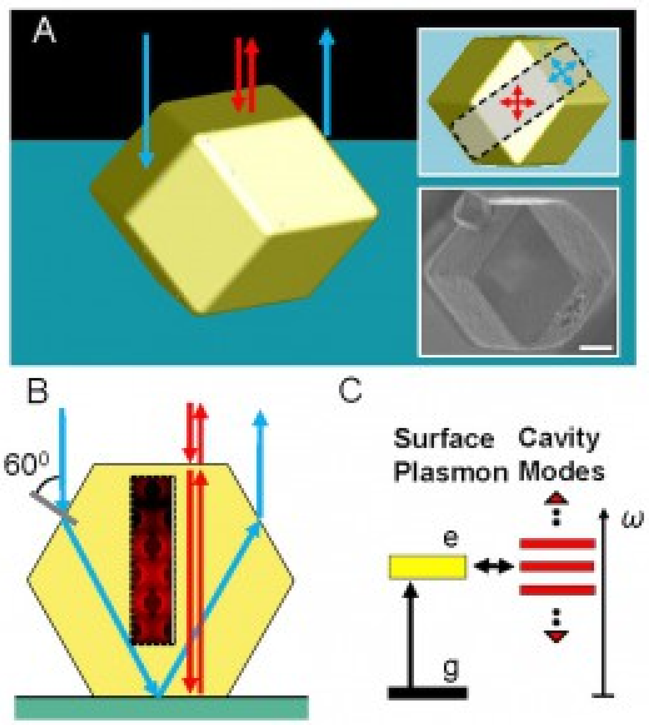


Fig.1. A polaritonic photonic crystal made by DNA-programmable assembly. (A) Three-dimensional illustration of a plasmonic PPC, in the shape of a rhombic dodecahedron, assembled from DNA-modified gold nanoparticles. Red arrows indicate light rays normal to the underlying substrate, impinging on and backscattering through a top facet of the crystal (FPMs). The blue ones represent light rays entering through the slanted side facets and leaving the PPC through the opposite side, not contributing to the FPMs (Fig. S2). The top right inset shows the top view of the crystal with two sets of arrows defining two polarization bases at the top and side facets. The bottom right inset shows an SEM image of a representative single crystal corresponding to the orientation of the top right inset. (Scale bar, 1 μm.)

(B) A 2D scheme showing the geometric optics approximation of backscattering consistent with the explanation in A. The hexagon outline is a vertical cross-section through the gray area in the top right inset of A parallel to its long edge. The box enclosed by a dashed line depicts the interaction between localized surface plasmons and photonic modes (red arrows; FPMs) with a typical near-field profile around gold nanoparticles. The contribution of backscattering through the side facets (blue arrows) to FPMs is negligible. (C) Scheme of plasmon polariton formation. The localized surface plasmons (yellow bar) strongly couple to the photonic modes (red bars; FPMs). Credit: Park DJ, et al. (2014) Plasmonic photonic crystals realized through DNA-programmable assembly. Proc Natl Acad Sci USA Published online before print on December 29, 2014.

To that end, scientists at Northwestern University recently reported strong light-plasmon interactions within 3D plasmonic photonic crystals that have lattice constants and nanoparticle diameters that can be independently controlled in the deep subwavelength size regime by using a DNA-programmable assembly technique – the first devices prepared by DNA-guided colloidal crystallization. The researchers have shown that they can tune the interaction between light and the collective electronic modes of gold nanoparticles by independently adjusting lattice constants and gold nanoparticle diameters, adding that their results in tuning interactions between light and highly-organized nanoscale collections of particles suggest the possibility of applications that include lasers, quantum electrodynamics and biosensing.

Prof. George C. Schatz discussed the paper that he, Prof. Chad A. Mirkin, lead author Daniel J. Park and their co-authors published in *Proceedings of the National Academy of Sciences* by first addressing the main challenges the scientists encountered in tuning the interaction between light and the collective electronic modes of gold nanoparticles by independently adjusting lattice constants and gold nanoparticle diameters. "The wavelength associated with photonic resonance modes" – such as the Fabry-Pérot interactions that occur with interferometers of the same name – "is defined by an interference condition that depends on geometry of the microstructure, as well as on the effective index of refraction of the material in the microstructure," Schatz tells *Phys.org*. "At the same time, the wavelength of plasmon resonances in a gold nanoparticle is determined by collective electron excitation in the particle and depends on the size and shape of the nanoparticle as well as on gold's refraction index." The researchers addressed this by fabricating superlattice materials that allow for independently tuning these two wavelengths, and therefore to study the interactions between the resonance modes. Moreover, he adds, the researchers found a range of superlattice and nanoparticle parameters where the photonic modes could be observed both below *and* above the plasmon energy – that is, its resonance wavelength – enabling them to observe a band gap that indicates strong coupling between the modes.

A second key aspect of their research was using DNA-guided colloidal crystallization to independently control strong light-plasmon interactions within 3D plasmonic photonic crystals that have lattice constants and nanoparticle diameters, as well as synthesizing plasmonic PPCs (polaritonic photonic crystals) from gold nanoparticles. "Prior to our paper and work published last year[1] by our colleagues at Northwestern in Prof. Mirkin's group, the DNA-guided crystallization method had been developed for making superlattice materials with variable gold particle size and lattice spacing," Schatz explains.

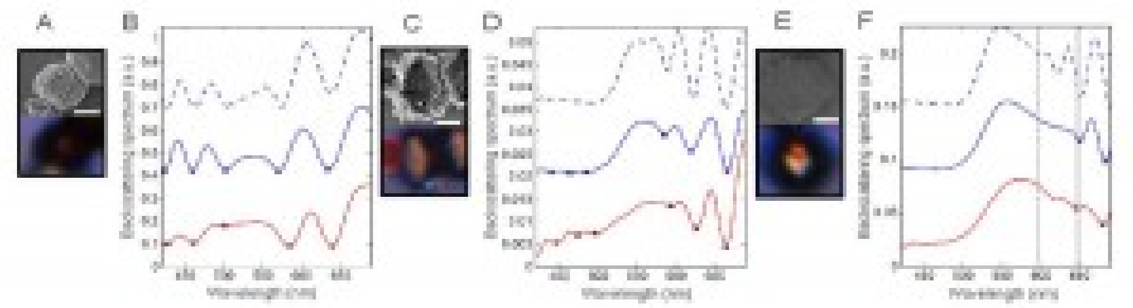


Fig.2. Experimental and theoretical backscattering spectra of PPC1–3. (A) SEM image (Top) and optical bright field reflection mode image (Bottom) of PPC1 on a silicon substrate. (Scale bar, 1 μm.) (B) Measured backscattering spectrum (red solid line) of PPC1 from the center red spot in A, Bottom.

Calculated backscattering spectra based on two infinite slab models with BCC crystal geometry (blue solid line) and EMT approximation (blue dashed line). FPMs are indicated by markers. (C–F) The same datasets for PPC2 and PPC3 as in A and B. PPC2 and PPC3 are on indium tin oxide (ITO)-coated glass slides. The optical images show bright spots at the center owing to backscattering from the top and bottom facets. Two vertical lines in F indicate spectral positions where FPMs are suppressed. (Scale bars, 1 μm.) Credit: Park DJ, et al. (2014) Plasmonic photonic crystals realized through DNA-programmable assembly. Proc Natl Acad Sci USA Published online before print on December 29, 2014.

"However," he continues, "the materials were polycrystalline, and therefore did not exhibit well-defined photonic modes that can allow for probing the interaction between light and surface plasmons. A key advance was the discovery[1] of a method for making superlattice single crystals with a well-defined crystal habit – that is, a rhombic dodecahedral shape – and variable size on the order of a few microns." Nevertheless, it was still unclear that there would be optical modes of high enough quality for Fabry-Pérot resonances to be observed and be tuned across the plasmon resonance. "It took several months to theoretically and experimentally probe and confirm the presence of Fabry-Pérot resonances," Schatz adds.

Schatz and his colleagues addressed these challenges by using measurements of backscattering – the reflection of waves, particles, or signals back to the source direction – to probe Fabry-Pérot modes. "Although backscattering measurements have been used in other contexts, this was the first application of this technology to DNA superlattice crystals, and it wasn't immediately clear to us that Fabry-Pérot resonances could be observed for this crystal habit and choice of material," Schatz notes. However, as detailed in their current paper, the scientists developed a realistic theoretical model of this experiment that predicted the existence of Fabry-Pérot modes and the possibility of observing them via backscattering while doing the experiments. "This stimulated us to do the experiments and persist with this work even though the early results were of poor quality. Furthermore, we used the computational model to guide in optimizing the experiment –

including the work in which we coated PPCs with silver.”

In their paper, the researchers discussed further photonic studies and possible applications in lasers, cavity quantum electrodynamics, quantum optics, quantum many-body dynamics, biosensing and other areas suggested by tuning nanoscale light-plasmon interactions. “Past work has observed quantum electrodynamics behavior in dielectric optical cavities, including enhanced and suppressed fluorescence from emitters in these cavities. The present experiments suggest that this type of measurement can be extended to cavities where hybrid plasmonic/photonic modes occur.” He emphasizes that while quantum electrodynamics phenomena via 2D hybrid plasmonic/photonic modes have already been observed for the last several years, their system opens a unique opportunity to utilize 3D crystal modes that contain plasmonic properties. “As a possible application, since plasmon-enhanced lasers have been observed with 2D lattices, the successful observation of 3D hybrid photonic-plasmonic modes suggests that such lasers can be prepared for 3D lattices.”

Another interesting finding is the tunability of DNA interconnects and the corresponding volume fraction of the plasmonic elements. “Tunability of the DNA interconnects provides the ability to change the lattice constant,” Schatz explains,” and with a certain size of nanoparticle, by varying the lattice constant we can tune the gold volume.”

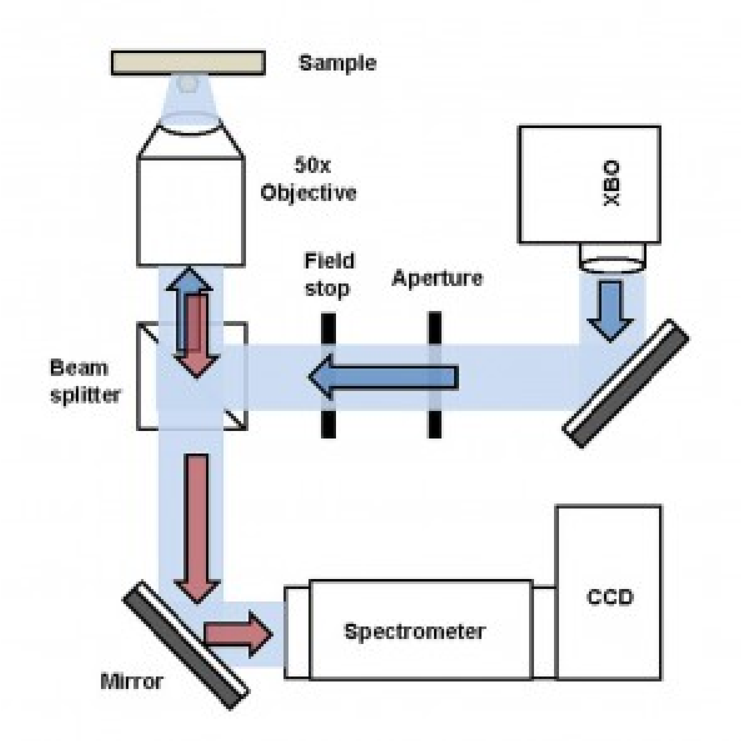


Fig.3. A schematic description of the backscattering signal detection setup. The blue arrows indicate the light incident on the sample and the red arrows the reflected light. Only the reflection mode, not the transmission mode, is reflected. Credit: Park DJ, et al. (2014) Plasmonic photonic crystals realized through DNA-programmable assembly. Proc Natl Acad Sci USA Published online before print on December 29, 2014.

When asked if their findings might interact with or contribute to developments in synthetic biology and synthetic genomics, as well as the accelerating integration of biotechnology and nanotechnology in translational medicine, Schatz pointed out that DNA provides a synthetic 'hook' that can be connected to synthetic biology. "We can therefore envision using the genetic programmability of DNA as input to the synthesis of fluorescent proteins in precise locations," adding that the medical applications of DNA-programmed superlattice materials are only at the concept stage. "From earlier work in the Mirkin group, we know how to use gold nanoparticles coated with DNA in medical diagnostics and therapeutics, so one can imagine future applications where these applications are extended to superlattices. A key point is that the superlattices provide a systematic tool for building structures that combine together inorganic components, such as metal or semiconductor nanoparticles with biomolecules."

Moving forward, Schatz says, the researchers need to generalize the menu of superlattice crystals. “The micron-scale crystal habits exhibit other photonic modes – that is, functionalities – such as whispering gallery resonance and light focusing. In addition, other nanoparticle components such as silver nanoparticles and quantum dots can be incorporated into superlattices.” This means that the scientists can play with a large number of photonic/electronic degrees of freedom within the framework of a DNA superlattice. “Therefore, we need to establish a well-defined set of photonic applications and studies utilizing and combining those physical degrees of freedom – and theory will play an important role in this process.”

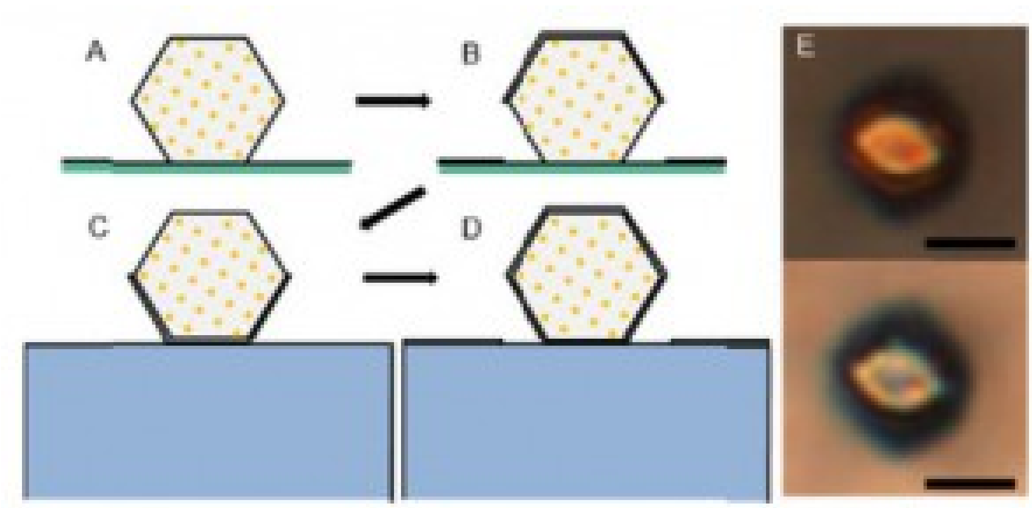


Fig.4. PPC silver coating process. (A) A PPC on a glass slide. (B) A silver layer is deposited on the PPC. (C) The uncoated bottom side of the PPC is exposed after sticking the PPC to the top surface of a PDMS pillar. (D) Another layer of silver is deposited on the uncoated side. (E) The top image shows a PPC at step (C), and the bottom step (D). A 100x objective was used and the scalebar is 2 μm. Credit: Park DJ, et al. (2014) Plasmonic photonic crystals realized through DNA-programmable assembly. Proc Natl Acad Sci USA Published online before print on December 29, 2014.

In terms of additional innovations, Schatz tells *Phys.org* that “now that we know that plasmon-photonic interactions can exhibit strong coupling, we need to expand this research, probably with different nanoparticles and with different types of photonic resonances. For example, we can incorporate anisotropic nanoparticles that exhibit more interesting plasmonic response to polarization of light – and utilizing other available photonic modes that exhibit light focusing features, we can think about developing optical components such as a plasmonic microlens. Finally, synthesizing quantum dot nanoparticle superlattices, we can perform fundamental physics studies related to the collective exciton emission."

Schatz concludes that other areas of research might also benefit from their study. "We're excited about the possibility of using superlattice materials not just in photonics, but also in energy-related applications, including photovoltaics, photocatalysis, and batteries."

Source: **http://phys.org/news/2015-01-dna-3d-plasmonic-photonic-crystals.html**

Explore further: Exploring extraordinary optical transmission in a plasmonic cavity

More information: Plasmonic photonic crystals realized through DNA-programmable assembly, *Proceedings of the National Academy of Sciences* published online before print December 29 2014, doi:10.1073/pnas.1422649112

Related:

[1]DNA-mediated nanoparticle crystallization into Wulff polyhedral, *Nature* (2014) **505**(7481):73–77, doi:10.1038/nature12739