1. The theoretical model

As depicted in Fig. S1, the whole space is divided into three regions separated by the planes at $y = 0$ and $y = h$.

Fig. S1 Sketch of the metallic slit array in a coordinate system. The slit array sits on the $y = 0$ plane. The $x = 0$ plane is at the center of a slit. The slit height, the slit width and the period are denoted as $h$, $a$ and $d$, respectively. The space is divided into three regions. Region I: above the $y = h$ plane; Region II: between the $y = h$ plane and the $y = 0$ plane; Region III: below the $y = 0$ plane.

Considering a TM plane wave incident on the slit array at a certain angle $\theta$, the light field (represented by the transverse magnetic field $H_z$) in region I and III are expressed by Rayleigh's expansion as following,
\[ H_1^I = \sum_{m=-\infty}^{\infty} \left\{ r_m \exp \left( i\chi_m^I (y-h) \right) + \delta_{m,0} \exp \left[ -i\chi_{0,y} \right] \right\} \exp \left( i\tilde{\alpha}_0 x \right) \exp \left( i\alpha_m x \right), \] (s1)

\[ H_{\tilde{z}}^\text{III} = \sum_{m=-\infty}^{\infty} t_m \exp \left( -i\chi_m^{\text{III}} y \right) \exp \left( i\tilde{\alpha}_0 x \right) \exp \left( i\alpha_m x \right), \] (s2)

where \( r_m \) and \( t_m \) are the \( m \)th order reflection and transmission coefficients, respectively. \( \delta_{m,0} \) equals to 1 at \( m = 0 \) and equals to 0 for other cases. \( \tilde{\alpha}_0 = k_0 \sin \theta \) denotes the \( x \) component of the wave vector; and \( \alpha_m = 2m\pi/d \) represents the \( m \)th order extra momentum given by the grating.

Correspondingly, \( \chi_m^I = \sqrt{k_0^2 - (\tilde{\alpha}_0 + \alpha_m)^2} \) and \( \chi_m^{\text{III}} = \sqrt{\varepsilon_d k_0^2 - (\tilde{\alpha}_0 + \alpha_m)^2} \) represent the \( y \)-directional momentum of the photons in region I and III, respectively. \( \varepsilon_d \) is the dielectric constant of the substrate. The light field in region I is considered as a superposition of incident and reflection light. The light field in region III represents the transmission. Two approximations are adopted to simplify the model. First, the metal is assumed to be perfectly conducting. Second, only the fundamental waveguide mode inside the slit is taken into account, which is acceptable when the light wavelength is much larger than the slit width. Then, the light field in region II writes

\[ H_{\tilde{z}}^\text{II} = \left( a^+ \exp \left( i\beta y \right) + a^- \exp \left( -i\beta y \right) \right) \exp \left( i\tilde{\alpha}_0 x \right). \] (s3)

The light field inside each slit is regarded as a superposition of two fundamental slit waveguide modes, i.e. \( a^+ \exp \left( i\beta y \right) \) and \( a^- \exp \left( -i\beta y \right) \), propagating in the positive and the negative \( y \) direction, respectively. Due to the perfect conductor approximation, the light field inside the metal is zero. \( \beta \) is the propagation constant of the fundamental slit waveguide mode. It is equal to \( k_0 \) when slits are empty, while changes into \( \sqrt{\varepsilon_d} k_0 \) when slits are filled by a material with a
dielectric constant of $\varepsilon_s$. By using the boundary conditions at the two interfaces of the three regions, the coefficients $a^+$, $a^-$, $r_m$ and $t_m$ are determined

$$ r_a = a^+ = \frac{\sum_{m=-\infty}^{\infty} a d \frac{\alpha_m a }{2} \frac{\varepsilon_d}{\varepsilon_s} \frac{1}{\chi_m} (i \beta) + 1}{\sum_{m=-\infty}^{\infty} a d \frac{\alpha_m a }{2} \frac{\varepsilon_d}{\varepsilon_s} \frac{1}{\chi_m} (i \beta) - 1} ,$$

$$ a^- = \frac{2 \exp(-i\chi'_m h)}{\exp(-i\beta h) \left( \sum_{m=-\infty}^{\infty} a d \frac{\alpha_m a }{2} \frac{\beta}{\varepsilon_s \chi_m} + 1 \right) - r_a \exp(i\beta h) \left( \sum_{m=-\infty}^{\infty} a d \frac{\alpha_m a }{2} \frac{\beta}{\varepsilon_s \chi_m} - 1 \right) } ,$$

$$ r_m = \frac{a d \frac{\alpha_m a }{2} \frac{\beta}{\varepsilon_s \chi_m} [a^+ \exp(i\beta h) - a^- \exp(-i\beta h)] + \delta_{m,0} \exp(-i\chi'_m h) ,$$

$$ t_m = \frac{a d \frac{\alpha_m a }{2} \frac{\varepsilon_d}{\varepsilon_s} \frac{1}{\chi_m} (i \beta) (a^+ - a^-) .$$

2. The zeroth order transmittance

Since the grating periods (from 200 nm to 500 nm) we studied are smaller than most part of the wavelength range (from 380 nm to 880 nm), the experimentally measured transmittance is mainly based on the zeroth order. Other higher order diffractions are either evanescent or out of the numerical aperture (0.75) of the microscope objective lens. The zeroth order transmitted light is expressed by

$$ H_c = t_0 \exp(-i\chi'_0 y) \exp(i\tilde{\alpha}_c x) ,$$

$$ E_x = \frac{-i\chi'_0}{(-i\omega)\varepsilon_s \varepsilon_d} t_0 \exp(-i\chi'_0 y) \exp(i\tilde{\alpha}_c x) ,$$

3
\[ E_y = \frac{-i\tilde{a}_0}{(-i\omega)\varepsilon_0\varepsilon_d} t_0 \exp(-iZ_0^\text{III} y)\exp(i\tilde{a}_0 x). \]  

(s10)

Thus, the time-averaged Poynting vector of the zeroth order transmitted light is derived as

\[ \langle S_i \rangle = \frac{1}{2} \left( \hat{e}_x |t_0|^2 \frac{-\tilde{a}_0}{\omega\varepsilon_0\varepsilon_d} + \hat{e}_y \left[ \sqrt{\varepsilon_d k_0^2 - \tilde{a}_0^2} \right] |t_0|^2 \right). \]  

(s11)

On the other hand, the time-averaged Poynting vector of the incident wave is

\[ \langle S_i \rangle = \frac{1}{2} \left( \hat{e}_x \frac{k_0 \sin \theta}{\omega\varepsilon_0} + \hat{e}_y (-1) \frac{k_0 \cos \theta}{\omega\varepsilon_0} \right). \]  

(s12)

The transmittance is the ratio of the incident power flowing into a unit area of the boundary to the transmitted power leaving a unit area of the boundary [1]. In this sense, the zeroth order transmittance works out as

\[ T_0 = |t_0|^2 \frac{\sqrt{\varepsilon_d k_0^2 - \tilde{a}_0^2}/\varepsilon_d}{\sqrt{k_0^2 - \tilde{a}_0^2}}. \]  

(s13)

Several figures in the manuscript, including the period-dependent spectra (Fig. 2 (a) and Fig. 6 (a)) and the angle-dependent spectra (Fig. 3 (c) and (d)) are based on Eq. (s13). At normal incidence and with empty slits, Eq. (s13) turns into Eq. 1 in the manuscript. In order to compare with experiments, the structural parameters are evaluated according to real measurements. For Fig. 2 (a), Fig. 3 (c) and (d), the slit width \( a \) is set to be 110nm, the slit height \( h \) to be 170nm, the dielectric constant of the slit \( \varepsilon_s \) to be 1 (empty slit) and the dielectric constant of the substrate \( \varepsilon_d \) to be 2.10 (fused silica).
3. Slit power enhancement factor

With the $\mathbf{H}$ field inside each slit being expressed as Eq. (s3), the $\mathbf{E}$ field which only has the $x$ component writes

$$E_x = \frac{(i\beta)}{(-i\omega)\varepsilon_o\varepsilon_s} \left[ a^+ \exp(i\beta y) - a^- \exp(-i\beta y) \right].$$  \hspace{1cm} \text{(s14)}

Then, the power flow works out

$$\langle S_{\text{slit}} \rangle = \hat{e}_y (-1) \frac{1}{2 \omega \varepsilon_o \varepsilon_s} \left( |a^-|^2 - |a^+|^2 \right).$$  \hspace{1cm} \text{(s15)}

At normal incidence, the incoming wave has a Poynting vector as

$$\langle S \rangle = \hat{e}_y (-1) \frac{1}{2 \omega \varepsilon_o}.$$  \hspace{1cm} \text{(s16)}

Thus, the slit power enhancement factor, which is defined as $\langle S_{\text{slit}} \rangle / \langle S \rangle$ writes

$$\frac{\langle S_{\text{slit}} \rangle}{\langle S \rangle} = \frac{\beta / \varepsilon_s}{k_0} \left( |a^-|^2 - |a^+|^2 \right).$$  \hspace{1cm} \text{(s17)}

This quantity is plotted in Fig. 4 (a) and (b) to reveal the intrinsic slit resonance. In this case, $\varepsilon_s$ is chosen to be 1 to mimic the slits filled with air in reality so that Eq. (s17) turns into Eq. 2 in the manuscript.

4. Analogy to a dielectric slab

The analogy was conducted by comparing the reflection coefficient or the transmission coefficient of the slit array with that of a dielectric slab. The reflected $\mathbf{H}$ field is expressed as
\[ H_r = r_0 \exp[i\chi_0^l(y-h)] \exp(i\alpha_0x), \]  
\text{(s18)}

where \( r_0 \) is derived as
\[ r_0 = \frac{a}{d} \frac{\beta}{\varepsilon_x \chi_0} \left[ a^+ \exp(i\beta h) - a^- \exp(-i\beta h) \right] + \exp(-i\chi_0^l h). \]  
\text{(s19)}

Here only the zeroth order diffraction is taken into account since it is the only propagating wave from a sub-wavelength structure. Substituting \( a^+ \) and \( a^- \) with Eq. (s4) and Eq. (s5), we obtain
\[ r_0 = \exp(-i\chi_0^l h) \left[ \frac{a}{d} \frac{\beta}{\varepsilon_x \chi_0} \frac{-2n_{\text{eff}}(1-n_{\text{eff}})\exp(i\chi_0^l h) + 2n_{\text{eff}}(1+n_{\text{eff}})\exp(-i\chi_0^l h)}{(1-n_{\text{eff}})^2\exp(i\chi_0^l h) - (1+n_{\text{eff}})^2\exp(-i\chi_0^l h)} + 1 \right], \]  
\text{(s20)}

where \( n_{\text{eff}} \) is defined as
\[ \sum_{m=-\infty}^{\infty} \frac{a}{d} \frac{\beta}{\varepsilon_x \chi_m} \frac{1}{\sin(\beta m \alpha / 2)} \]  
At wavelengths much longer than the period, the higher orders in the sum only introduce a small imaginary correction, and then \( \frac{a}{d} \frac{\beta}{\varepsilon_x \chi_0^l} \approx \frac{1}{n_{\text{eff}}}. \)

Thus, \( r_0 \) rewrites
\[ r_0 = \exp(-i\chi_0^l h) \left\{ \frac{(n_{\text{eff}}^2 - 1)\sin(\chi_0^l h)}{(1 + n_{\text{eff}}^2)\sin(\chi_0^l h) + 2in_{\text{eff}}\cos(\chi_0^l h)} \right\}. \]  
\text{(s21)}

With the incident field \( H_i = \exp(-i\chi_0^l y) \exp(i\alpha_0x) \), the reflection coefficient in terms of the ratio between \( H_r \) and \( H_i \) at \( y = h \) works out as
\[ r = \frac{(n_{\text{eff}}^2 - 1)\sin(\chi_0^l h)}{(1 + n_{\text{eff}}^2)\sin(\chi_0^l h) + 2in_{\text{eff}}\cos(\chi_0^l h)}. \]  
\text{(s22)}
Comparing it with the reflection coefficient of a normal dielectric slab

\[
 r = \frac{(n_{\text{slab}}^2 - 1) \sin(n_{\text{slab}}\chi_0' h_{\text{slab}})}{(1 + n_{\text{slab}}^2) \sin(n_{\text{slab}}\chi_0' h_{\text{slab}}) + 2in_{\text{slab}} \cos(n_{\text{slab}}\chi_0' h_{\text{slab}})}, \tag{s23}
\]

it is found that the slit array can be regarded as a dielectric slab with refractive index of \( n_{\text{eff}} \) and thickness of \( h/n_{\text{eff}} \). Eq. (s23) is the reflection coefficient of an etalon. A consistent result can be worked out by comparing the transmission coefficients.

5. Reflection at an effective medium of slit array

Assuming the slit array is infinitely long in \( y \) direction and fills half space, the light field is then expressed by

\[
 H_{\text{z}}^I = \sum_{m=-\infty}^{+\infty} \left\{ r_m \exp[i\chi_m'(y - h)] + \delta_{m,0} \exp[-i\chi_0'y] \right\} \exp(i\tilde{\alpha}_0 x) \exp(i\alpha_m x), \tag{s24}
\]

\[
 H_{\text{z}}^H = a^- \exp(-i\beta y) \exp(i\tilde{\alpha}_0 x). \tag{s25}
\]

Now there are only two regions. Region I denotes the free space above \( y = h \) and Region II denotes the slit array. Since there is no exiting end of the slit array, when light flows into the slits, it only propagates in negative \( y \) direction as expressed by Eq. (s25). By using the boundary conditions, the light field can be worked out. Based on that, the reflection coefficient at the interface writes

\[
r = 1 - \frac{2a}{d} \frac{\beta}{\varepsilon_{\chi_0'}} \frac{1}{1 + \sum_{m=-\infty}^{+\infty} \frac{a}{d} \sin\left(\frac{\alpha_m a}{2}\right) \frac{\beta}{\varepsilon_{\chi_m'}}}. \tag{s26}
\]
The R0_acc plotted in Fig. 5 (d) is based Eq. (s26).

By using the definition

\[ n_{\text{eff}} = \sum_{m=-\infty}^{\infty} \frac{a}{d} \frac{\beta}{\varepsilon_s \chi_m} \left( \frac{a}{2} \right) \sin \left( \frac{\alpha_m}{2} \right) \]

and the approximation

\[ \frac{a}{d} \frac{\beta}{\varepsilon_s \chi_0} \approx 1 \]

the reflection coefficient rewrites

\[ r = \frac{n_{\text{eff}} - 1}{n_{\text{eff}} + 1}. \]  

Eq. (s26) is the accurate reflection coefficient derived from the theoretical model and Eq. (s27) is the reflection coefficient based on the effective index. Both of them are plotted in Figure 5 (d) in the manuscript for comparison. They are almost identical in the sub-wavelength range, which ensures the validity to use an effective index to describe the impedance mismatch.

6. Comparison between the theoretical model and the real case

Our theoretical model is based on an assumption that the metal slit array is made of a perfect conductor. The validity of this approximation in describing the transition from a spectrum filter to a polarizer in a real metal slit array was discussed in the main text. Here, a few more evidences are presented. Fig. S2 shows the zeroth order transmittance and reflectance predicted by the theoretical model together with the measured data and the RCWA simulation of an Al slit array. In principle, the theoretical model shows the similar features, i.e. the grating resonances (represented by the sharp dips in transmittance or peaks in reflectance) and the slit resonance (represented by the broad peak in transmittance or dip in reflectance), as the measurement and the RCWA simulation. Concerning the discrepancies, the lower intensity of the slit resonance in the Al slit array than the theoretical prediction is due to the loss of Al as a real metal. The red-
shift of both the slit resonance and the grating resonances in the Al slit array with respect to the theoretical model is due to the surface plasmon polariton (SPP) excited at the grating surface and at the side walls of each slit in a real metal case.

The SPP occurs either at the grating surface or at the side walls in each slit, as illustrated by Fig. S3 (a) and (b). The former is similar to the SPP wave on a continuous metal film. The later forms an metal-insulator-metal (MIM) SPP waveguide mode. At a grating resonance, a surface wave is excited by phase matching. It could be a pure diffracted light along the surface in the case of a perfect metal or an SPP wave in the case of a real metal. In either these two cases, the
propagation constant \((\beta_1)\) of the surface wave excited by a normal incident light is required to be an integer multiple of \(2\pi/d\), where \(d\) is the grating period. \(\beta_1 = 2\pi/d\) represents to the first order grating resonance. The diffracted light along the surface is a plane wave as illustrated in Fig. S3 (a) so that the dispersion follows the light in free space (blue curve in Fig. S3 (c)) and the resonant frequency works out to be \(2\pi c/d\), where \(c\) is light speed. On the other hand, the SPP wave has a dispersion of \(\beta_1 = k_0\sqrt{\varepsilon_m\varepsilon_i}/(\varepsilon_m + \varepsilon_i)\) (e.g. red curve for Al or green curve for Ag in Fig. S3 (c)), where \(\varepsilon_m\) is permittivity of the metal and \(\varepsilon_i\) is that of the dielectric. Thus, the resonant frequency works out to be \(2\pi c\sqrt{\varepsilon_m + \varepsilon_i}/d\sqrt{\varepsilon_m\varepsilon_i}\), which is lower than \(2\pi c/d\). As illustrated in Fig. S3 (c), the propagation constant of the surface wave excited by the first order grating resonance in a 400nm-period slit array is marked by a dashed line. The intersections of the dashed line and the dispersion curves show that the SPP wave is excited at a lower frequency than the light diffracted along the surface. This accounts for the red-shift of the grating resonances in the real measurement with respect to the theoretical model. Since the plasma frequency of Al (22.43×10^{15} Hz ~ 84nm) is pretty high so that the dispersion of Al SPP almost follows the free light in the visible-near IR range and thus the red-shift of the grating resonances is not prominent. For a further confirmation of the SPP effect, Ag is taken into account as a third counterpart. Due to its smaller plasma frequency (13.70×10^{15} Hz ~ 138nm), the dispersion of Ag SPP (green curve in Fig. S3 (c)) deviates more from the light cone than that of Al SPP. Consequently, as shown in Fig. S3 (e), the red-shift of the grating resonances in a Ag slit array is more significant than that in an Al slit array.
Fig. S3 Comparison between a slit array made of a perfect metal and that made of a real metal. (a) Sketch of surface light diffraction in a perfect metal slit array and the SPP wave in a real metal one. (b) Sketch of the TEM waveguide mode in a perfect metal slit and the MIM SPP mode in a real metal slit. (c) Dispersion plots of light in free space (blue curve), SPP wave at the Al/air interface (red curve) and SPP wave at the Ag/air interface (green curve). (d) Dispersion plots of TEM waveguide mode (blue curve), Al/air/Al SPP mode (red curve) and Ag/air/Ag SPP mode (green curve) in a slit 110nm wide. (e) Transmittance of a slit array made from a perfect metal (theoretical prediction: blue curve), Al (measured data: black dots; RCWA simulation: red curve) and Ag (RCWA simulation: green curve). The period is 400nm, the slit width 110nm and the slit height 170nm.

Similarly, the waveguide mode in each slit could be a TEM waveguide mode in the case of a perfect metal or an MIM SPP waveguide mode in the case of a real metal. In either cases, the slit
resonance (i.e. the F-P resonance of the waveguide mode) requires the propagation constant $\beta_2$ approximately equal to $\pi/h$, where $h$ is the slit height. The TEM mode follows the light dispersion in free space while the MIM SPP mode with a symmetric $E_z$ field distribution follows the dispersion

\[
\tanh \left( \frac{a}{2} \sqrt{\beta^2 - \varepsilon_r (\omega/c)^2} \right) = -\frac{\varepsilon_i \sqrt{\beta^2 - \varepsilon_m (\omega/c)^2}}{\varepsilon_m \sqrt{\beta^2 - \varepsilon_r (\omega/c)^2}},
\]

where $a$ denotes the slit width. The dispersion plots in Fig. S3 (d) shows that at the same slit resonance the MIM SPP waveguide mode is excited at a lower resonant frequency than the TEM waveguide mode. This accounts for the red-shift of the slit resonance in the measured spectrum of an Al slit array with respect to the theoretical model (Fig. S3 (e)).

However, the discrepancies do not affect the analysis of the transition from a spectrum filter to a polarizer, which is based on the decoupling of the grating/slit coupled resonance and the diminishing of the slit resonance. As confirmed by the comparison between the period dependent transmission spectrum predicted by the theoretical model and that simulated by RCWA for an Al slit array (Fig. S4), the two spectra evolve with period similarly. Therefore, the usage of the theoretical mode to describe our experiment is reasonable, especially for Al slit array whose SPP dispersion is close to light in free space.
Fig. S4 2D plot of a period dependent zeroth order transmission spectra based on the theoretical model (a) and the RCWA simulation of an Al slit array (b).
References

[1] Born, M. & Wolf, E. *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light* (Cambridge University Press, 1999)