EMERGENT PROPERTIES FROM WS_2 EMPOWERED BY LASER SCULPTING AND AU NANOPARTICLES LANDSCAPING

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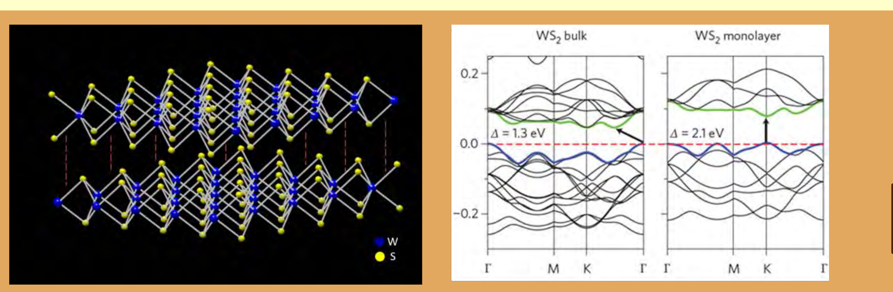
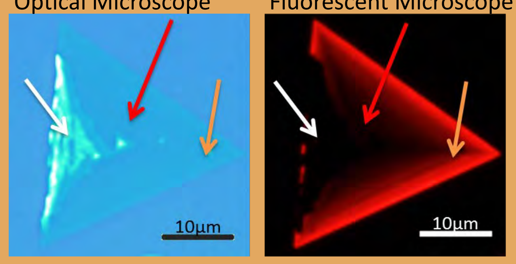
Introduction



- Transition Metal Dichalcogenides (TMDs): exciting systems to engineer its properties en route to future optoelectronic applications
- When bulk layer TMDs is peeled down to monolayer, it transforms from a system with an indirect bandgap to one with direct bandgap

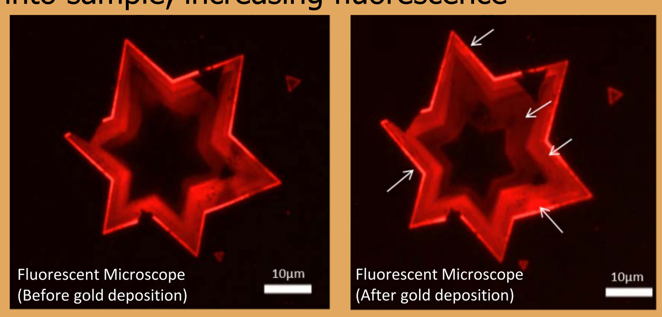


- Hence, monolayer TMDs are photoluminescent in nature unlike bulk layer TMDs

- Growing WS_2 using the Chemical Vapour Deposition (CVD) method yields more bulk layer than monolayers
- useful if we modify bulk layer WS_2 to obtain photoluminescence (PL) similar to monolayer WS_2

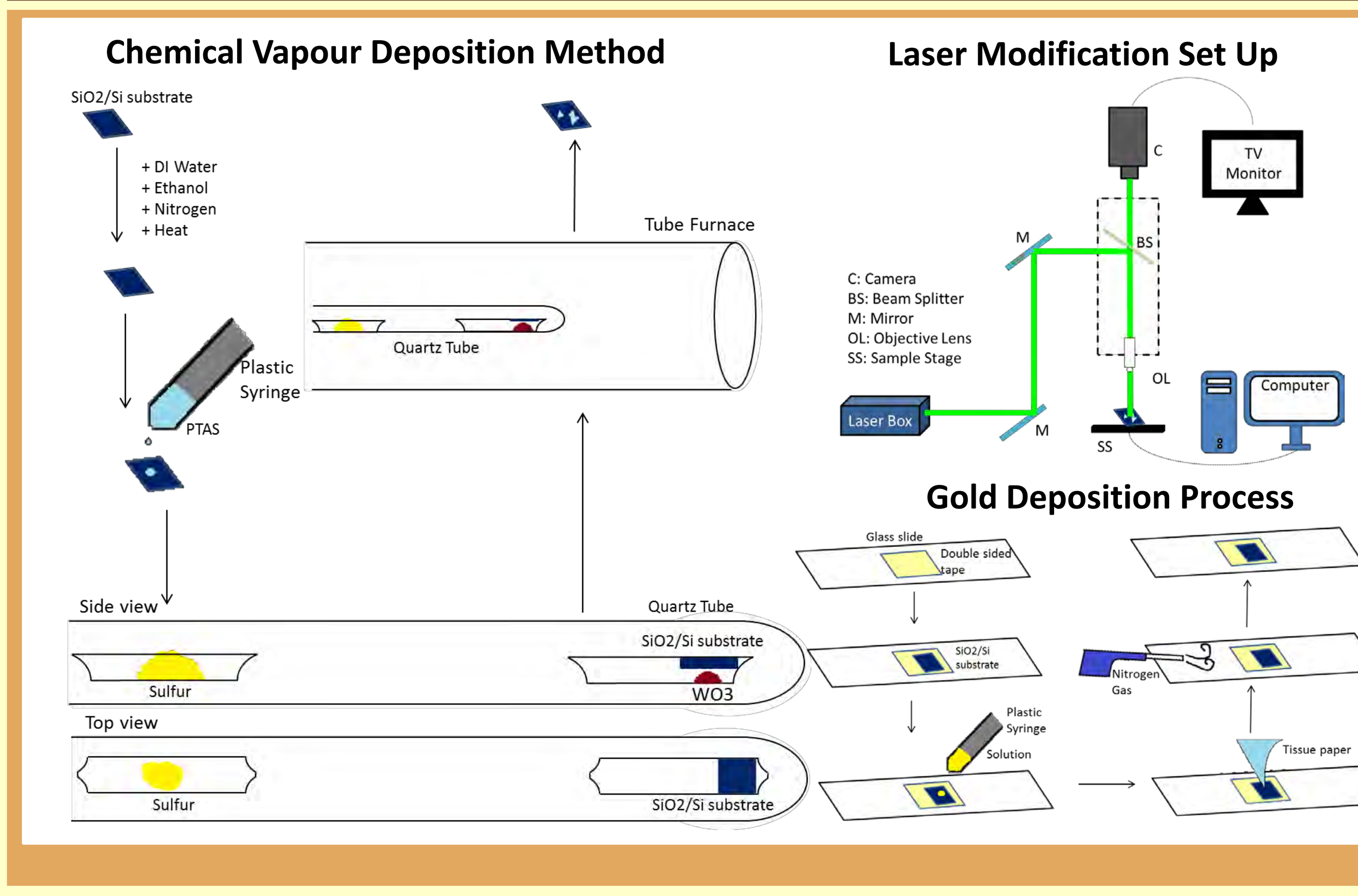
Past research to increase photoluminescence

- Laser modification of bulk layers: oxygen is introduced into sample, increasing fluorescence



- Decoration of gold nanoparticles (Au NPs) increases fluorescence by plasmonic coupling and reveals intricate details of WS_2
- Au NPs can be added to modified bulk layers to see if there is any increase in PL intensity and if there is any change in Au NP deposition morphology

Methodology



- WS_2 was synthesised using the Chemical Vapour Deposition Method

Laser Modification Set Up:

- Focused laser beam technique
- Laser light (green) enters optical microscope and reaches a beam splitter
- Laser light then passes through 100x objective lens to reach the sample
- Laser is fixed and sample is moved to create laser modified regions

Gold Deposition Process:

- Sample was placed on polysine slide
- 9μL of 0.01M $AuCl_3$ dissolved in ethanol was deposited on the sample for 10 or 20 seconds
- Thin tissue paper and nitrogen gas blowing was used to remove excess solution
- Systematic characterisation was carried out

Objective

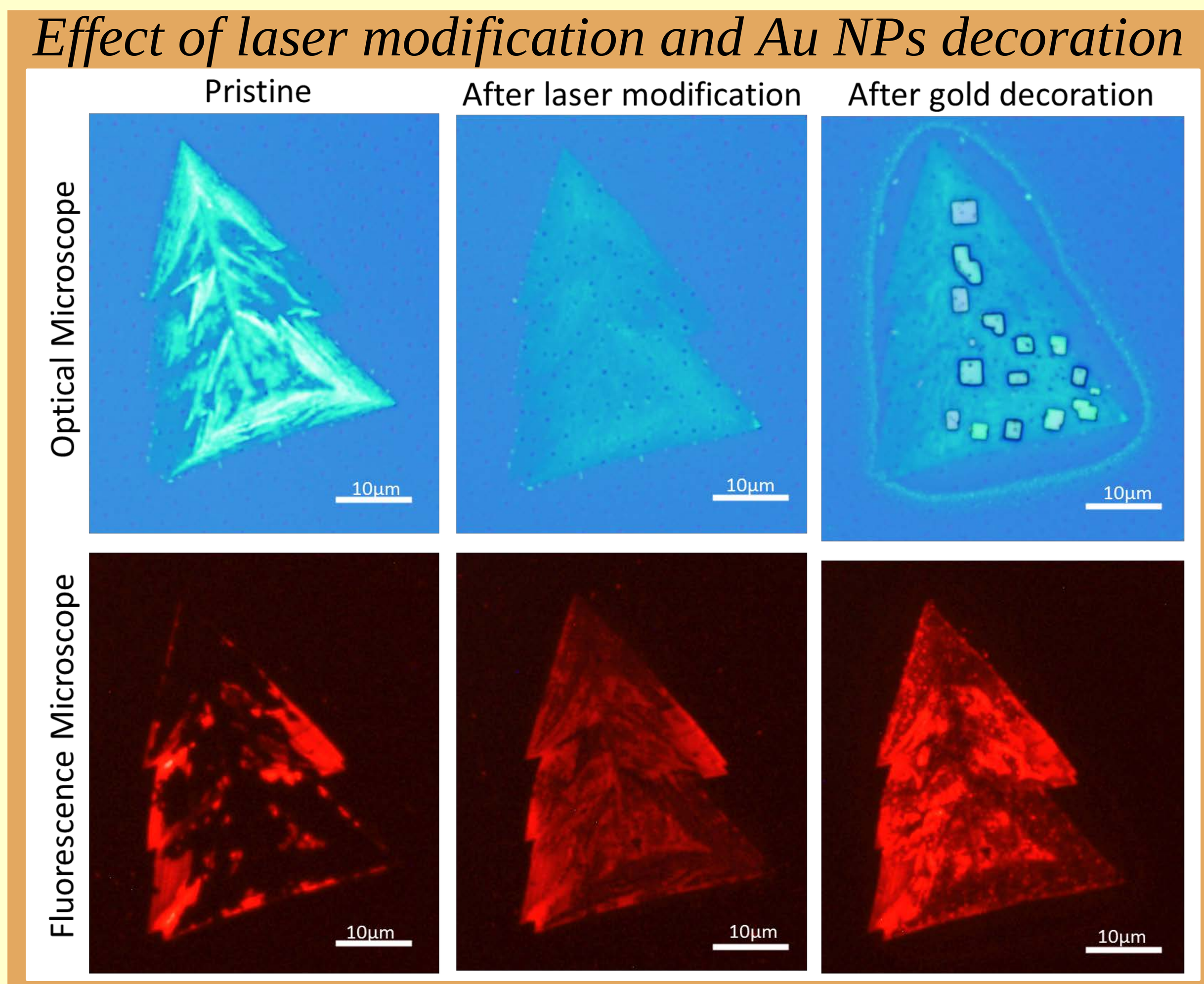
- Enable Au NPs to further enhance a laser modified region of WS_2
- To control location of gold deposition on the microflake
- Investigate the mechanism laser modification and gold deposition on laser modified WS_2

Hypothesis

- Au NPs deposition would increase the PL intensity further by facilitating electron transfer
- Higher density of Au NPs deposition due to increase in defects at laser modified regions
- Laser modification: thins down bulk layer to monolayers, increases the PL intensity by modifying the chemical composition of WS_2 with the addition of oxygen species into the material

Results & Discussion

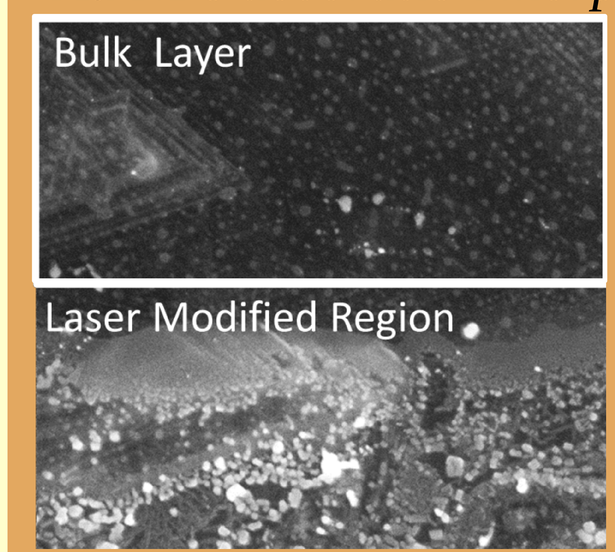
Effect of laser modification and Au NPs decoration



- Sample is part monolayer part bulk layer
- Laser modified regions are green in colour
- Chemical modification after gold deposition

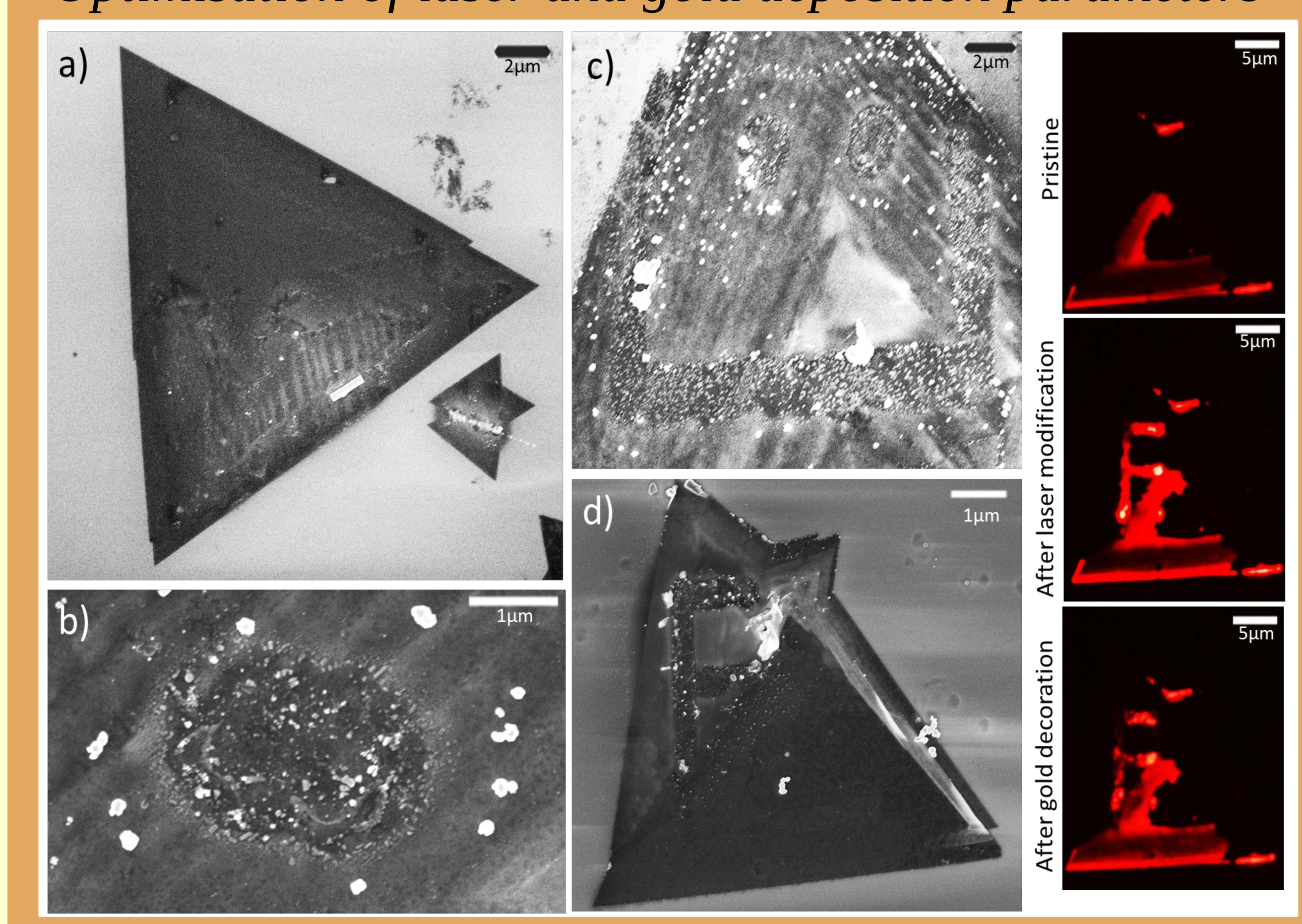
- Only monolayers exhibit fluorescence in pristine sample
- Slight enhancement of photoluminescence after laser modification
- Marked enhancement of laser modified regions due to gold decoration

Au NPs decoration morphology



- Pristine bulk layer region: Au NPs deposit in an orderly fashion which follows the layering of bulk layer
- Laser modified region: deposition is haphazard, does not follow original morphology
- Average size of Au NPs is 0.476 times of normal bulk layers
- Density of deposition is 1.59 times higher
- **Laser modification possibly creates more defects and sulfur vacancies which act as nucleation sites for deposition**

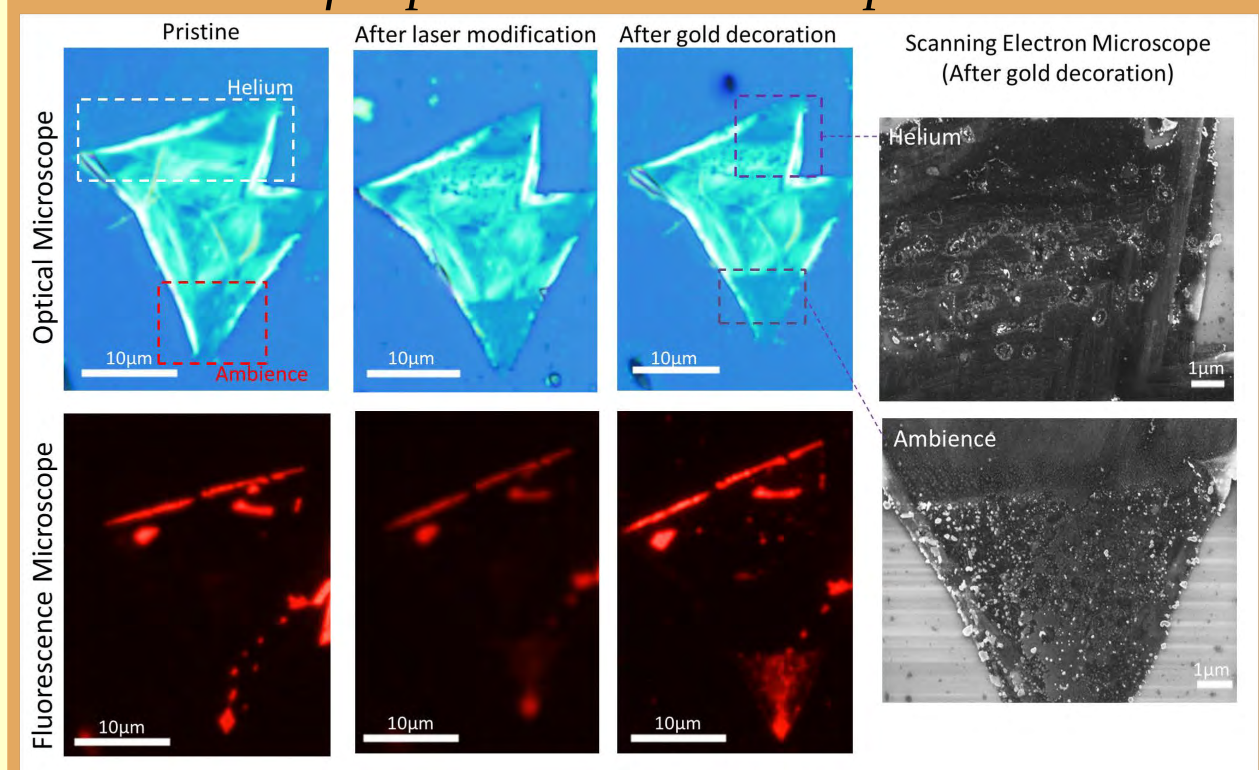
Optimisation of laser and gold deposition parameters



(a) laser modified bulk layers attract more Au NPs compared to pristine monolayers
(b) bulk layer regions attract larger Au NPs at low densities, laser modified regions produce much higher density of Au NPs at smaller sizes
(c) smiley face
(d) "E" encrypted on sample

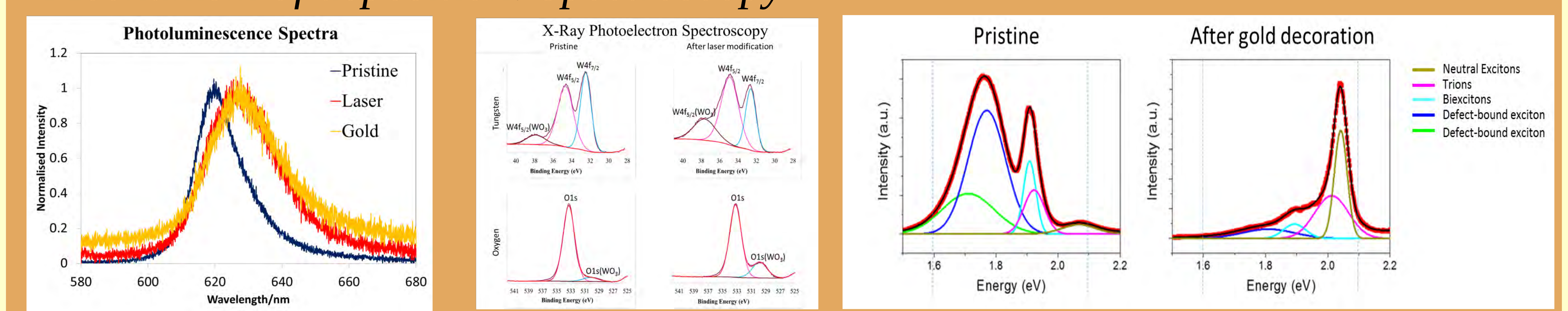
- Optimum laser modification where bulk layer is thin down to near monolayers
- Gold deposition produced differential brightness intensities corresponding to density deposition

Mechanism of deposition: Helium Experiment



- Sample was more difficult to cut in helium: oxygen facilitates the laser modification process
- Helium region: does not burn bulk layer fully, show slight increase in PL intensity
- Ambience: bulk layer burned down fully, significant increase in PL intensity after Au NPs deposition with large Au NPs
- **Oxygen facilitates laser modification process**

Mechanism of deposition: Spectroscopy

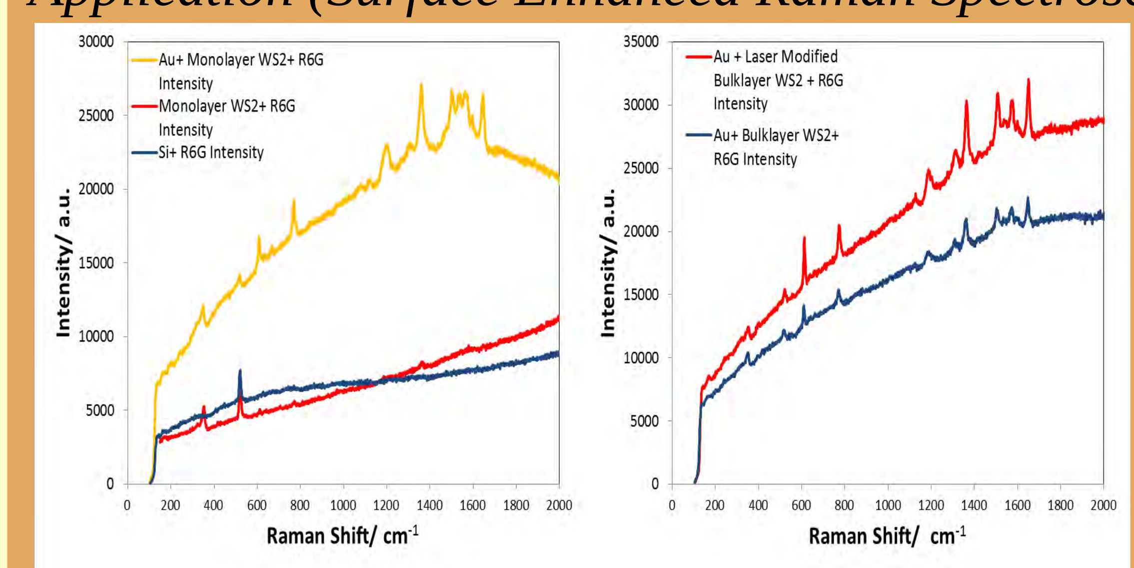


- Chemical modification with peak wavelength shift of 4.8nm after laser modification
- No peak wavelength shift after gold decoration

- Increase in oxygen after laser modification
- **Oxygen facilitates laser modification process**

- Gold decoration on pristine monolayers show amplification of neutral exciton peak, suppression of other peaks
- Au NPs can re-emit fluorescent light of much narrower energy spread
- Gold reduces electron cloud shielding between electron-hole pairs

Application (Surface Enhanced Raman Spectroscopy)



- Feasibility of decorated WS_2 as a Surface Enhanced Raman Spectroscopy substrate to detect aromatic molecules (R6G) was investigated
- At resonant wavelength excitation, presence of Au NPs aided in the Raman enhancement of fabricated SERS substrate

- Enhancement factor of Au NPs- WS_2 hybrids is 65.1
- Viable approach to enhance Raman signals of aromatic molecules not adsorbed efficiently on plasmonic metals
- Modified bulk layer-Au NPs substrates are also feasible SERS substrates: enhancement factor of 2.1 compared to bulk layer- Au NPs substrates

Conclusion

- Au NPs have the ability to sharpen the fluorescence re-emitted by WS_2 : Au NPs increase the fluorescence of the sample through both plasmonic coupling and reducing electron cloud shielding between electron-hole pairs
- Laser modification causes Au NPs to deposit at higher densities and smaller particle size: laser modification not only dopes oxygen into the system, but creates more nucleation sites allowing more effective Au NPs deposition
- We have created a hybrid device with tunable morphology, functionality and properties.

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