Supporting Information: Photoluminescence from metal nanostructures - dependence on size

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Additional Figures

Supporting Information contains Fig. S1-9, including absorption cross-section of spheres, absorption characteristics across spectrum, thermal and non-thermal contribution to PL of sphere, PL of sphere excited off-resonance, PL calculated for higher order mode responses, the thermo-optic effect on absorption and PL calculation for films.

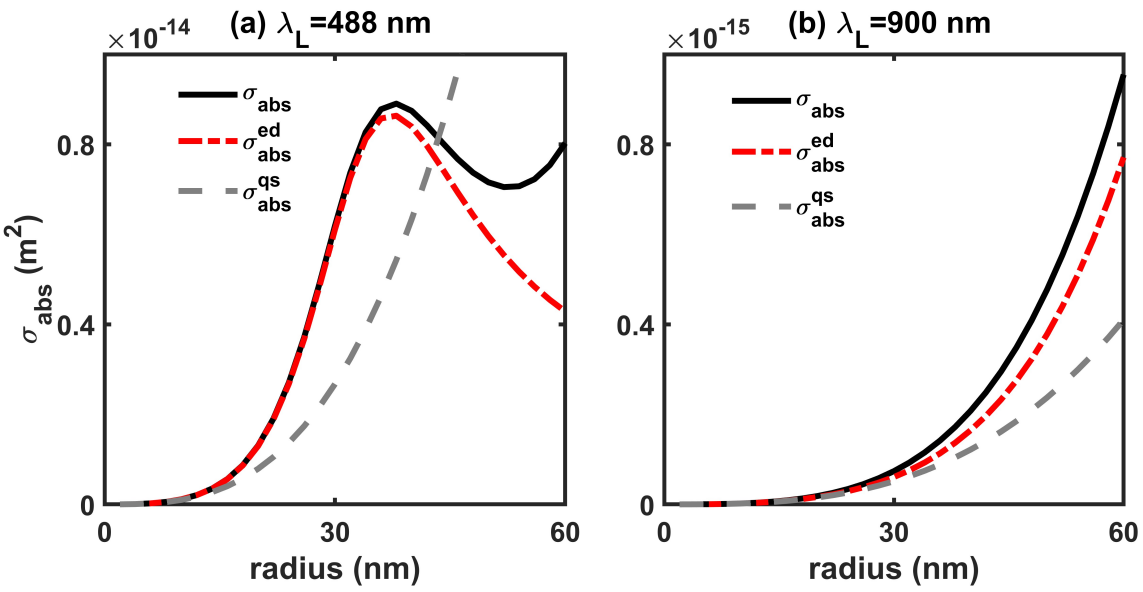

Figure S1: (Color online) The absorption cross-section (σ_{abs}),[S1,S2] the dipolar contribution to the absorption cross-section (σ^{ed}_{abs}) and the absorption cross section in the quasi-static limit (σ^{qs}_{abs})[S1] are calculated for Ag spheres in oil at the wavelengths (a) 488 nm and (b) 900 nm.

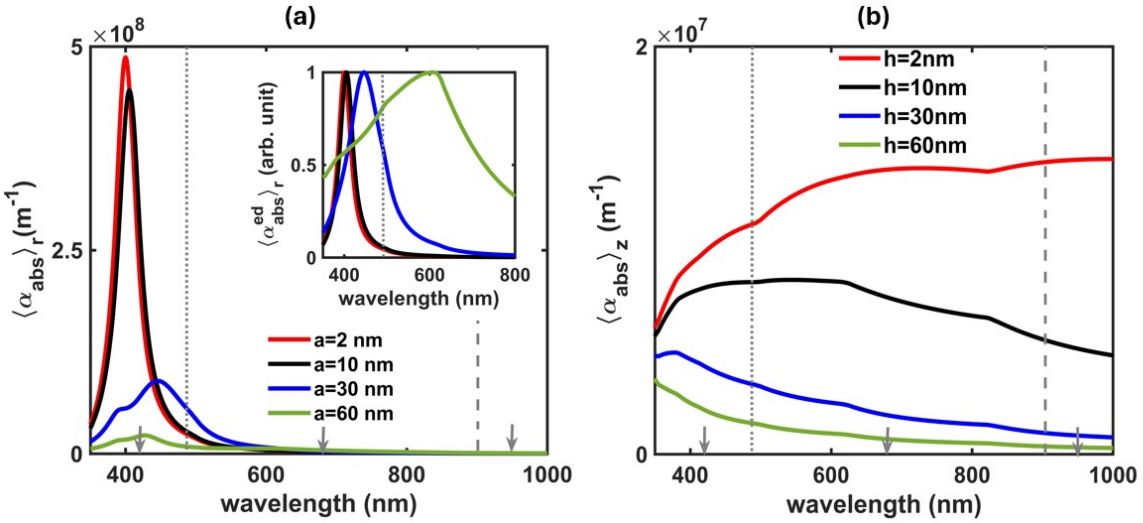

Figure S2: (Color online) (a) The spectral dependence of the volume-averaged absorption cross section density, $\langle \alpha_{abs}(\omega, \mathbf{r}) \rangle_r$, calculated for Ag nano-spheres of radius a ranging from 2 nm to 60 nm in oil. The contribution from the electric dipole mode alone, represented by $\langle \alpha^{ed}_{abs}(\omega, \mathbf{r}) \rangle_r = \sigma^{ed}_{abs}/V$, is shown in the inset. (b) The spectral dependence of $\langle \alpha_{abs}(\omega, \mathbf{r}) \rangle_z$ calculated for Ag films of thickness h varying from 2 nm to 60 nm. In both cases, dotted and Dashed gray vertical lines indicate the absorption wavelengths 488 nm and 900 nm, respectively, and the arrows indicate emission wavelengths 420 nm, 680 nm and 950 nm. Red, black, blue and green color indicates radii $a = 2,\ 10,\ 30$ and 60 nm, respectively, in (a) and thicknesses $h = 2,\ 10,\ 30$ and 60 nm, respectively in (b).

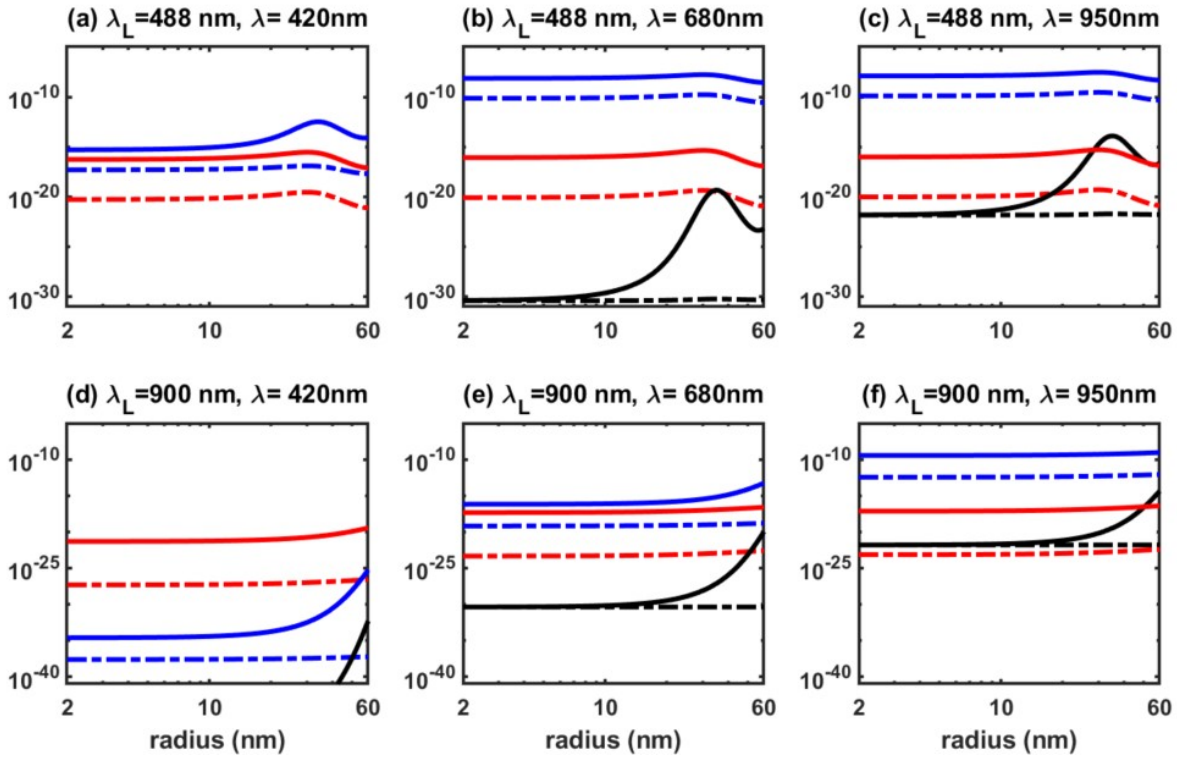

Figure S3: (Color online) The thermal and nonthermal contributions to I_e (i.e., the terms in Eq. (4)): $\langle \mathcal{E}_{BB}(\omega; T_e)\rangle$ (black), $2\langle \mathcal{E}_{BB}(\omega - \omega_L; T_e)\rangle \delta_E$ (blue), $\langle \mathcal{E}_{BB}(\omega - 2\omega_L; T_e)\rangle \delta_E^2$ (red) calculated for Ag spheres immersed in oil due to continuous wave illumination with (a)-(c) $\lambda_L = 488$ nm and (d)-(f) $\lambda_L = 900$ nm. Calculations are done at emission wavelengths $\lambda = 420$ nm ((a) and (d)), $\lambda = 680$ nm ((b) and (e)) and $\lambda = 950$ nm ((c) and (f)) corresponding to $I_{in} = 0.25$ MW/cm^2 (indicated by continuous line) and $I_{in} = 2.5$ kW/cm^2 (indicated by dash-dot line) for (a)-(c) and $I_{in} = 3.5$ MW/cm^2 (indicated by solid line) and $I_{in} = 3.5$kW/cm^2 (indicated by dash-dot line) for (d)-(f). The thermal emission $\langle \mathcal{E}_{BB}(\omega; T_e)\rangle$ is notably low for aSE beyond the considered range, see (a) and (d).

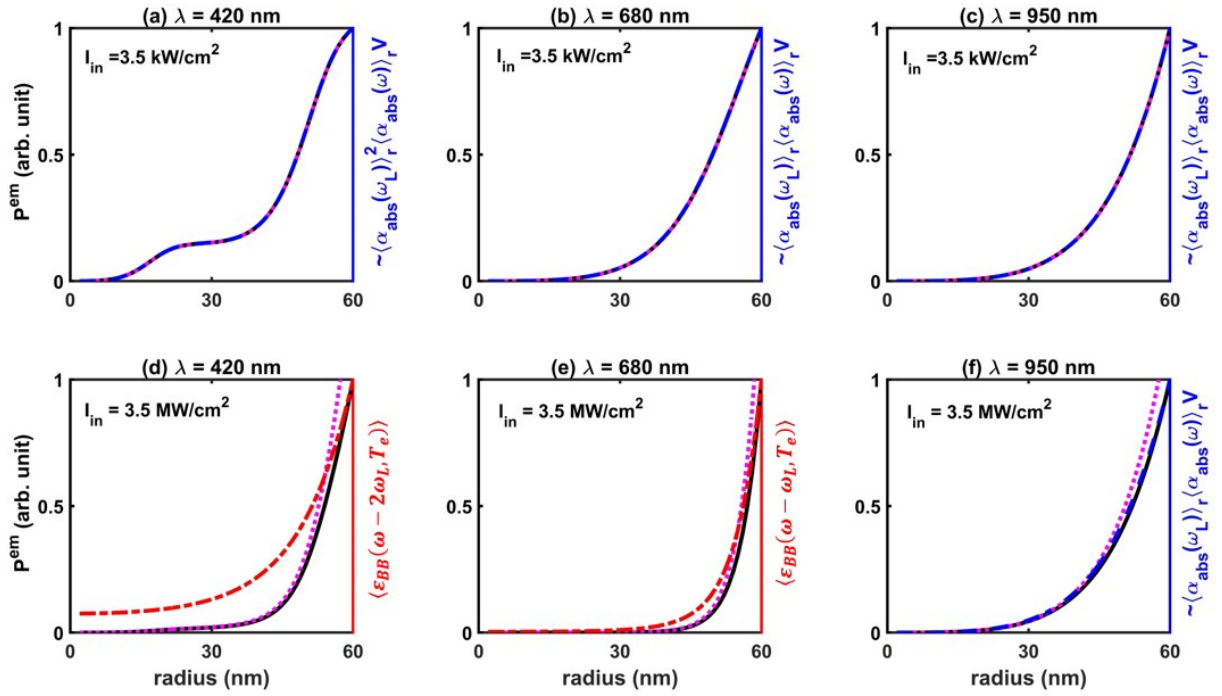

Figure S4: (Color online) The PL calculated for spheres using the homogenized approximation (Eq. (12); black solid line) under CW illumination, excited off-resonance at $\lambda_L = 900$ nm, and emission wavelengths of $\lambda = 420$ nm ((a) and (d)), $\lambda = 680$ nm ((b) and (e)) and $\lambda = 950$ nm ((c) and (f)). For these calculations, $p_{sat} \sim 10^{24}$ W/m^3 and the incident intensity, I_{in} used for the calculation are (a)-(c) 3.5 kW/cm^2 and (d)-(f) 3.5 MW/cm^2. The dashed blue lines represent $V\langle\alpha_{abs}(\lambda_L)\rangle_r\langle\alpha_{abs}(\lambda)\rangle_r$, and the red dash-dot lines represent $\langle\mathcal{E}_{BB}\rangle_r$. The magenta dotted line shows the PL calculation (Eq. (12) when the thermo-optic effect is included. Frequency and wavelength are used interchangeably, as convenient.

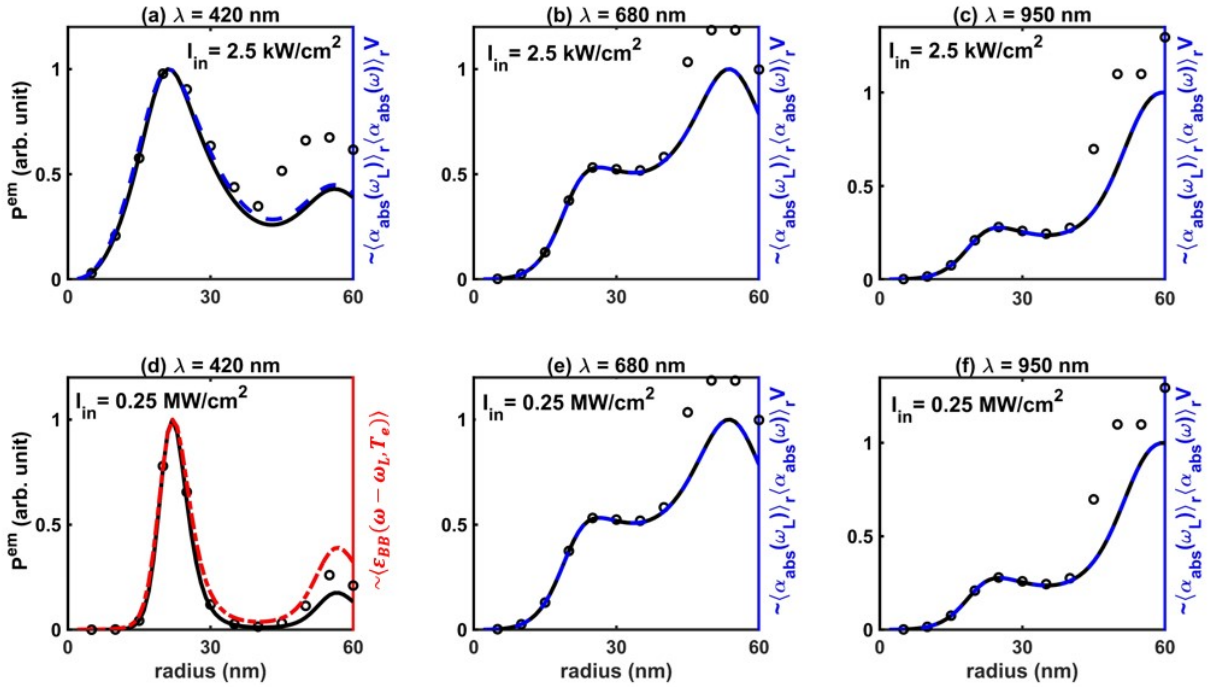

Figure S5: (Color online) The total PL (Eq. (9); circles) and its homogenized approximation (Eq. (12); black continuous line) calculated for spheres for background refractive index 1.8, under CW illumination at $\lambda_L = 488$ nm and emission wavelengths of $\lambda = 420$ nm ((a) and (d)), $\lambda = 680$ nm ((b) and (e)), and $\lambda = 950$ nm ((c) and (f)). I_{in} used for the calculation are (a)-(c) 2.5 kW/cm^2 and (d)-(f) 0.25 MW/cm^2. The dashed blue lines represent $a^3\langle\alpha_{abs}(\lambda_L)\rangle_r\langle\alpha_{abs}(\lambda)\rangle_r$ and the red dash-dot lines represent $\langle\mathcal{E}_{BB}\rangle$. Frequency and wavelength are used interchangeably, as convenient.

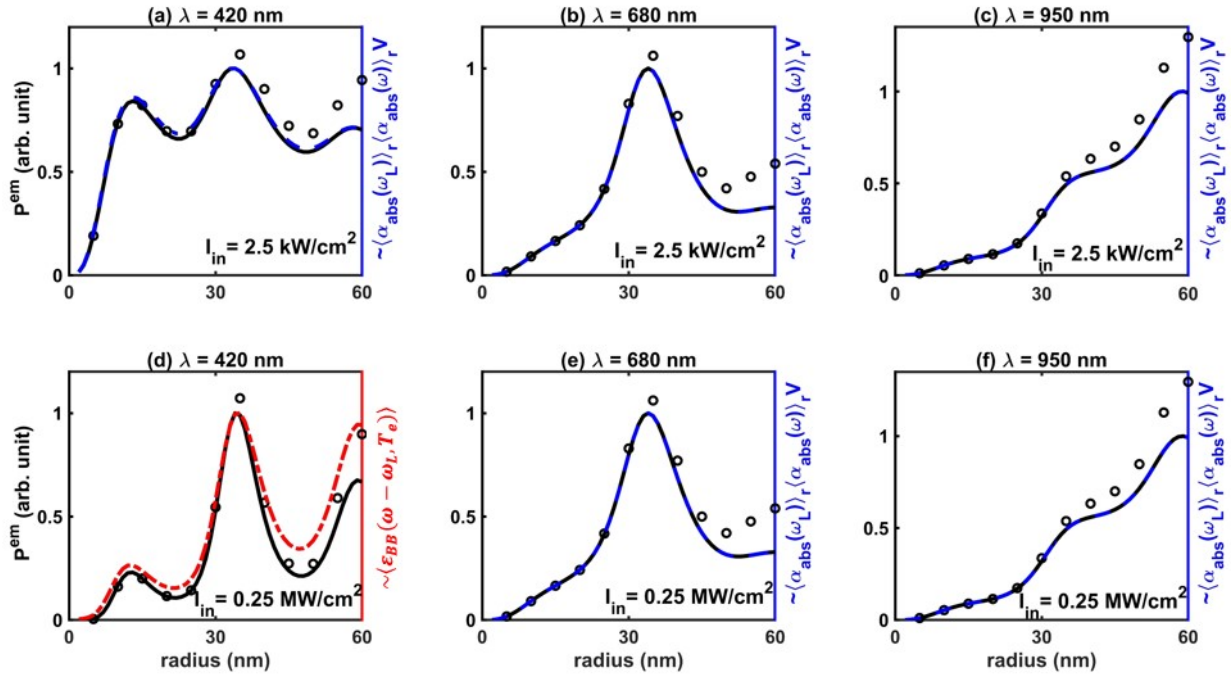

Figure S6: (Color online) Same as Fig. S5 for background refractive index 2.2.

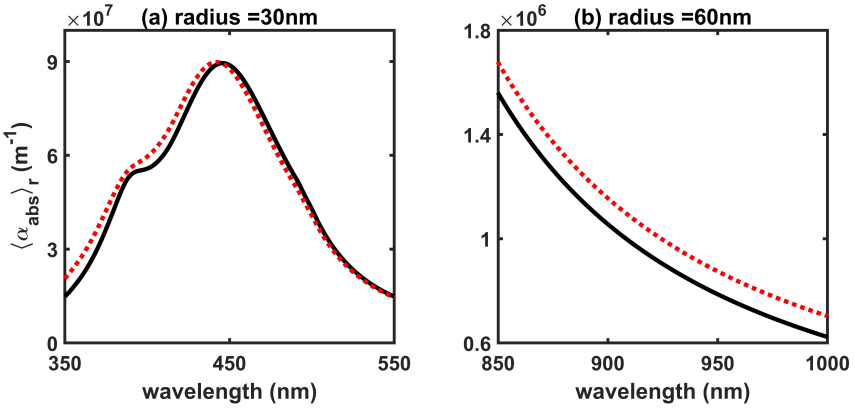

Figure S7: (Color online) $\langle \alpha_{abs} \rangle_r$ calculated for Ag nano-spheres of radius (a) $a = 30$ nm, (b) $a = 60$ nm, immersed in oil at room temperature (black solid line) and at $450°K$ (red dotted line).

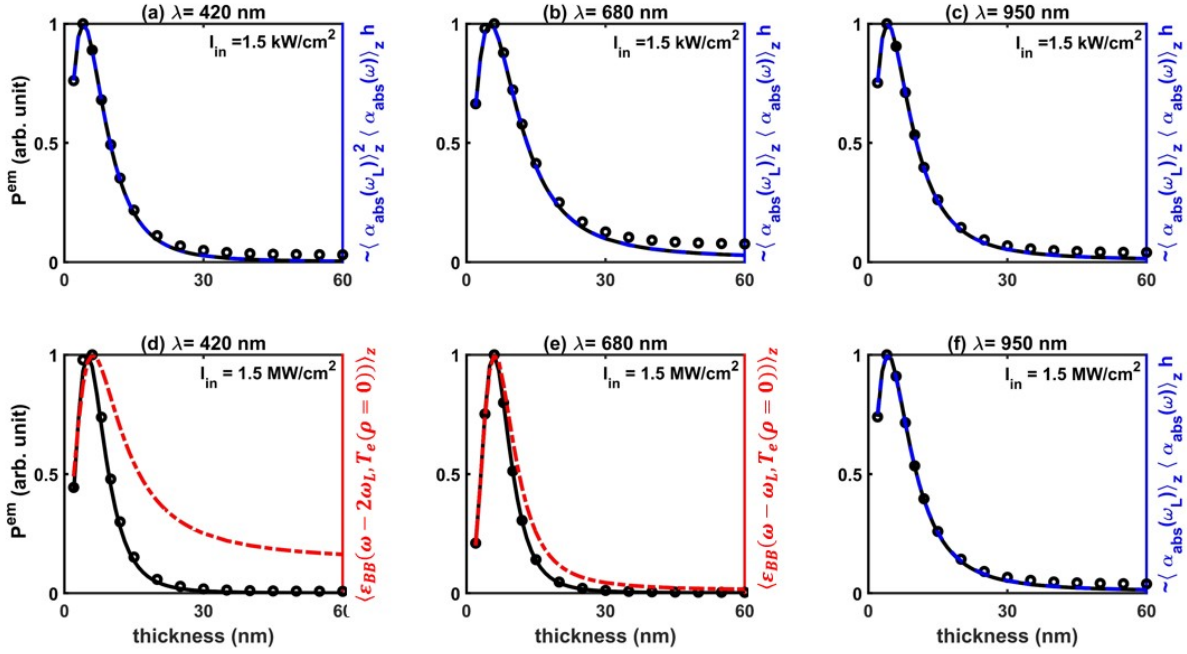

Figure S8: (Color online) The total PL calculated for the films using Eq. (9) (circles) and that using uniform field approximation (black continuous line) under CW illumination at $\lambda_L = 900$ nm and emission wavelengths of $\lambda = 420$ nm ((a) and (d)), $\lambda = 680$ nm ((b) and (e)) and $\lambda = 950$ nm ((c) and (f)). I_0 values are (a)-(c) 1.5 kW/cm^2 and (d)-(f) 1.5 MW/cm^2. The dashed blue lines represent $\langle\alpha_{abs}(\omega_L)\rangle_z\langle\alpha_{abs}(\omega)\rangle_z h$ and the red dash-dot lines represent $\langle\mathcal{E}_{BB}\rangle$.

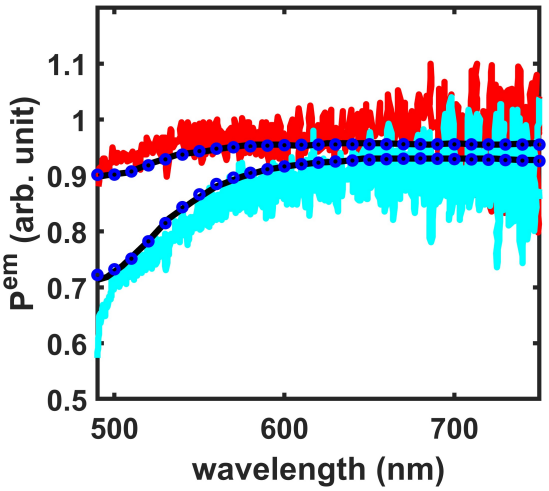

Figure S9: (Color online) The experimental results for the PL from gold layers, for thicknesses $h = 47$ nm (sky blue solid line) and $h = 79$ nm (red solid line) and the corresponding simulations (black solid lines) taken from,[S5] showing the ratio $\frac{\mathrm{PL}(h)}{\mathrm{PL}(h=113\mathrm{nm})}$ as a function of emission wavelength for the excitation conditions of $\lambda_L = 488$ nm, $I_{in} = 0.162\mathrm{mW}/\mu\mathrm{m}^2$. The corresponding calculations using (Eq. (9)) are shown as blue circles.

References

(S1) Bohren, C. F.; Huffman, D. R. *Absorption and scattering of light by small particles*; Wiley & Sons, 1983.

(S2) Kalyan, I.; Krishnamurthy, C. V. Morphology dependent resonance modes in highly porous TiO2 microspheres. *Journal of Applied Physics* **2018**, *124*, 133102.

(S3) Bowman, A. R.; Echarri, A. R.; Kiani, F.; Iyikanat, F.; Tsoulos, T. V.; Cox, J. D.; Sundararaman, R.; de Abajo, F. J. G.; Tagliabue, G. Quantum-mechanical effects in photoluminescence from thin crystalline gold films. *Light: Science and Applications* **2024**, *13*, 91.

(S4) Ref. S3, Fig. 3(b).

(S5) Ref. S3, Fig. 3(b).