Nano Focus

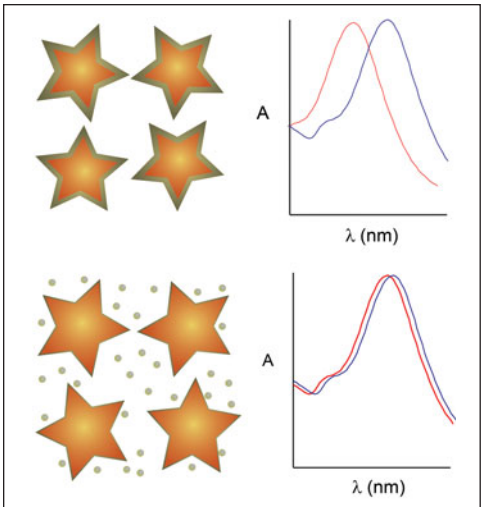
Inverse sensitivity achieved in plasmonic nanosensors

The highly sensitive shifts of the surface plasmon resonance of metal nanoparticles in response to their environment make these structures very useful as molecular sensors. However, even lower limits of detection are needed for early diagnosis of disease or detection of environmental contamination. To this end, L. Rodrigo-Lorenzo at the University of Vigo, R. de la Rica at Imperial College London and colleagues have recently found a way to invert the conventional sensing paradigm and create plasmonic sensors that actually give a stronger signal at lower molecular concentrations.

Their research, described in the July issue of *Nature Materials* (DOI: 10.1038/nmat3337; p. 604), uses star-shaped gold nanoparticles, termed "nanostars" as plasmonic sensors. These were covalently modified with solutions of the enzyme glucose oxidase, resulting in a surface coverage proportional to the concentration of enzyme used. This enzyme oxidizes glucose to generate hydrogen peroxide, which can in turn be used to reduce silver ions to solid silver. For high concentrations of enzyme, more hydrogen peroxide is produced and the rate of silver precipitation is high enough for individual silver nanoparticles to nucleate. At lower concentrations, the silver only grows as a layer on the gold nanostars. This silver coating has a much larger effect on the absorption spectrum of the nanostars than the precipitated silver nanoparticles, such that the low concentration scenario produces a greater sensor response, allowing down to 10^{-20} g ml^{-1} of glucose oxidase to be detected.

The researchers were able to adapt this inverse sensing mechanism to detect the cancer biomarker prostate specific antigen, which requires detection at ultralow concentrations for the early diagnosis of cancer recurrence in prostatectomy patients. For this, both the nanostars and glucose oxidase were modified with antibodies that bind specifically to the antigen, thus directly relating the coverage of surface enzyme to the concentration of antigen. A lower limit of 10^{-18} g ml^{-1} could be detected, which is an order of magnitude lower than previous methods.

The researchers said that the varied chemistry of crystal growth should enable adaptation of this unusual sensing mechanism to incorporate more subtle effects such as crystal size and morphology, and hopefully allow even lower limits to be attained.



Gold nanostars modified with a low concentration of enzyme become coated with silver and show a large shift in absorption spectrum (top), whereas nanostars with high enzyme concentration cause nucleation of silver nanocrystals and little change to the spectrum (bottom). Reproduced with permission from *Nature Mater.* **11** (7) (2012), DOI: 10.1038/nmat3337; p. 604. ©2012 Macmillan Publishers Ltd.

Tobias Lockwood

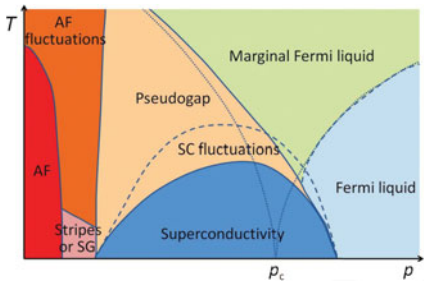
Energy Focus

Quantum critical regime enables higher T_c superconductivity

Physicists at the University of Miami may have discovered what has been preventing the steady progression of higher critical temperatures (T_c) in superconducting systems. In a theoretical physics article published in the May issue of *Europhysics Letters* (DOI: 10.1209/0295-5075/98/47011), Josef Ashkenazi and Neil F. Johnson from the University of Miami show that it is the quantum critical regime, in which different symmetry-breaking instability states are combined, which makes the suppression of superconductivity by such states diminish or disappear. The emergence of instabilities has been blocking progress to superconductivity at high temperatures. Such instabilities occur also in the cuprate system, where they are known as "striped" states; within the quantum critical zone, striped states containing different orientations and magnetic phases are combined.

"What we realized is that the existence of this quantum critical regime does take a combination of these different states," Ashkenazi said. "When these different states are combined, then the suppression of superconductivity by the instability goes away, or at least diminishes a lot."

So how are broken symmetry states combined? There has been a lot of discussion about a type of "glue" that would hold paired charge carriers together, in particular the two electrons in a Cooper pair. In Johnson and Ashkenazi's auxiliary Bose condensates (ABC) theory, a strong glue arises in the cuprates in a quantum critical regime while, by contrast, the system moves outside this



Proposed phase diagram for hole-doped cuprates, under changing temperature and doping level p. Solid and dashed lines represent phase and gradual transitions, respectively. Dotted lines represent gradual transitions in the case that pairing is suppressed down to $T = 0$. AF stands for antiferromagnetic, SG for spin glass, and SC for superconducting. *Image credit*: Josef Ashkenazi and Neil F. Johnson, University of Miami.

https://doi.org/10.1557/mrs.2012.190 Published online by Cambridge University Press

regime at low and high levels of doping. At low doping levels the glue becomes inactive because of a broken symmetry instability state that blocks superconductivity, while at high doping levels the glue "fades away," the researchers said.

"The reason that superconductivity could not advance above low T_c in the past was not because there were no strong coupling constants," Ashkenazi said. Strong coupling due to phonons, and non-phononic magnetic excitations, or other excitations, do exist. "But the system could not progress to very high T_c because of the competing symmetry-breaking instabilities, which would kill it."

The researchers suggested a phase diagram by plotting the absolute temperature T versus the hole-doping concentration p for the cuprate system. If pairing is suppressed down to $T = 0$, a quantum critical point p_c defines the starting point for a quantum phase transition. In the absence of pairing, the quantum critical regime starts at this point and includes the area between the dotted lines in the figure, representing extensions of the Fermi liquid phase and the pseudogap phase of the system. The occurrence of pairing extends the range of quantum criticality into the superconductivity and pseudogap regimes.

As far as what this discovery might mean to experimentalists, Ashkenazi said, "I think this work is an important breakthrough toward a more focused way to give instruction to experimentalists to look for where to go to find high T_c superconductors and, hopefully, maybe even room-temperature superconductors. In general you have to look close to phase transitions—in particular, the proximity of a metal–insulator Mott transition is a good place to look for higher T_c materials—but our work sets the stage for more work to be done."

Tim Palucka

Nano Focus

Defects in carbon nanotubes heal themselves under the right conditions

Following reports on the experimental growth of carbon nanotubes up to one meter in length, computational simulations have now shown why this is possible. Using density functional theory (DFT) calculations of the energy landscape and the kinetics of carbon nanotube growth, researchers at Hong Kong Polytechnic University, Rice University in Houston, and Tsinghua University have shown that "healing" mechanisms exist at the carbon/catalyst interface that heal and restore potential topological defects—pentagons, heptagons, and pentagon-heptagon (5|7) pairs—to hexagons before they move more than an atomic layer or two beyond the interface.

"In our theoretical analysis we show that at practical temperatures and given the values of energy barriers, the rates of formation and removal of defects are balanced," said Boris Yakobson of Rice University. "They form with some probability and then at a higher rate they are deleted or 'healed.'"

According to Feng Ding from Hong Kong Polytechnic University, this finding, reported in the June 15 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.108.245505; 245505), puts to rest the theory that nanotubes form initially with lots of defects, which are then annealed out at elevated temperatures over time. In fact, any defect that makes it beyond a couple of atomic layers from the interface without being healed is permanently embedded in the carbon structure, leading to nano-cones, nano-horns, or other defective shapes.

Such defective shapes are undesirable for carbon nanotubes intended for use in practical devices because defects change the chiral indices, which are related to the circumference, of the nanotube along its length. The chiral indices define the electronic structure and bandgap of the material, which must be well controlled to define the properties of a nanotube. The ideal is to fabricate perfect nanotubes with the same chiral indices. "The moment you change the chiral index in a tube, you change from one material to another," Yakobson said. "It may change from a metal to a semiconductor the moment you introduce one 5|7 defect."

For these simulations, the researchers abandoned the molecular dynamics approach, which Yakobson said forces calculations to be done too fast for this type of study, producing too many defects along the way. Instead, they decided to slow down the simulation and use DFT for a carbon/Fe catalyst system to calculate and carefully analyze the energy barriers in the system. They followed the changes in atomic positions and calculated the rates of change. Next, they applied kinetic rate theories to evaluate how often defects are formed and how rapidly they are healed.

The researchers concluded that by controlling the temperature and the rate of carbon introduction to the catalyst, sustained, defect-free nanotube growth would be possible in the range of 10^8–10^{11} carbon atoms, setting an upper limit of about one meter on the length of these perfect nanotubes. "Our work shows that defects should not be there to begin with, except in the first one or two atomic rows, but not deeper," Yakobson said. "If you nucleate one tube, it can grow for a very long time and preserve the same chirality."

But can the researchers choose and control the chirality of the carbon nanotube from the nucleation of the first atomic layer at the catalyst surface? Whether the nanotube has a zigzag or an armchair configuration is determined at this crucial moment. "One of the big problems is that nanotubes grow mixed," Yakobson said. "You have a bucket with billions of nanotubes and each is a different type, which is a bad thing for many applications." Though tedious methods exist to separate the different types, "the dream of this business is to create nanotubes in one type, or at least in some narrow distribution," Yakobson said. That is the focus of future research.

Tim Palucka

https://doi.org/10.1557/mrs.2012.190 Published online by Cambridge University Press