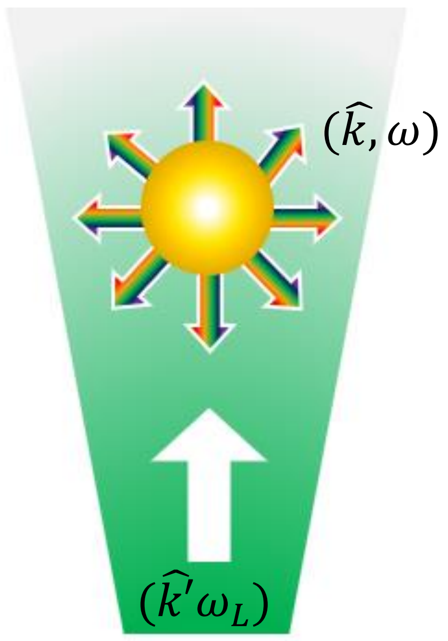
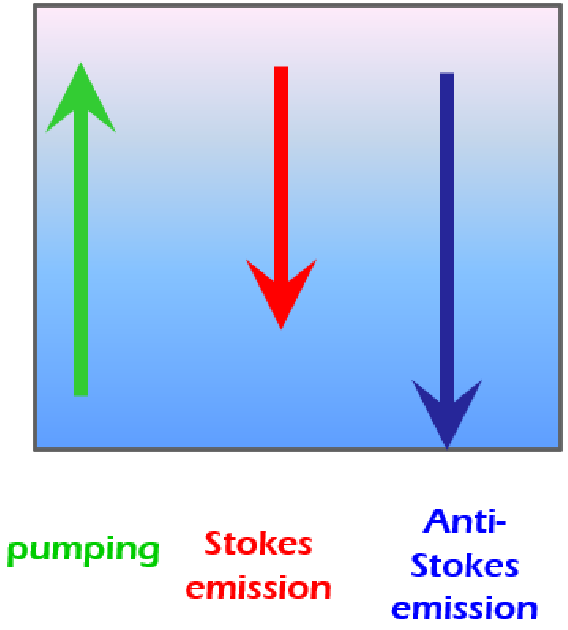
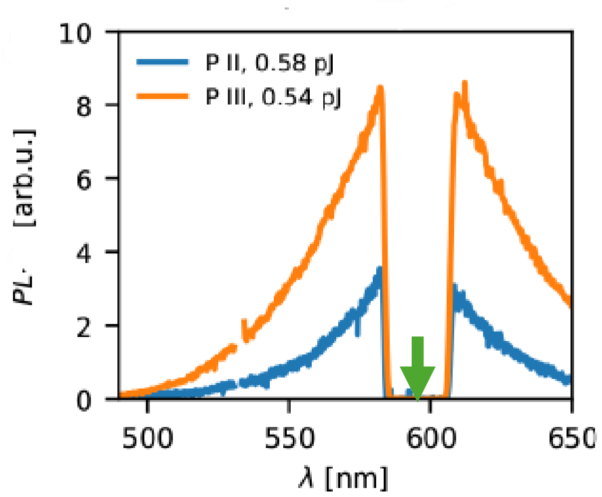
Photoluminescence from metal films

19-11-2024

Theory of metal luminescence







$$\Gamma \sim \underbrace{\rho(\omega)}_{\text{“Photonic part”}} \int \underbrace{\left|\langle f|\vec{\mu}|i\rangle\right|^2 f(\varepsilon+\hbar\omega)\left[1-f(\varepsilon)\right]}_{\text{"electronic" part}} d\varepsilon$$

Jollans et. al., J. Phys. Chem. A, 124, 6968−6976 (2020)

Theory of metal luminescence: Electronic contribution

- Rate of emitted photons from a point inside metal structure:

$$\Gamma \sim \underbrace{\rho(\omega)}_{\text{"Photonic part"}} \int \underbrace{\left|\langle f|\vec{\mu}|i\rangle\right|^2 f(\varepsilon+\hbar\omega)\left[1-f(\varepsilon)\right]}_{\text{"electronic" part}} d\varepsilon$$

I_e

Electronic part→ solving Boltzmann equation for steady state

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\substack{photon\\absorption}} + \left(\frac{\partial f}{\partial t}\right)_{\substack{e-e\\scattering}} + \left(\frac{\partial f}{\partial t}\right)_{\substack{e-ph\\scattering}}$$

$$f(\mathcal{E},T_e;|E_{loc}|^2) \cong f^T(\mathcal{E},T_e) + \Delta f_e^{NT}$$

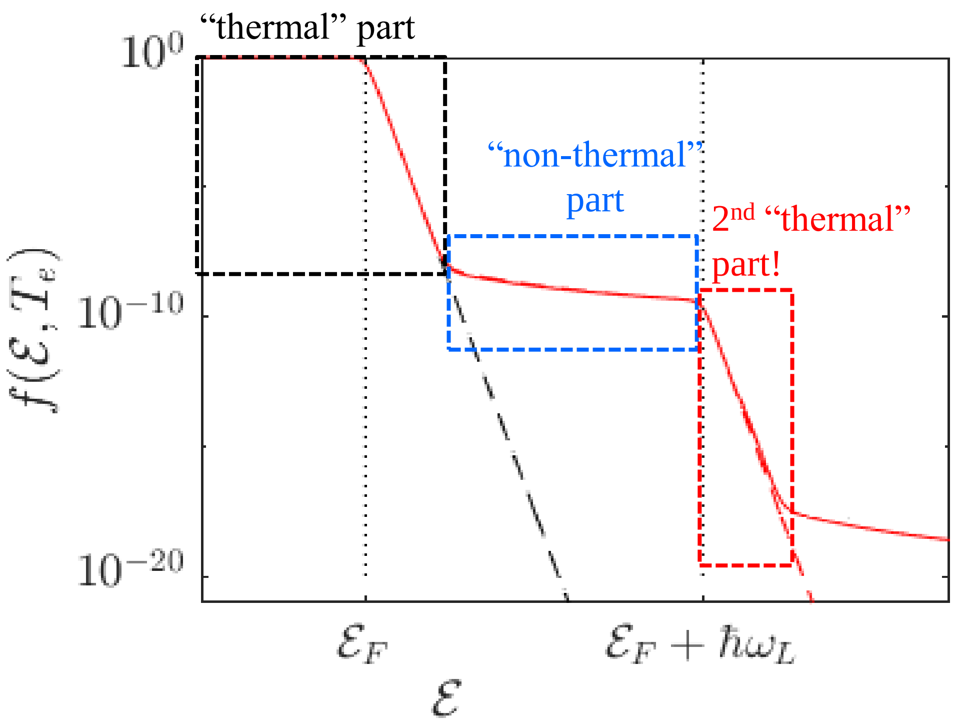
$$\Delta f_e^{NT} \approx \delta_E f^T(\mathcal{E}-\hbar\omega_L,T_e),$$

$$\delta_E(\boldsymbol{r};\omega_L) = p_{abs}(\boldsymbol{r};\omega_L)/p_{sat}, \qquad p_{abs}(\boldsymbol{r};\omega_L) = \frac{\omega\epsilon_0}{2}\epsilon''_m|E_L|^2 = \underbrace{\alpha_{abs}}_{\text{Absorption cross section density}}(\boldsymbol{r};\omega_L)I_{in}$$

$$p_{sat} = \frac{3n_e(\hbar\omega_L)^2}{4\varepsilon_F\tau_{e-e}}$$

τ_{e-e} =effective e – e collision rate

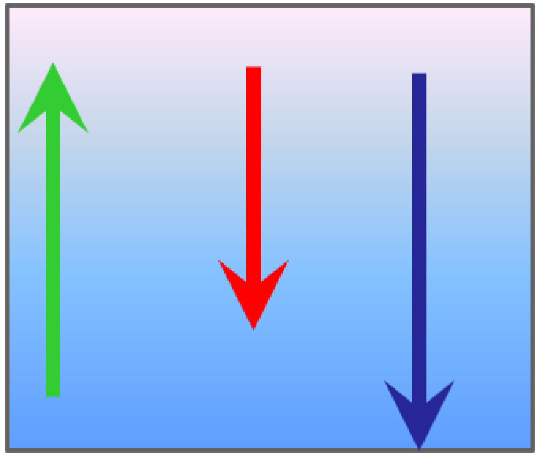
n_e= is the electron density



Sivan, Dubi, ACS Nano 15, 8724−8732 (2021)

Dubi & Sivan, Light: Science & Applications 8, 89 (2019)

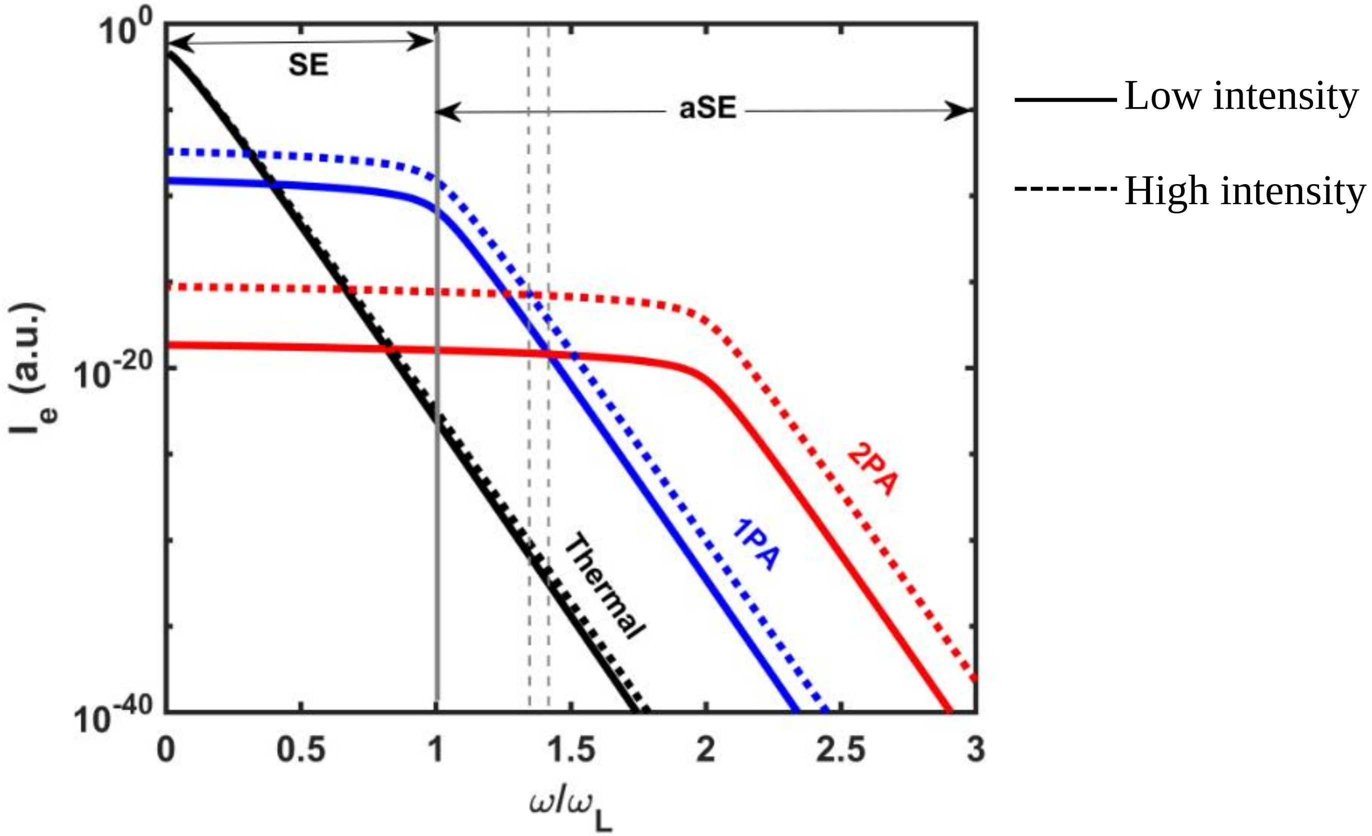
Theory of metal luminescence



pumping

Stokes emission (SE)

Anti-Stokes emission (aSE)



$$I_e \sim \underbrace{\frac{\hbar\omega}{e^{\hbar\omega/k_B T_e}-1}}_{\varepsilon_{BB}(\omega,\,\omega_L T_e)} + \alpha\,\frac{\hbar(\omega-\omega_L)}{e^{\hbar(\omega-\omega_L)/k_B T_e}-1}\,|E_L|^2 + \beta\,\frac{\hbar(\omega-2\omega_L)}{e^{\hbar(\omega-2\omega_L)/k_B T_e}-1}\,|E_L|^4 + \cdots$$

Photonic part ??

Theory of metal luminescence

Luminescence from an extended structure

$$dP^{em}(\omega,\omega_L,\hat{k}) \cong \frac{\omega^2}{8\pi^3c^2}\sum_{pol=s,p}\int_V \underbrace{\eta(\boldsymbol{r}';\omega,pol,\hat{k})}_{\text{Emissivity density}} I_e\left(\omega,\omega_L,T_e(\boldsymbol{r}'),p_{abs}(\boldsymbol{r}';\omega_L,pol,-\hat{k})\right)dr'^3 d\Omega$$

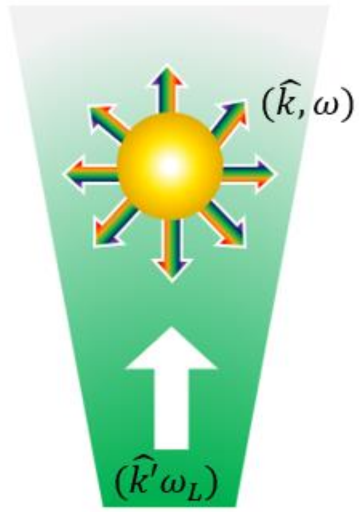
local Kirchhoff Law:

Emissivity density =Absorption cross section density

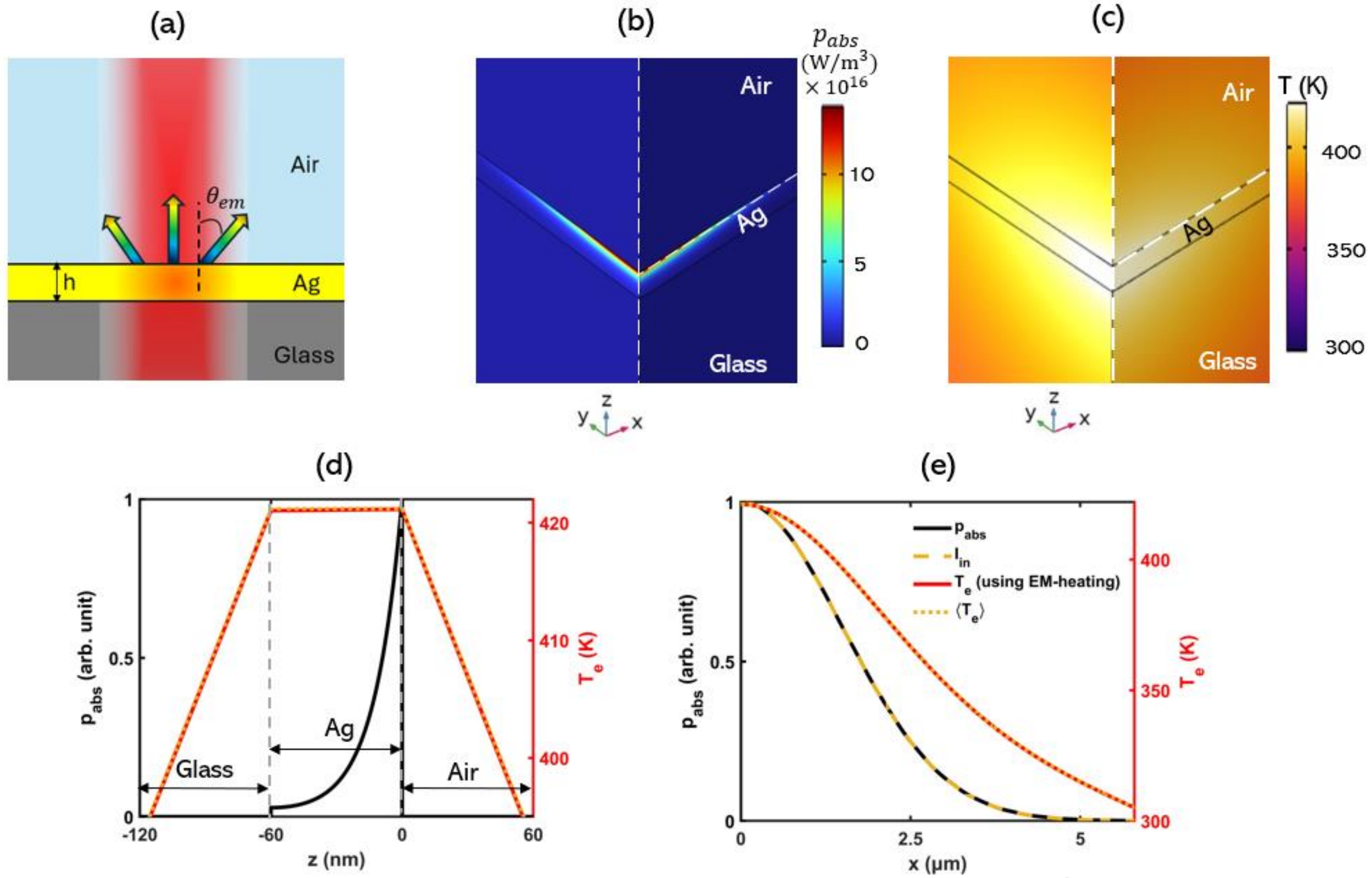
$$\eta(\boldsymbol{r}';\omega,pol,\hat{k}) = \alpha_{abs}(\boldsymbol{r}';\omega,pol,-\hat{k})$$

$$\alpha_{abs}(\boldsymbol{r};\omega_L) = \frac{p_{abs}(\boldsymbol{r};\omega_L)}{I_{in}}$$

$$\boxed{\begin{gathered}\alpha_{abs}(\boldsymbol{r}';\omega_L,pol,-\hat{k})\\ \alpha_{abs}(\boldsymbol{r}';\omega,pol,\hat{k})\\ T_e(\boldsymbol{r}')\end{gathered}}$$



Luminescence from metal film



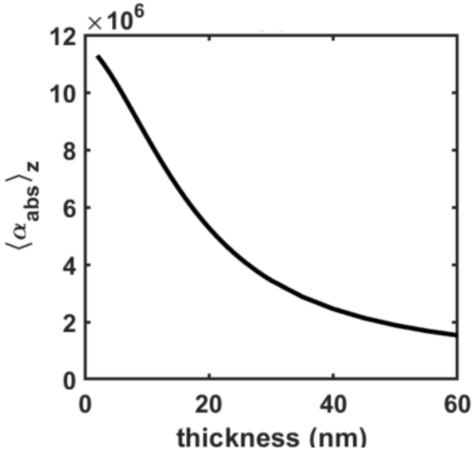
- Along the plane of the film (xy-plane): $p_{abs} \sim I_{in}$ But T_e has a broader distribution
- Along the Thickness of the film (z-axis): $p_{abs} \sim e^{-kn''z}$ But T_e ~ constant

$$p_{abs}(\boldsymbol{r}'; \omega_L, pol, -\hat{k}) = I_{in}(\rho; \omega_L, pol, -\hat{k})\alpha_{abs}(z; \omega_L, pol, -\hat{k})$$

$$T_e(\rho)$$

Calculation: Luminescence from silver film

$\lambda_L = 488\ nm$



$$\alpha_{abs}(\boldsymbol{r};\omega_L) = \frac{p_{abs}(\boldsymbol{r};\omega_L)}{I_{in}}$$

transfer matrix method

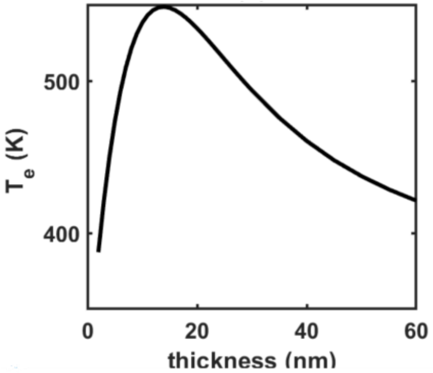
o $\alpha_{abs}(\boldsymbol{r};\omega_L)$

— $\langle\alpha_{abs}(\boldsymbol{r};\omega_L)\rangle_z$

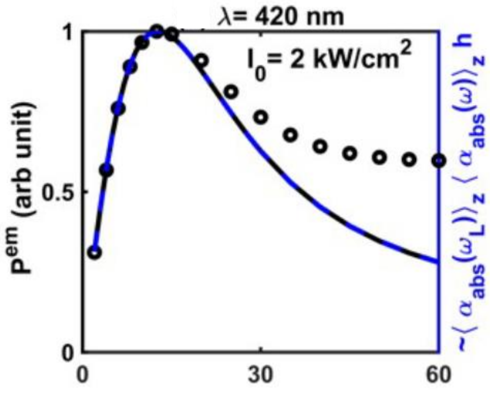
$$\langle\alpha_{abs}\rangle_z = \frac{A}{h} = \frac{1-T-R}{h}$$

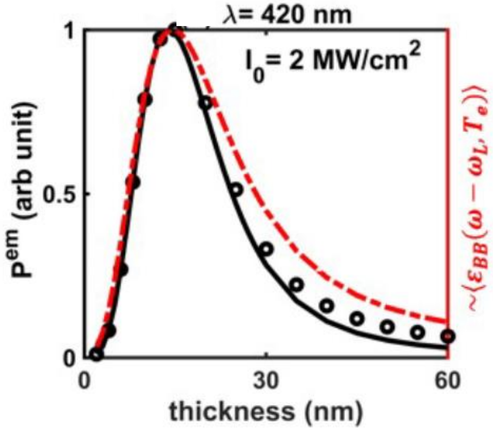
$I_{in} = 2\ kW/cm^2$
$T_e \sim 300K$

$I_{in} = 2\ MW/cm^2$

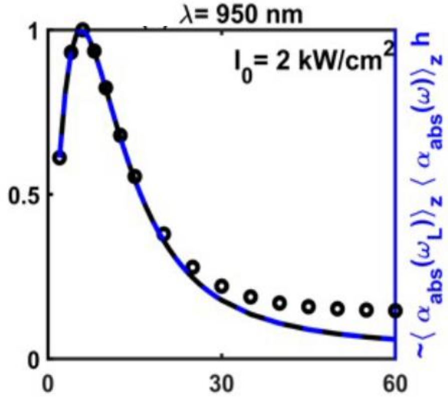


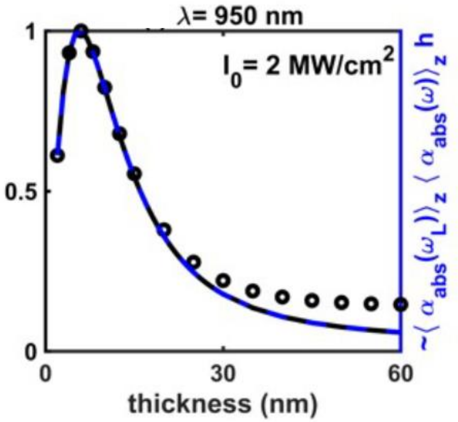
aSE





SE

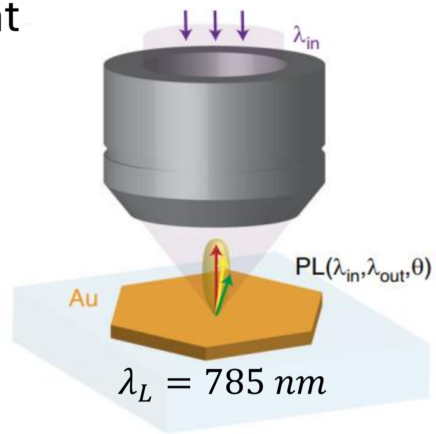


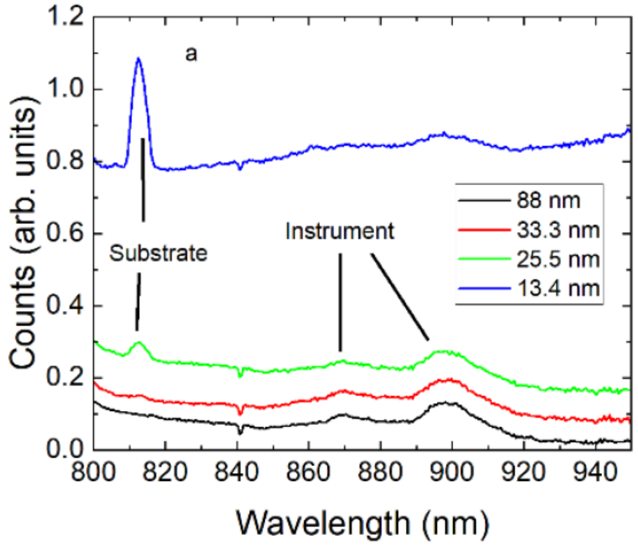


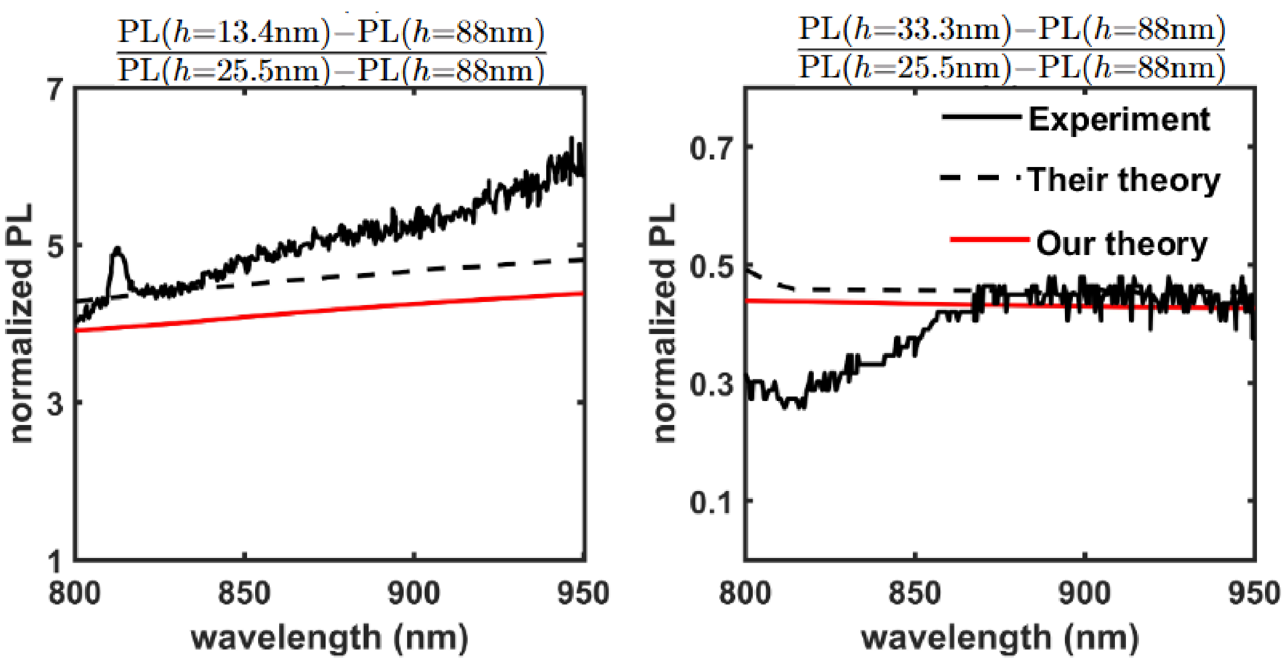
- PL initially increases (volume effect) and then decreases (surface effect) for thicker films
- T_e~room temperature→ PL is independent of temperature
- SE→ PL is independent of temperature
- aSE & $T_e > 300\ K$→ PL is temp dependent

Comparison to experiment

Experiment







Their theory:

- Quantum mechanical calculations –discrete electron states treatment
- Summation of the individual dipole emissions
- A detailed DFT-based calculation of the permittivity

Our theory:

- Calculation of temperature
- Calculation of absorption cross section density

Our simple theory estimates the size dependent trends closely to that of experiment

Thank you