Nano Focus

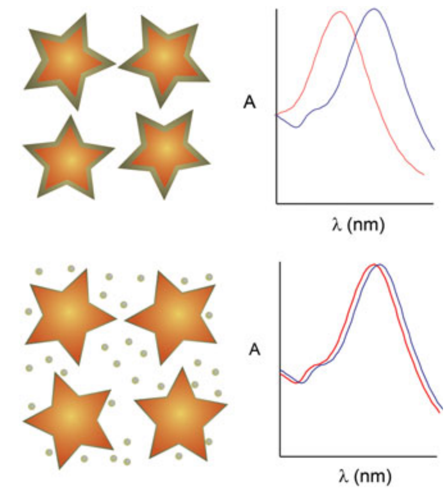
Inverse sensitivity achieved in plasmonic nanosensors

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

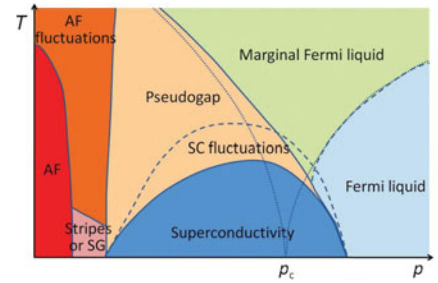
Energy Focus

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.

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