Annual Review of NSTC-AFOSR

Tunable Plasmonic Resonances in Gradient-deposited Gold

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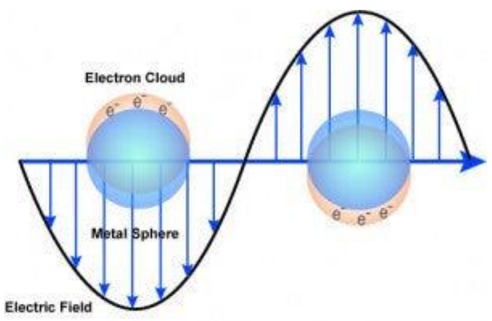
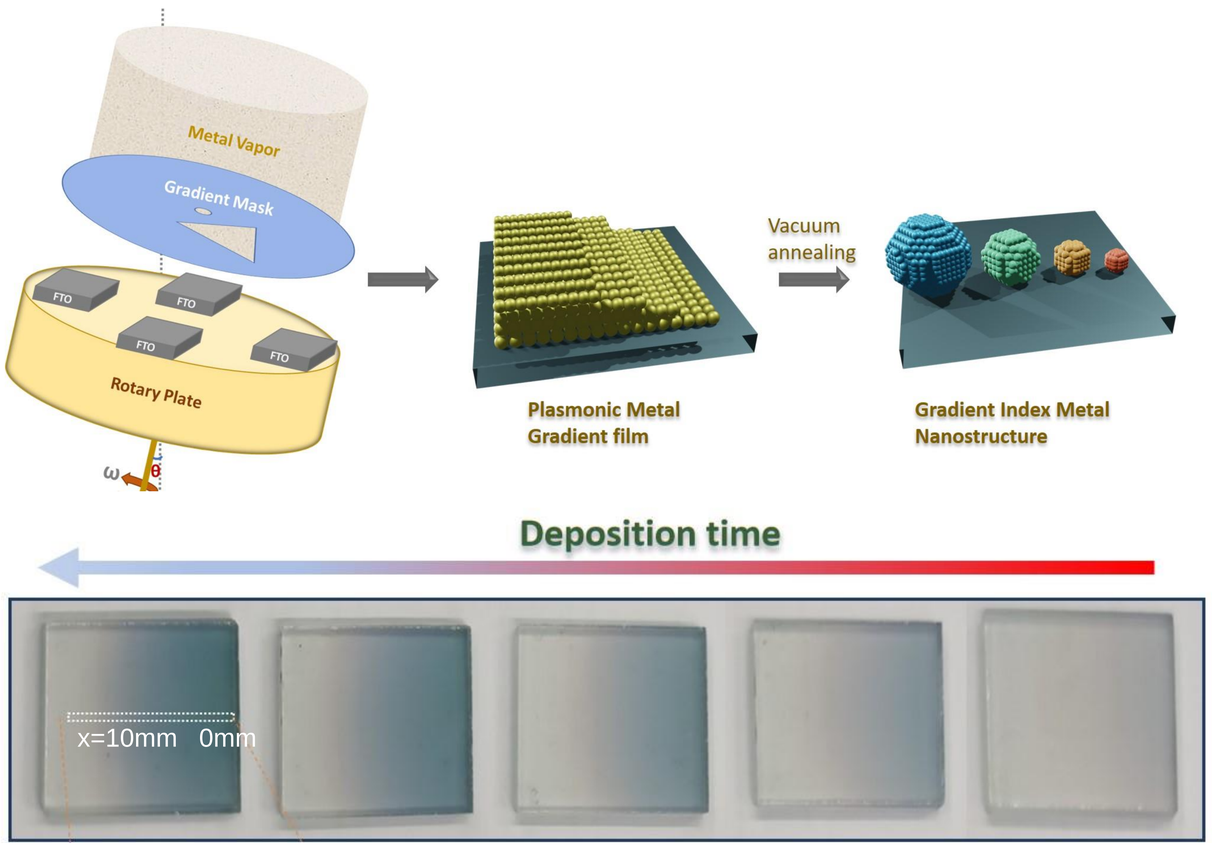
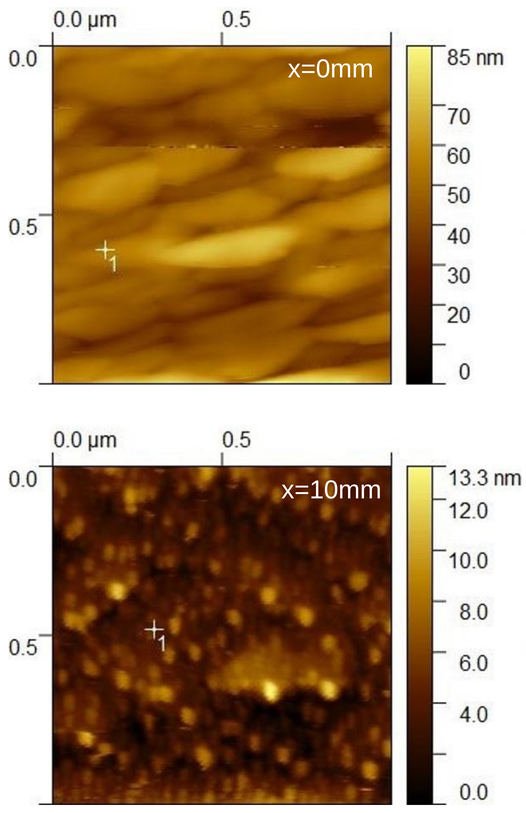
Thin film plasmonics with a twist

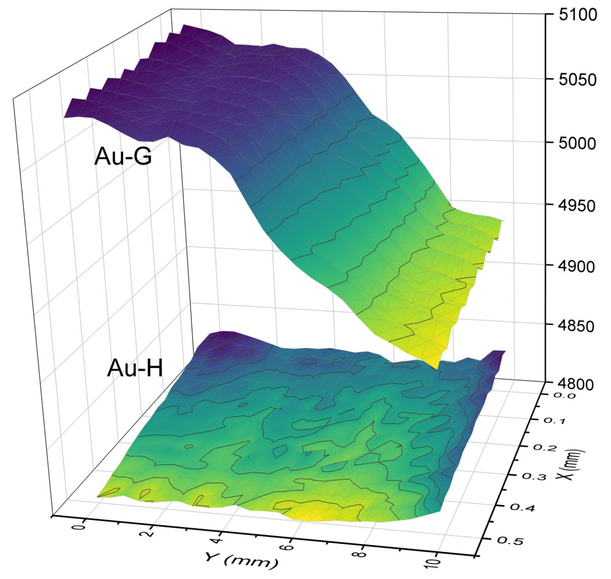


- Plasmons are resonant collective oscillations of the conduction electrons upon light excitation of metallic structures
- Conventional plasmonics focuses on individual nanoparticles
- We investigate large-scale assemblies of nanoparticles with spatially varying dimensions
- Such assemblies can be produced with high precision using a novel gradient mask approach

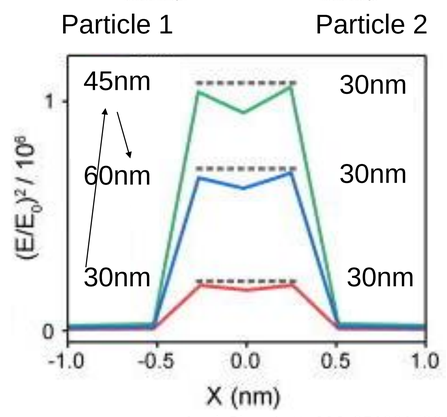


Emergent characteristics



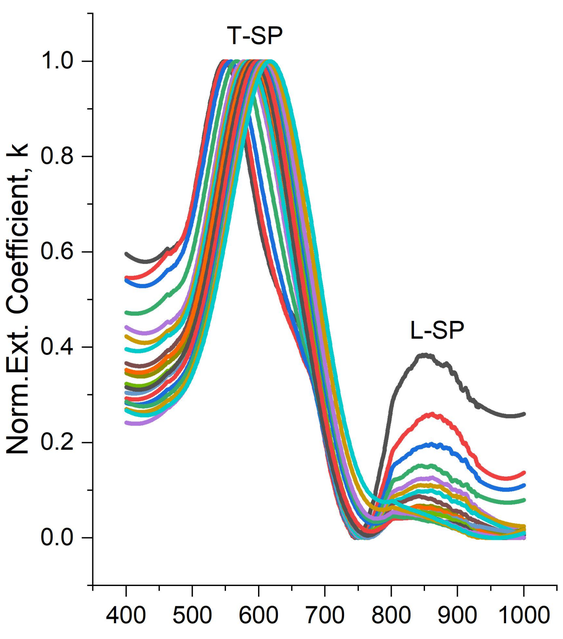


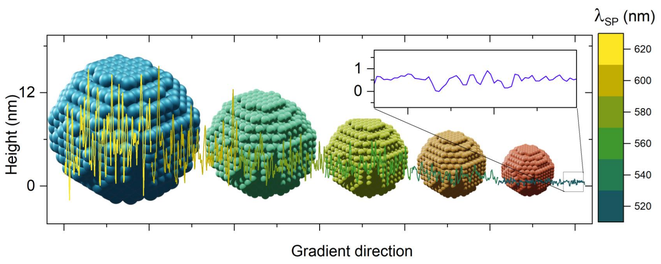
- We observe a spatially varying morphology with changes in particle shape and size
- KPM reveals a clear lateral gradient in work function due to the varying particle properties
- Theoretical work suggests that laterally varying particle sizes could improve the electric field enhancement within their hot-spots



Appl. Phys. Lett. **114**, 251901 (2019)

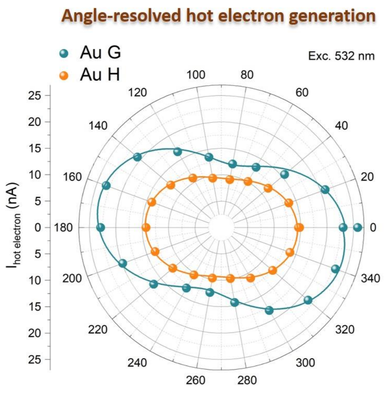
Optical Response

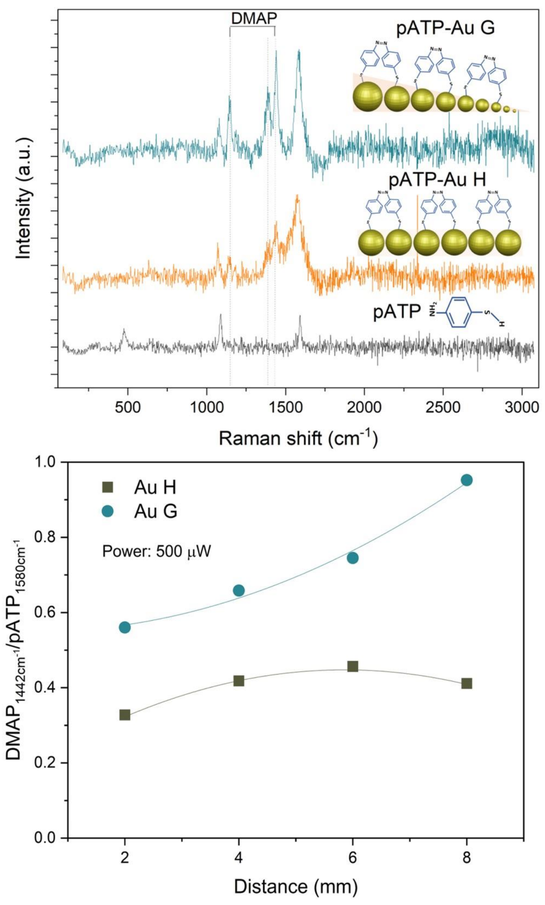




- In addition to conventional transverse surface plasmons, a new peak occurs at 850nm
- This feature is a longitudinal plasmon peak originating from the coupling between larger and smaller particles along the gradient

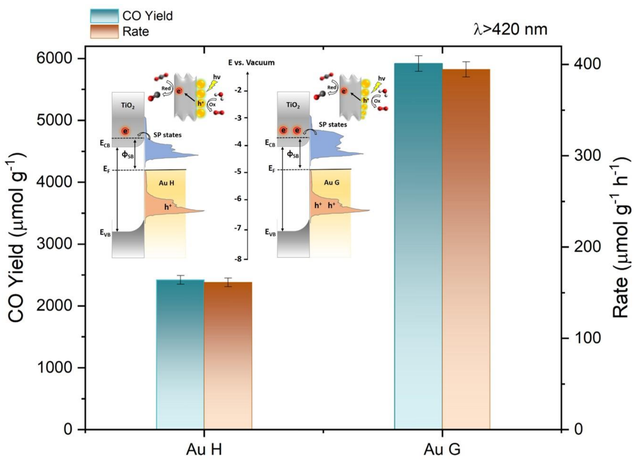
Hot electron emission

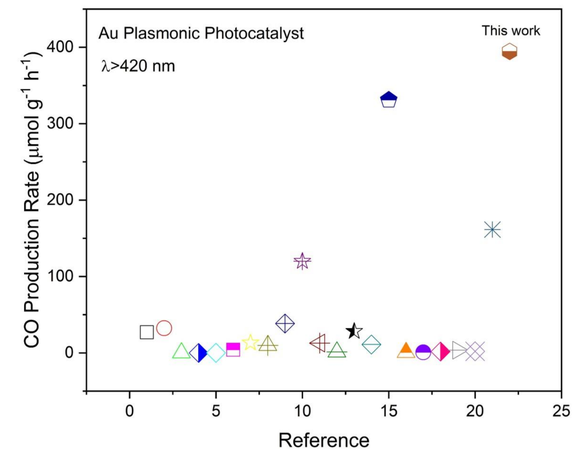




- Hot electron photocurrent measurements confirm a pronounced anisotropy in gradient samples
- We observe a significant enhancement in hot electron emission for gradient structures compared to planar gold films
- High electron yield is also evidenced by photodegradation measurements
  - ❑ Local SERS on Gradient shows a strong hot electron assisted conversion of pATP to DMAP
  - ❑ For gradient samples, the hot electron yield increases with size

Applications





- Photocatalytic reduction was achieved through hot-electron injection into gaseous CO_2
- Superior photocatalytic activity with CO yield of 5890 µmol g^{-1}
- Outstanding performance compared to previously reported gold nanostructures