Electron spill-out in plasmonic systems enhances second-harmonic generation

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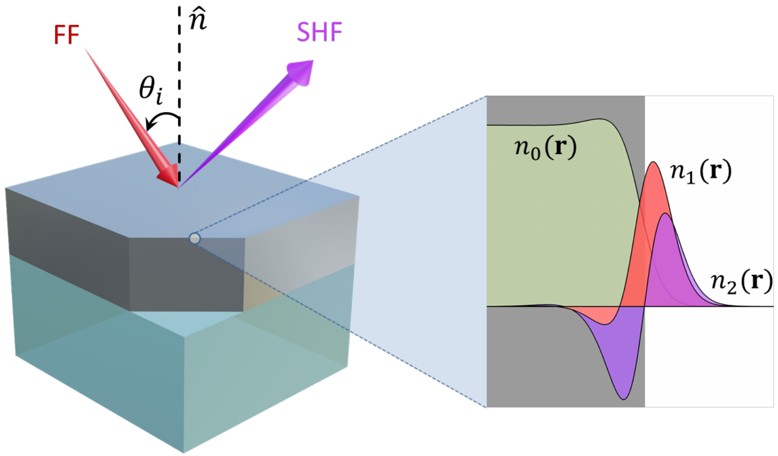
Second-harmonic generation (SHG)

- SHG process can be supported by an **angstrom-scale thin layer** near the metallic interface.

- At such length scale, **classical electrodynamics fails** to address microscopic details.

- **Nonlocal and quantum mechanical effects** may become crucial for an accurate description.



- **Spatial variation of the charge density** can play a significant role and can boost the **nonlinear efficiencies by several orders of magnitude**.

- **Nonlinear quantum hydrodynamic theory** for nonlinear microscopic electron dynamics.

Quantum Hydrodynamic Theory (QHT)

Full nonlinear hydrodynamic equation of motion of an electronic system:

$$m_e\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla+\gamma\right)\mathbf{v}=-e(\mathbf{E}+\mathbf{v}\times\mathbf{B})\;-\nabla\frac{\partial G[n]}{\partial n}$$

$G[n]$ is the energy functional of free electron gas, given as:

$$G[n]=T_{\mathrm{TF}}[n]\;+\;\lambda\,T_{\mathrm{W}}[n,\nabla n]\;+\;v_{XC}[n]$$

Thomas-Fermi   von Weizsäcker   Exchange-correlation

where λ is the range, defining decay of the electron density and is usually taken as: $1/9\le\lambda\le1$.

Considering $\mathbf{J}=-en\mathbf{v}$, we can write:

$$\frac{\partial\mathbf{J}}{\partial t}+\gamma\mathbf{J}=\frac{e^2n_1}{m_e}\mathbf{E}-\frac{e}{m}\mathbf{J}\times\mathbf{B}+\frac{en}{m_e}\nabla\frac{\partial G[n]}{\partial n}+\frac{1}{e}\left(\frac{\mathbf{J}}{n}\nabla\cdot\mathbf{J}-\mathbf{J}\cdot\nabla\frac{\mathbf{J}}{n}\right)$$

- C. Ciracì and F. D. Sala, Phys. Rev. B **93**, 205405 (2016).

Quantum Hydrodynamic Theory (QHT)

Writing the fields as the sum of few harmonics:

$$\mathbf{V}(\mathbf{r},t) = \mathbf{V}_0(\mathbf{r}) + \mathbf{V}_1(\mathbf{r})e^{-i\omega_1 t} + \mathbf{V}_2(\mathbf{r})e^{-i\omega_2 t} + \text{c. c.}$$

Using undepleted pump approximation and $\mathbf{J} = \frac{\partial \mathbf{P}}{\partial t}$:

$$-\frac{en_0}{m_e}\nabla\left(\frac{\delta G}{\delta n}\right)_1 - (\omega_1^2 + i\gamma\omega_1)\mathbf{P}_1 = \varepsilon_0\omega_p^2\mathbf{E}_1$$

$$-\frac{en_0}{m_e}\nabla\left(\frac{\delta G}{\delta n}\right)_2 - (\omega_2^2 + i\gamma\omega_2)\mathbf{P}_2 = \varepsilon_0\omega_p^2\mathbf{E}_2 + \mathbf{S}_{\mathrm{NL}}$$

where $\omega_p(r) = \sqrt{e^2 n_0(r)/(m_e\varepsilon_0)}$ is the space-dependent plasma frequency and the nonlinear source term $\mathbf{S}_{\mathrm{NL}}$:

$$\mathbf{S}_{\mathrm{NL}} = \frac{e^2 n_1}{m_e}\mathbf{E}_1 + \mathrm{i}\omega_1\frac{\mu_0 e}{m_e}\mathbf{P}_1\times\mathbf{H}_1 - \frac{\omega_1^2}{en_0}\left(\mathbf{P}_1\nabla\cdot\mathbf{P}_1 + \mathbf{P}_1\cdot\nabla\mathbf{P}_1 - \mathbf{P}_1\cdot\mathbf{P}_1\frac{\nabla n_0}{n_0}\right) +$$

$$+\frac{en_1}{m_e}\nabla\left(\frac{\delta G}{\delta n}\right)_1 + \frac{en_o}{m_e}\nabla\left(\frac{\delta G}{\delta n}\right)_2^{\mathrm{NL}}$$

Equilibrium charge density

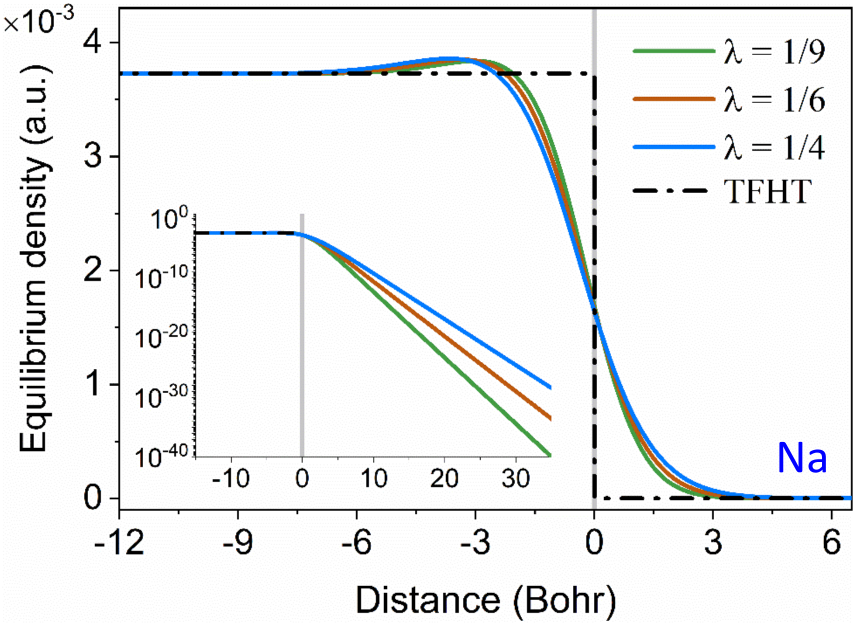
Equilibrium electron density n_0 was computed by the following nonlinear static equation:

$$\nabla \varepsilon_\infty(\mathbf{r}) \cdot \nabla \left(\frac{\delta G[n]}{\delta n}\right)_{n=n_0} + \frac{e^2}{\varepsilon_0}(n_0 - n^+) = 0$$

n^+ indicates the positive background charge.

ε_∞ is the core dielectric constant.

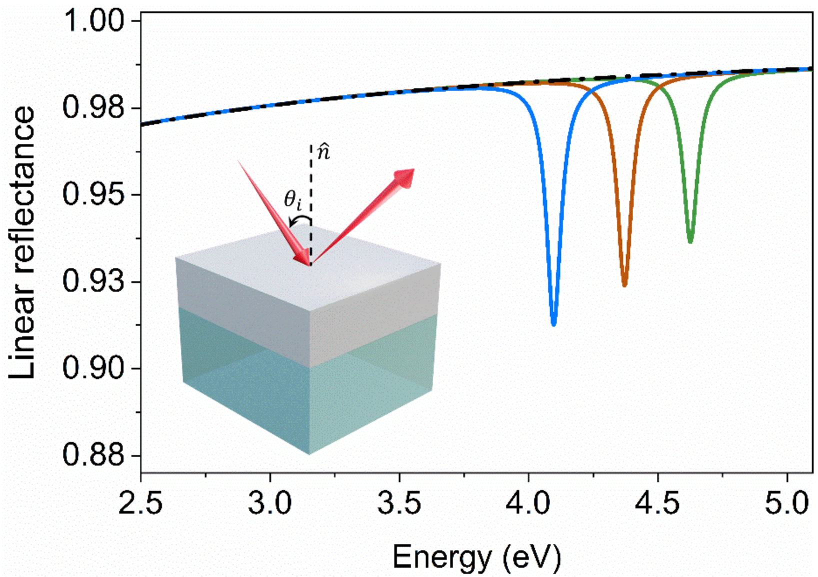
A constant electron density inside the metal with no spatial dependence is assumed in the **Thomas-Fermi hydrodynamic theory** (TFHT).

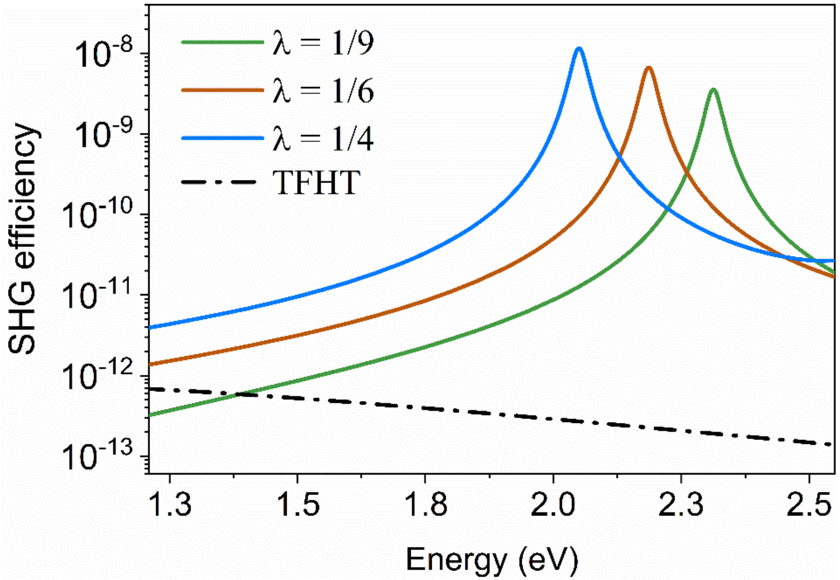


- $t_{film} = 400$ nm
- $\varepsilon_\infty = 1$
- $r_s = 4$ a.u.

Simple Drude-like metal: Na

- Spatial dependence of the electron density in QHT predicts a dip in the reflection spectra.
- No structure in the case of TFHT as no spill-out is considered.
- These resonances are due to excitation of the multipolar surface plasmons.
- Large enhancement in the SHG efficiency.
- By controlling the amount of electron spill-out, **resonances cab be tuned** to the frequency of interest.





- $t_{film} = 400$ nm
- $\hbar\gamma = 0.066$ eV
- $r_s = 4$ a.u.

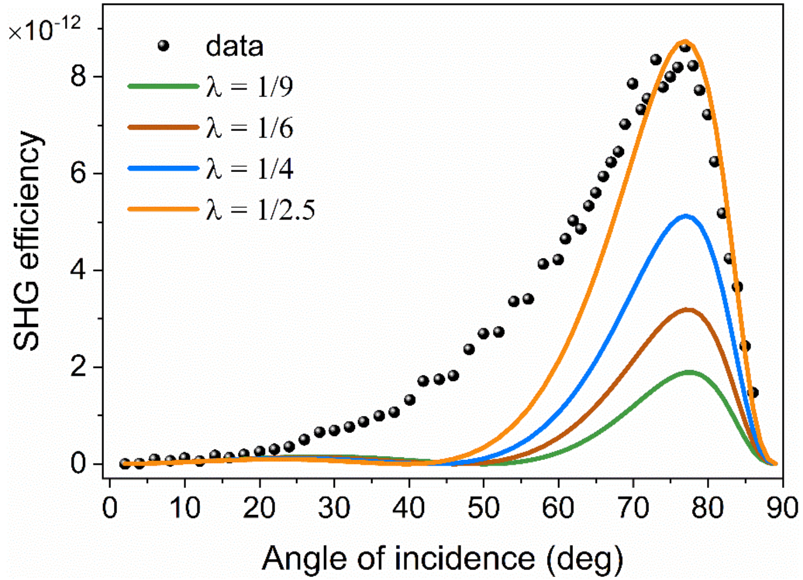
Fitting experimental data: Ag

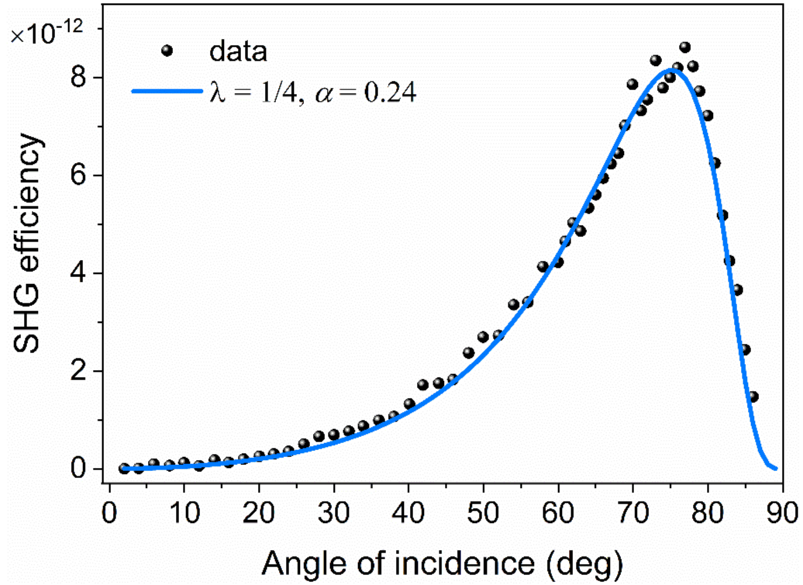
- For smaller values of λ the efficiency is largely underestimated and increases as λ increases.
- Full self-consistent nonlinear QHT can approximate peak of the data but the angular dependence is not fully reproduced.
- To fit the data, we introduce a parameter α such that:

$$\lambda T_W[n, \nabla n] = \lambda[T_W^L + \alpha T_W^{NL}]$$

L and NL indicate linear and nonlinear terms, respectively.

- Unlike Na, the clean **Ag film does not show any resonance** structure in the efficiency spectra, due to:
  - lower spill out
  - polarizable background





† O'Donnell and R. Torre, New J. Phys. **7**, 154 (2005).

- $t_{film} = 400$ nm
- $\hbar\gamma = 0.03$ eV
- $r_s = 3$ a.u.
- $\varepsilon_\infty = 5.8$

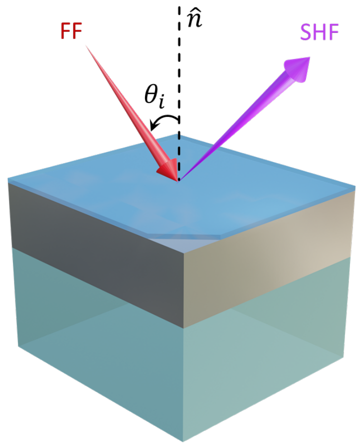
Ag film with a dielectric coating

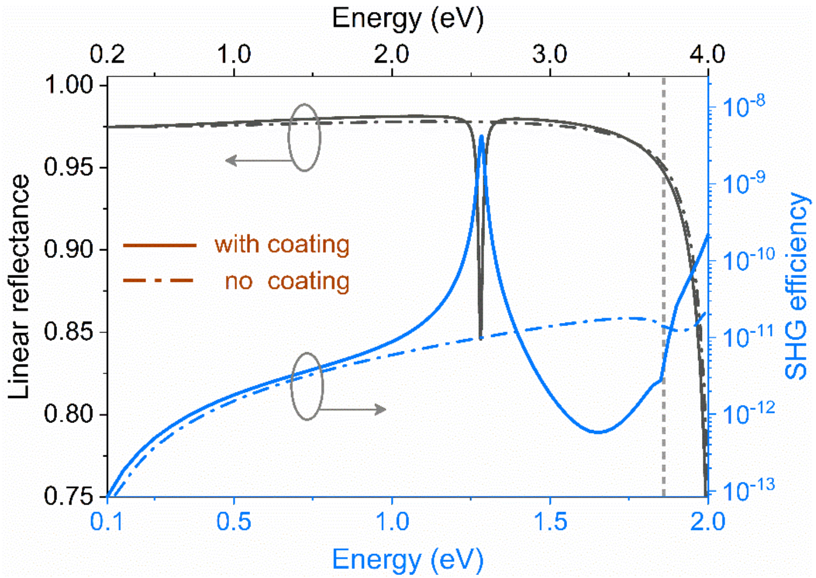
- Electron spill-out can be enhance by reducing the work function at the metal interface.

- Coating the Ag film with a sub-wavelength thin layer of a dielectric material (ε_r).

- Coated film shows a **dip in the linear spectra**, resulting in a strong enhancement in the SHG efficiency spectra.

- Ag film with **no coating** shows **no resonance** structure in the spectra.

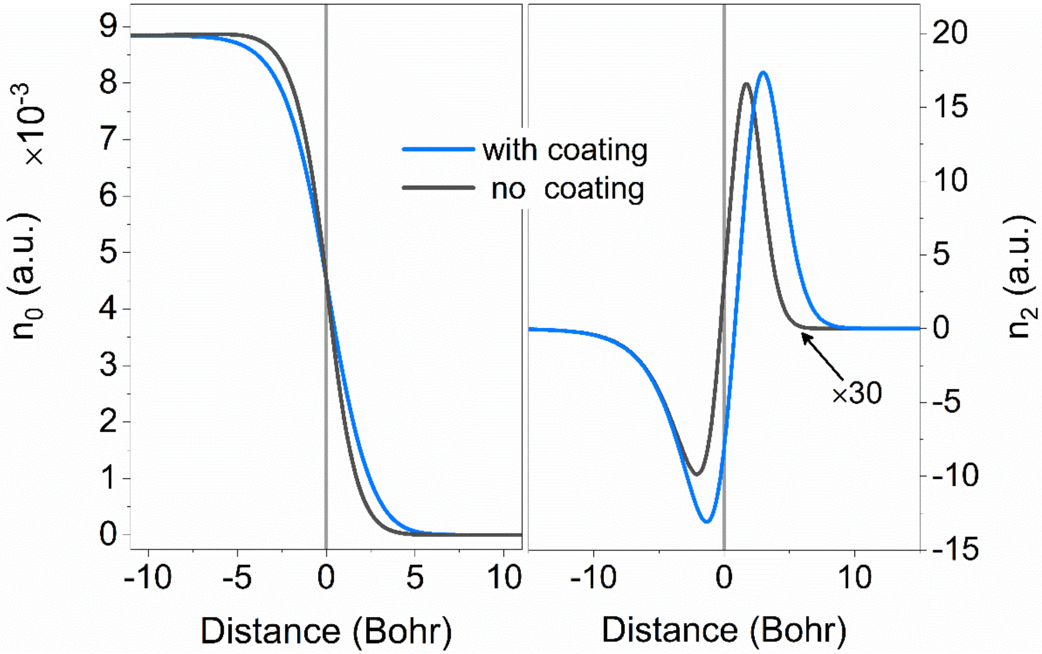




M. Khalid and C. Ciracì, ArXiv: arXiv:2004.07012v1.

- $t_{film} = 400$ nm
- $\lambda = 1/4$
- $t_{coating} = 10$ nm
- $\varepsilon_r = \varepsilon_\infty$

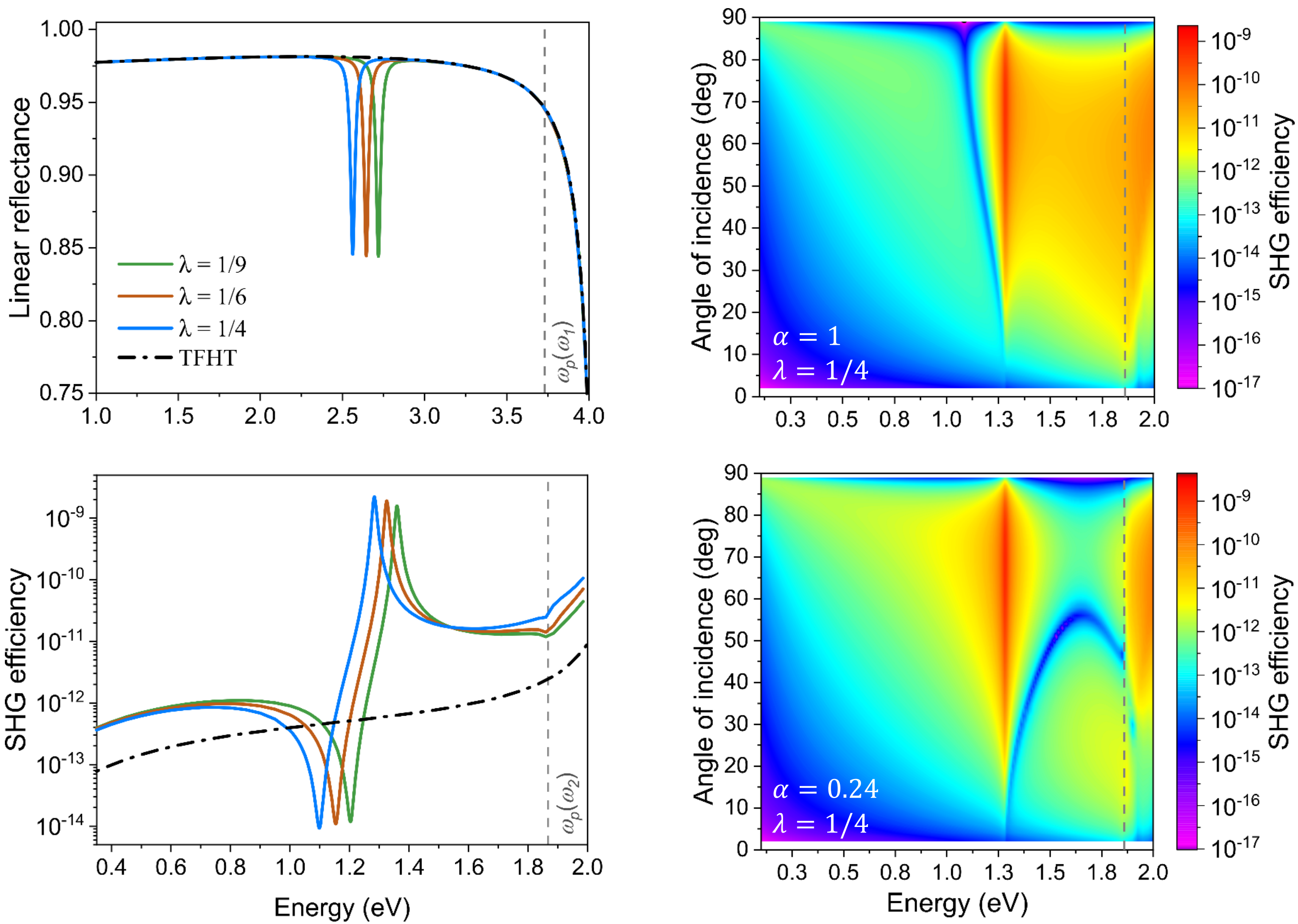
Ag film with a dielectric coating



- Optical response is very sensitive function of the ground-state electron density.
- With a **dielectric coating, the spill-out is more pronounced** as compared to uncoated film.
- The induced charge density for the coated film is larger in width and magnitude, and is shifted farther away from the metal surface.

- $t_{film} = 400$ nm
- $\lambda = 1/4$
- $t_{caoting} = 10$ nm
- $\varepsilon_r = \varepsilon_\infty$

Ag film with a dielectric coating



- $t_{film} = 400$ nm
- $t_{coating} = 10$ nm
- $\varepsilon_r = \varepsilon_\infty$

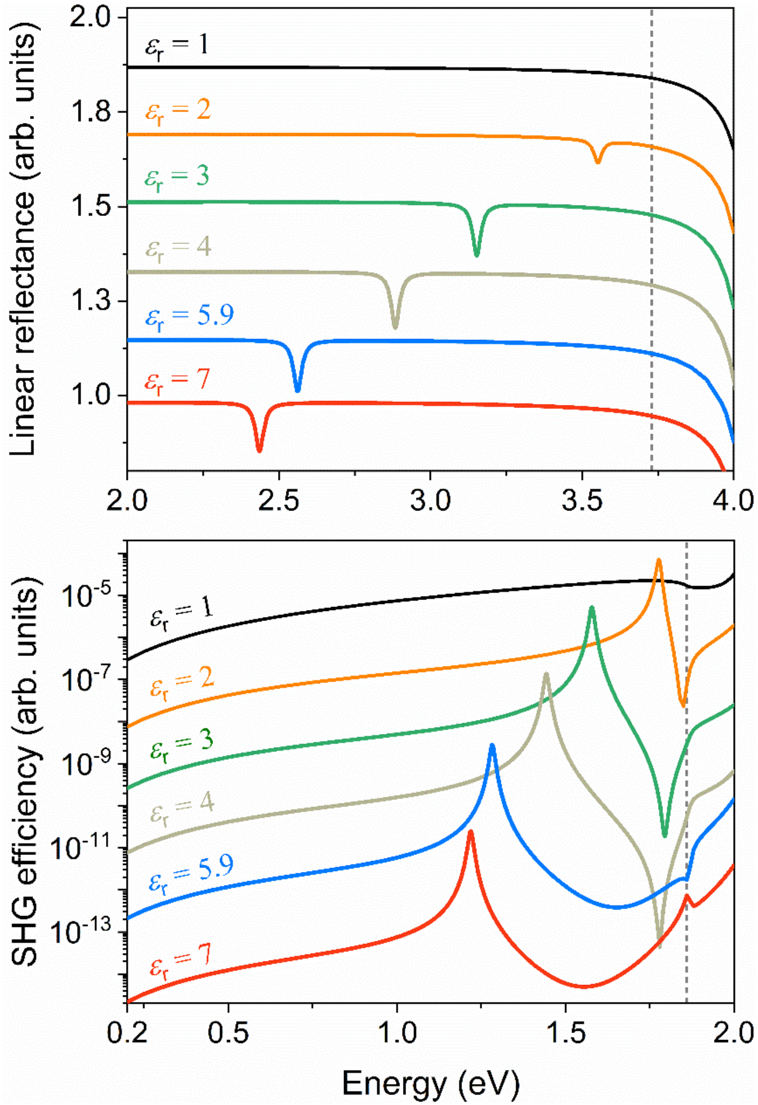
Ag film with dielectric coating

- Optical response of the Ag film for various values of the dielectric constant ε_r of the coating material.

- For each $\varepsilon_r > 1$, a dip in the linear spectra can be observed, although it becomes less intense when $\varepsilon_r \rightarrow 1$ and disappears for $\varepsilon_r = 1$.

- The generated signal with very enhanced efficiency.

- SHG process can be tuned by coating the Ag film with a suitable dielectric material.



M. Khalid and C. Ciracì, ArXiv: arXiv:2004.07012v1.

- $t_{film} = 400$ nm
- $\lambda = 1/4$
- $t_{coating} = 10$ nm
- $\alpha = 0.24$

Conclusions

- We have proposed a theoretical model based on the quantum hydrodynamic theory to probe **second-order nonlinearities at metal surfaces**.
- **Realistic profiles of the ground state density** can be efficiently incorporated.
- We found **very large enhancement** in the SHG efficiency **induced by electron spill-out**.
- Resonances can be tuned with the aid of **dielectric coating** of the film.
- Nonlinear conversion rates can be further enhanced using **plasmon-based field enhancement techniques**.

Acknowledgments

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