Watching and controlling single molecules in nm-scale plasmonic cavities

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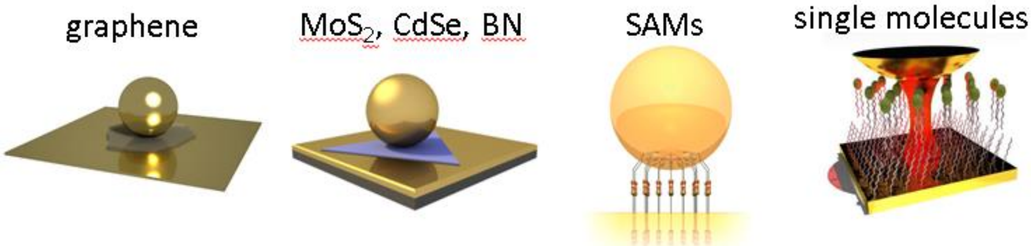
Coupling between plasmonic nano-components generates strongly red-shifted resonances combined with intense local field amplification on the nanoscale. This allows directly seeing molecules as well as excitations in semiconductors. We have recently explored plasmonic coupling which can be tuned dynamically, through reliable bottom-up self-assembly. The crucial aspect of these systems is the extreme sensitivity to separation, and how quantum tunneling starts to be directly seen at room temperature in ambient conditions. We recently demonstrated how quantum plasmonics controls the very smallest space that light can be squeezed into.[1-3]



We also demonstrate the possibility to track few molecules using the extreme enhancements. We show how the new generation of 2D semiconductors can couple to such nano-scale gaps utilizes our nanoparticle on mirror geometry. We find that changing just a single atom on each molecule of a self-assembled monolayer can shift the plasmon by over 50nm, and produce surprising vibrational signatures.[4-8] These have encouraging prospective applications in (bio)molecular sensing as well as fundamental science.[9-15] We also now demonstrate strong coupling with single molecules in appropriately designed optical and molecular nano-structures. The ability to track and watch molecules interact and react opens up the ability to study chemistry molecule-by-molecule and potentially to control single reaction pathways.

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[3] *Nano Lett* **13**, 5033 (2013); Controlling sub-nm plasmonic gaps using graphene
[4] *ACS Nano* **9**, 825 (2014); Monitoring Morphological Changes in 2D Monolayer Semiconductors …
[5] *Nano Letters* **15**, 669 (2015); Nano-optics of molecular-shunted plasmonic nanojunctions
[6] *Science Reports* **4**, 5490 (2014); Watching individual molecules flex within lipid membranes using SERS
[7] *Nature Comm*. **5**, 4568 (2014); Threading plasmonic nanoparticle strings with light
[8] *Nature Comm*. **5**, 3448 (2014); DNA origami based assembly of gold nanoparticle dimers for SERS detection
[9] *Scientific Reports* **4**, 6785 (2014); Quantitative multiplexing with nano-self-assemblies in SERS
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