Supplementary Information

Experimental and Theoretical Investigation of Macro-Periodic and Micro-Random Nanostructures with Simultaneously Spatial Translational Symmetry and Long-Range Order Breaking

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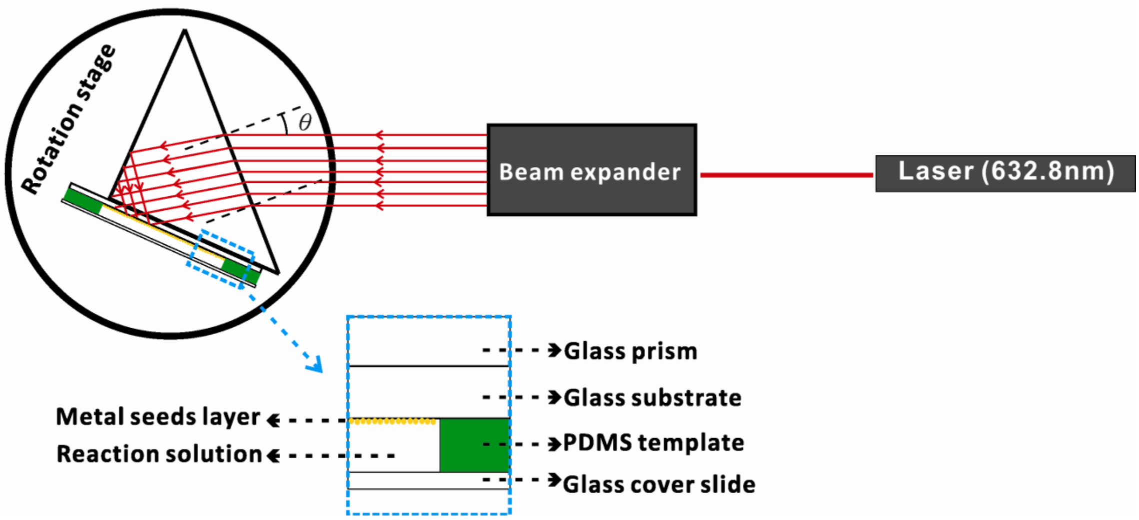


Figure S1. Schematic diagram of the setup and designed arrangement of substrate mounting for fabricating silver macro-periodic and micro-random structures.

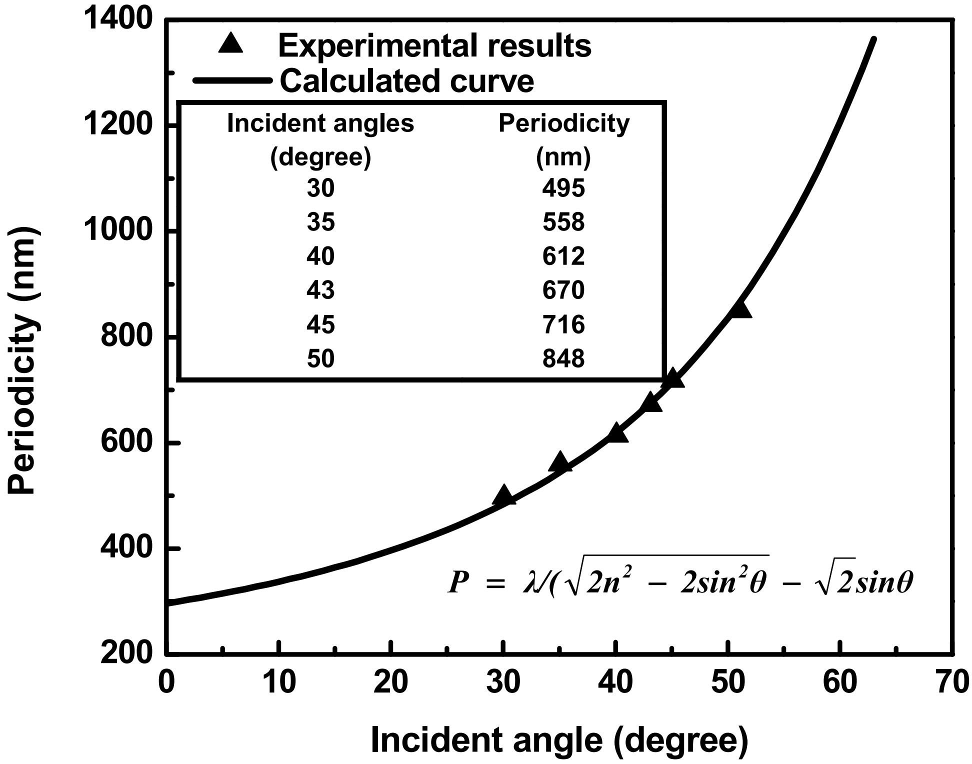


Figure S2. Periodicity (P) of pattern as a function of incident angle of light. The triangular dots are experimental results as summarized in the inset table. Theoretical calculation is represented by the black line. In the equation, λ is the wavelength of light source, θ is the incident angle, and n is the refractive index of glass substrate.

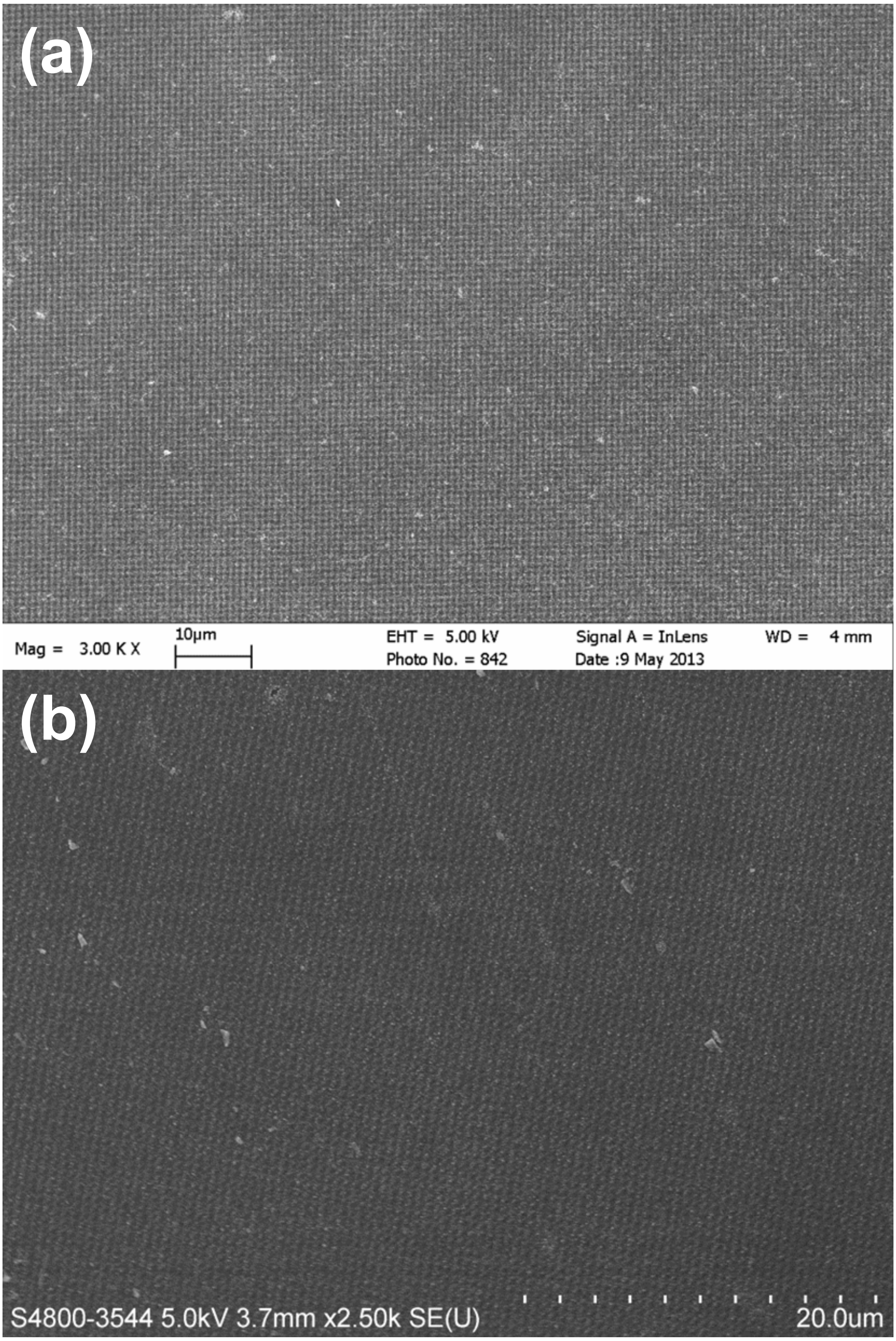


Figure S3. 2D periodic silver nanostructures prepared from (a) double exposures and (b) three beams interference.

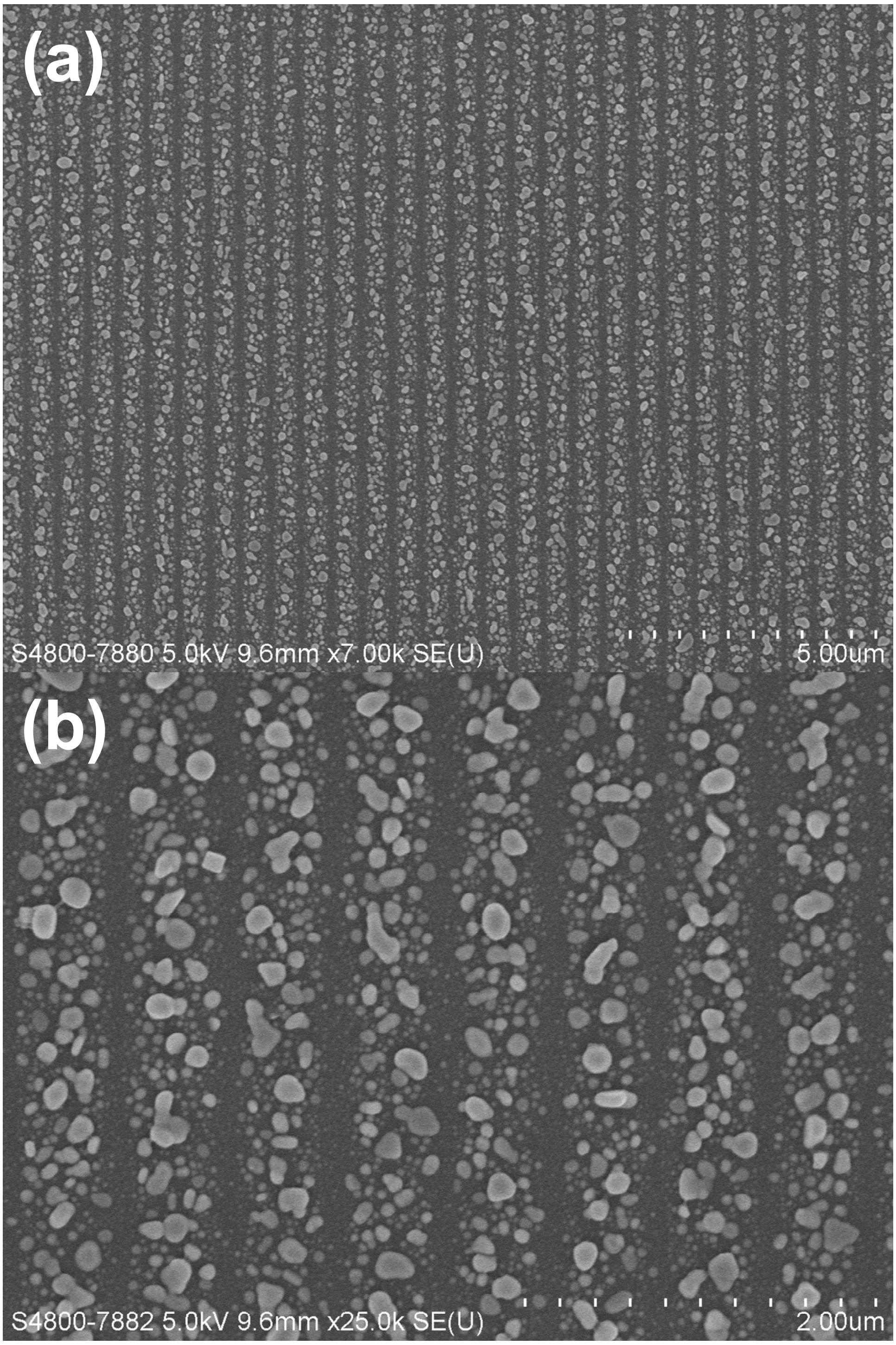


Figure S4. SEM image of (a) silver nanoplate based macro-periodic and micro-random structure after thermal annealing and (b) the magnified image.

A schematic structure with one dimensional periodicity (Λ_x) was shown in Figure S5 (a). Taking TM polarization (electric field is along *x*-direction) as example, the incident magnetic field can be written as:

$$H_{inc,y} = \exp[-jk_0 n_{\mathrm{I}}(\sin\theta x + \cos\theta z)] \quad (1)$$

The normalized fields in region I (*z<0*) and III (*z>d*) is expressed as:

$$H_{\mathrm{I},y} = H_{\mathrm{inc},y} + \sum_i r_i \exp[-j(k_{xi}x - k_{\mathrm{I},zi}z)] \quad (2)$$

$$H_{\mathrm{III},y} = \sum_i t_i \exp\{-j[k_{xi}x + k_{\mathrm{III},zi}(z-d)]\} \quad (3)$$

where $k_{\mathrm{I},zi}, k_{\mathrm{III},zi}$ and k_{xi} are the wave numbers and can be determined by dispersion relation and Floquet theorem, r_i (t_i) (*i* is integer) are normalized magnetic field amplitudes of the *i*-th reflected (transmitted) wave in region I (III) which are unknowns. In the grating region II (*0<z<d*), the periodic permittivity is expanded in the Fourier series as $\varepsilon_{rd}(x) = \sum_h \tilde{\varepsilon}_h \exp(j2\pi/\Lambda_x)$ where $\tilde{\varepsilon}_h$ is the *h*-th Fourier component of the permittivity in grating region. It should be note that this expansion is not valid for macro-periodic and micro-random structures which will be dealt with in our modified RCWA method. The tangential magnetic (*y*-component) and electric fields (*x*-component) can be expanded in Fourier series in terms of space harmonics fields:

$$H_{\mathrm{II},y} = \sum_{i=-N}^{N} U_{yi}(z)\exp(-jk_{xi}x) \quad (4)$$

$$E_{\mathrm{II},x} = j\eta_0 \sum_{i=-N}^{N} V_{xi}(z)\exp(-jk_{xi}x) \quad (5)$$

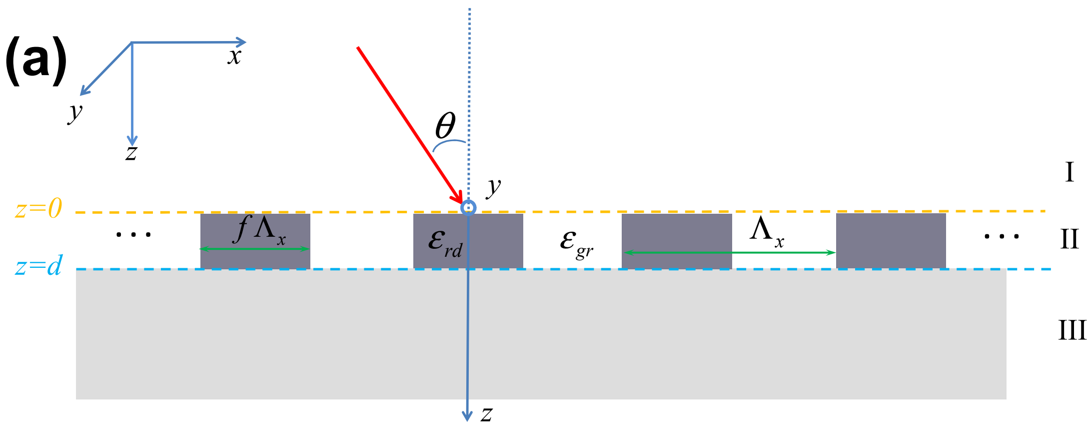
where $U_{yi}(z)$ and $V_{xi}(z)$ are the normalized amplitudes of the *i*-th space harmonic fields and η_0 is wave impedance in free space. Substituting expression (1-5) into Maxwell's equations, a second order matrix differential equation will be obtained:

$$\frac{\partial^2}{\partial \tilde{z}^2}\mathbf{U}_y = \boldsymbol{\varepsilon}\boldsymbol{\Omega}\mathbf{U}_y \quad (6)$$

where $\tilde{z} = k_0 z$ and $\boldsymbol{\Omega} = \mathbf{K}_x \boldsymbol{\varepsilon}^{-1}\mathbf{K}_x - \mathbf{I}$ is expressed in terms of wave vectors and Fourier components of permittivity, $\mathbf{K}_x$ is a diagonal matrix of k_{xi} and $\boldsymbol{\varepsilon}^{-1}$ is the matrix formed by $\tilde{\varepsilon}_h$, $\mathbf{I}$ is unit matrix. With calculating the eigenvalues and eigenvectors of $\boldsymbol{\Omega}$, matching the boundary condition at z=0 and z=d, the unknowns of r_i and t_i can be analytically determined. The reflection and transmission of grating structures are respectively determined by:

$$R = \sum_i r_i r_i^* \,\mathrm{Re}[\frac{k_{I,zi}}{k_0 n_I \cos\theta}] \quad (7)$$

$$T = \sum_i t_i t_i^* \,\mathrm{Re}[\frac{k_{\mathrm{II},zi}}{n_{\mathrm{II}}^2}\frac{n_{\mathrm{I}}}{k_0 \cos\theta}] \quad (8)$$



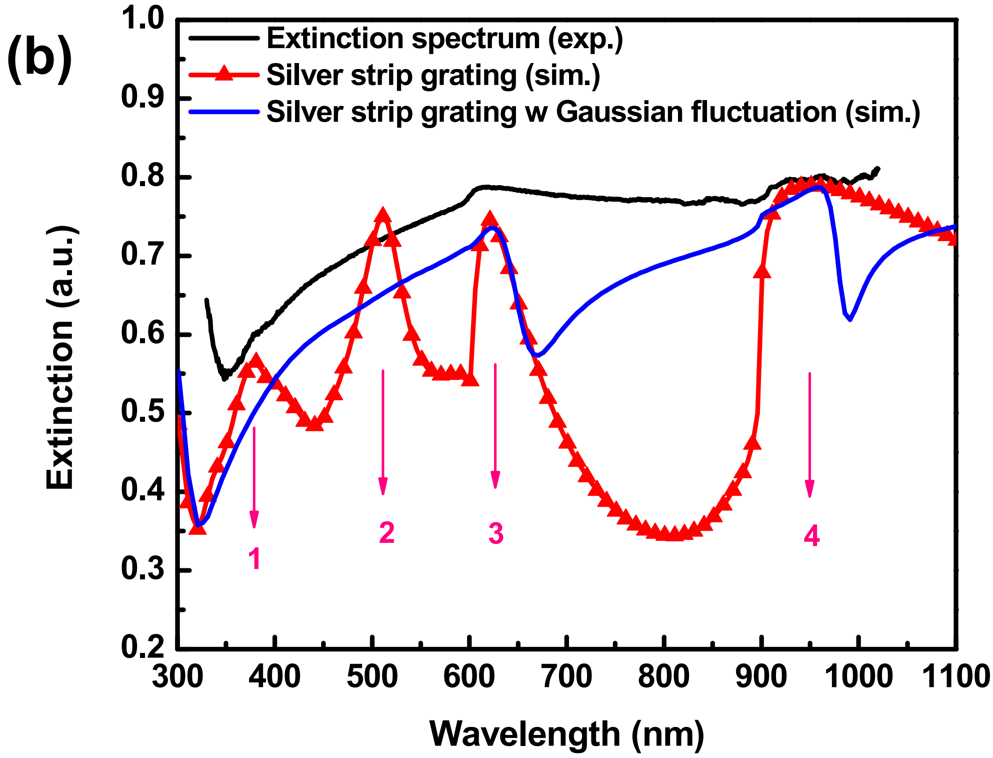


Figure S5. (a) A schematic of grating structures. Λ_x is the period in *x*-direction, $f\,\Lambda_x$ is the width of grating strip, ε_{gr} and ε_{rd} are, respectively, the permittivities of groove and ridge region of grating, θ is incident angle of light. (b)Experimental (exp.) and simulation (sim.) extinction spectra of silver strip grating on glass substrate. The black curve is the experimental extinction spectrum of our silver nanoplate comprised macro-periodic and micro-random structure. Triangle red line is the perfect silver strip grating and the blue line is silver strip grating after including Gaussian fluctuation (σ =0.15). The periodicity, width and height of silver strip for simulation are 610nm, 400nm and 50 nm, respectively.

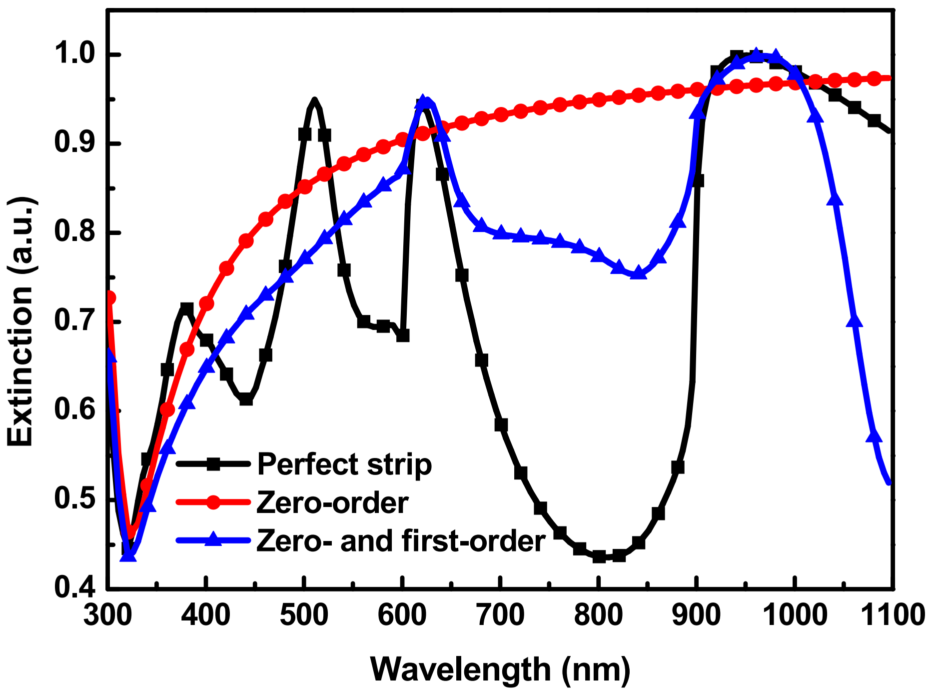


Figure S6. Simulated extinction spectra of perfect grating. The black square curve is calculated by including all order components of Floquet spectrum of silver refractive indices. The red dot curve is the spectra of zero-order component, and the blue triangle curve is the zero- and first-order component combined spectrum respectively.