



# Chapter 7

## Perovskite-coated gratings

Despite their structural simplicity, 1D grating samples can sustain many electromagnetic modes, from diffractive interference effects to more localised and waveguided modes. In plasmonic gratings we can distinguish between such ‘photonic’ gratings modes and the ‘plasmonic’ modes that involve interactions with excited surface plasmon oscillations, as described in Sec. 3.2. The dispersion and efficiency of grating modes in optical spectra depend on the coupling with incoming/outgoing photons, and is very sensitive to factors such as the polarisation of light, changes in geometry and the refractive index of any coating materials.

In this Chapter the optical behaviour of perovskite-coated 1D gratings are explored, and CHPI-coated Ag gratings are used to understand the interactions between excitons and SPPs.

### 7.1 Experimental methods

The fabrication of dielectric-coated metal gratings is shown in Fig. 7.1(a). Gratings are fabricated in ethylene tetrafluoroethylene (ETFE) from nanopatterned silicon stamps using nanoimprinting. A sheet of ETFE (thickness 0.8 mm) is placed on a silicon stamp, heated to 200°C and placed under 30 Bar pressure for 300 s. The ETFE is cooled to 90°C while maintaining the same pressure, then released from the stamp. An optically opaque metal layer ( $\sim$ 120 nm thick Ti/Ag) is deposited onto the polymer to form metal gratings. Chemically synthesised CHPI powder [Sec. 2.3.2] is dissolved in tetrahydrofuran and spin coated onto the gratings in a dehydrated atmosphere to produce a conformal coating. For polystyrene (PS)-coated gratings,  $M_w = 500000$  PS powder is dissolved in toluene and spin coated onto the gratings. All samples are kept under a nitrogen atmosphere to prevent oxidation. Measurements by SEM and AFM of the metal and dielectric-coated gratings are used to

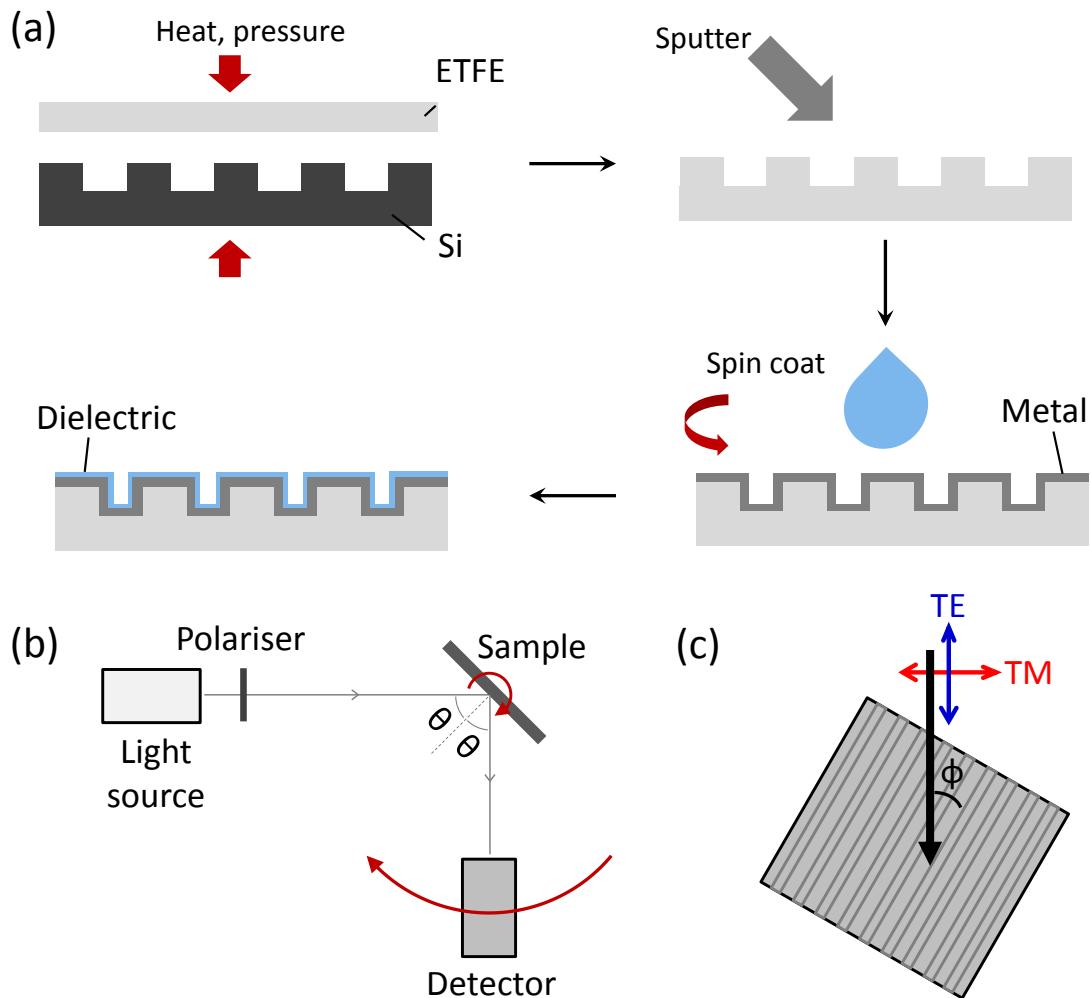


Fig. 7.1 (a) Fabrication of dielectric-coated metal grating. (b) Setup of angle-dependent reflectivity measurements. (c) Relationship between the polarisation of incoming light and azimuthal angle  $\phi$ .

extract the dimensions of the nanostructures. Polarised specular reflection measurements are made as a function of the incident polar ( $\theta$ ) and azimuthal ( $\phi$ ) angles using a polarised broadband white light source (215 – 2500 nm) [Figs. 7.1(b,c)]. The sample properties are uniform over  $\text{cm}^2$  areas, with small variations due to the depth and morphology of the coatings.

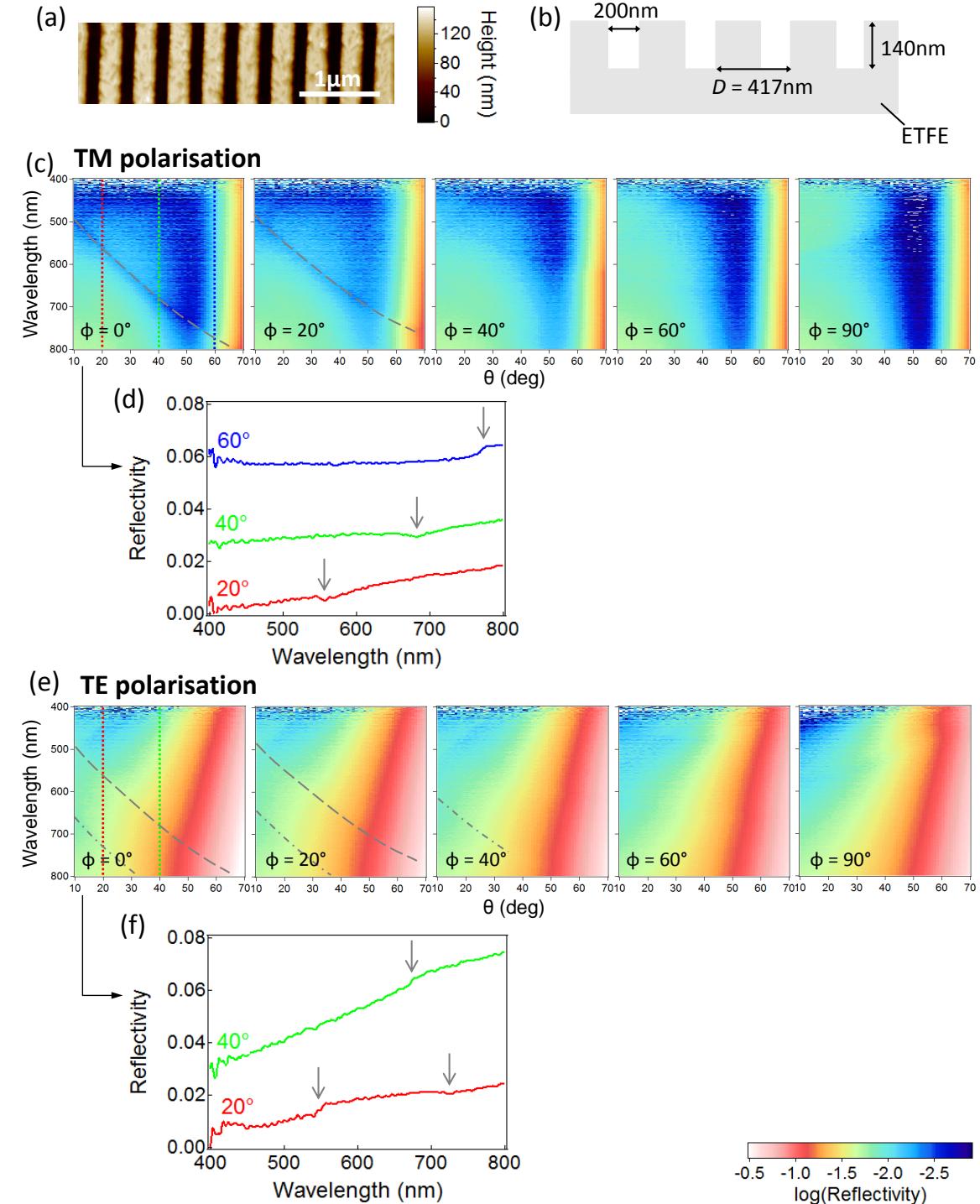


Fig. 7.2 (a) AFM image and (b) schematic structure of  $D = 417\text{ nm}$  ETHE grating. (c) TM polarised reflectivity scans of ETHE grating, and (d) reflectivity spectra for  $\phi = 0^\circ$ . Spectra are offset for clarity. (e,f) Same as above for TE polarisation. Photonic grating modes are indicated by grey lines/arrows on reflectivity scans/spectra.

## 7.2 Dielectric gratings

### 7.2.1 ETFE gratings

AFM scans of the imprinted  $D = 417$  nm ETFE grating [Fig. 7.2(a)] show the formation of a square-wave grating with depth 140 nm and slit width 200 nm [Fig. 7.2(b)]. TM and TE polarised reflectivity scans show  $m = -1$  photonic modes in air according to Eq. 3.11 [grey dashed lines on Figs. 7.2(c,e)] appearing as dips in the reflectivity [Figs. 7.2(d,f)]. In TE polarisation we also see the appearance of a redshifted photonic mode (grey dot-dashed line on Fig. 7.2(e)), attributed to light that has penetrated the transmissive ETFE. This mode fits well to Eq. 3.11 with  $n = 1.4$ , the reported ETFE refractive index<sup>200</sup>. For both polarisations the grating modes are no longer visible for  $\phi > 60^\circ$ . Note also a dip in the reflectivity of TM scans at  $\theta \approx 50^\circ$  due to the Brewster angle of ETFE.

### 7.2.2 CHPI-coated ETFE gratings

The exciton resonance at 505 nm dominates both the TM and TE reflectivity scans of CHPI-coated  $D = 417$  nm ETFE gratings [Figs. 7.3(a,c)]. The  $m = \pm 1, n = 1.4$  diffractive photonic grating modes are again visible [grey dot-dashed lines on Figs. 7.3(a,c)], and appear as Fano resonances in reflectivity [Figs. 7.3(b,d)]. In TM polarisation the diffractive modes are strongest for  $\phi = 90^\circ$ , while for TE they are strongest at  $\phi = 0^\circ$ , thus coupling with photons is strongest when the  $\vec{E}$  field is parallel to grating lines. Note there are no interactions between grating modes and excitons in this system. The Brewster angle in TM scans has now changed to  $\theta \approx 62^\circ$  due to the larger refractive index of CHPI.

## 7.3 Non-plasmonic metal gratings

### 7.3.1 Ti gratings

SEM image of a  $D = 417$  nm Ti grating shows the roughness of sputtered Ti film on ETFE [Fig. 7.4(a)], while AFM measurements reveal a trapezoidal grating profile as a result of the nanoimprinting process. Heating and cooling of ETFE during sputtering also appears to have changed the grating periodicity  $D$ , as the photonic grating modes in reflectivity scans [Figs. 7.4(c,e)] are best fit to  $D = 410$  nm [Eq. 3.11]. Aside from the change in geometry, the appearance of  $m = -1$  grating modes in optical spectra is very similar to what has been observed in ETFE gratings, with modes appearing as dips in reflectivity. However the

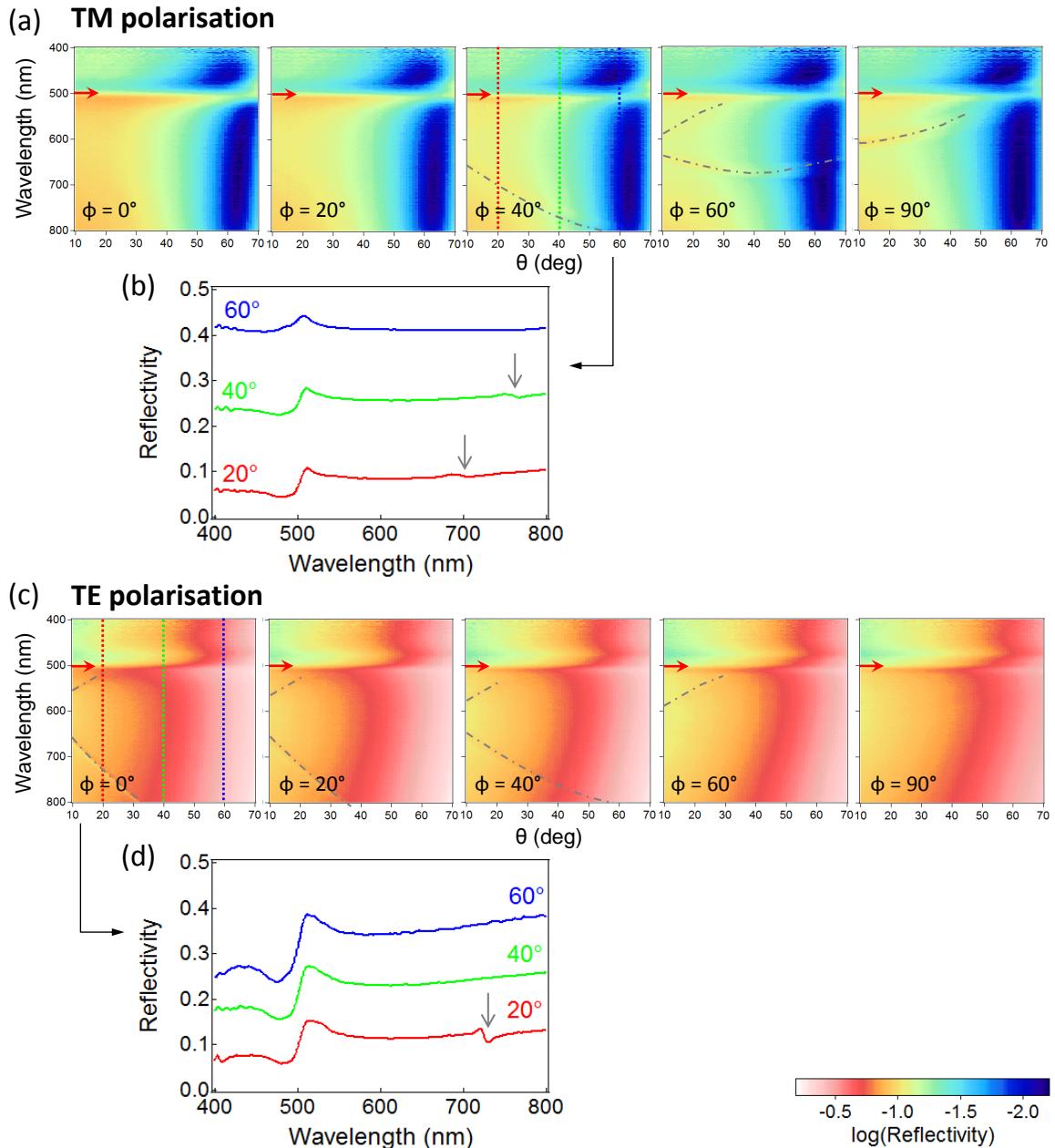


Fig. 7.3 (a) TM polarised reflectivity scans of  $D = 417$  nm CHPI-coated ETFE grating, and (b) reflectivity spectra for  $\phi = 40^\circ$ . Spectra are offset for clarity. (c) Same as (a) for TE polarisation and (d) reflectivity spectra for  $\phi = 0^\circ$ . Photonic grating modes are indicated by grey lines/arrows on reflectivity scans/spectra, and excitons by red arrows.

coupling to photons is much weaker in TE polarisation, as the  $\vec{E}$  field is parallel to grating lines [Sec. 3.2].

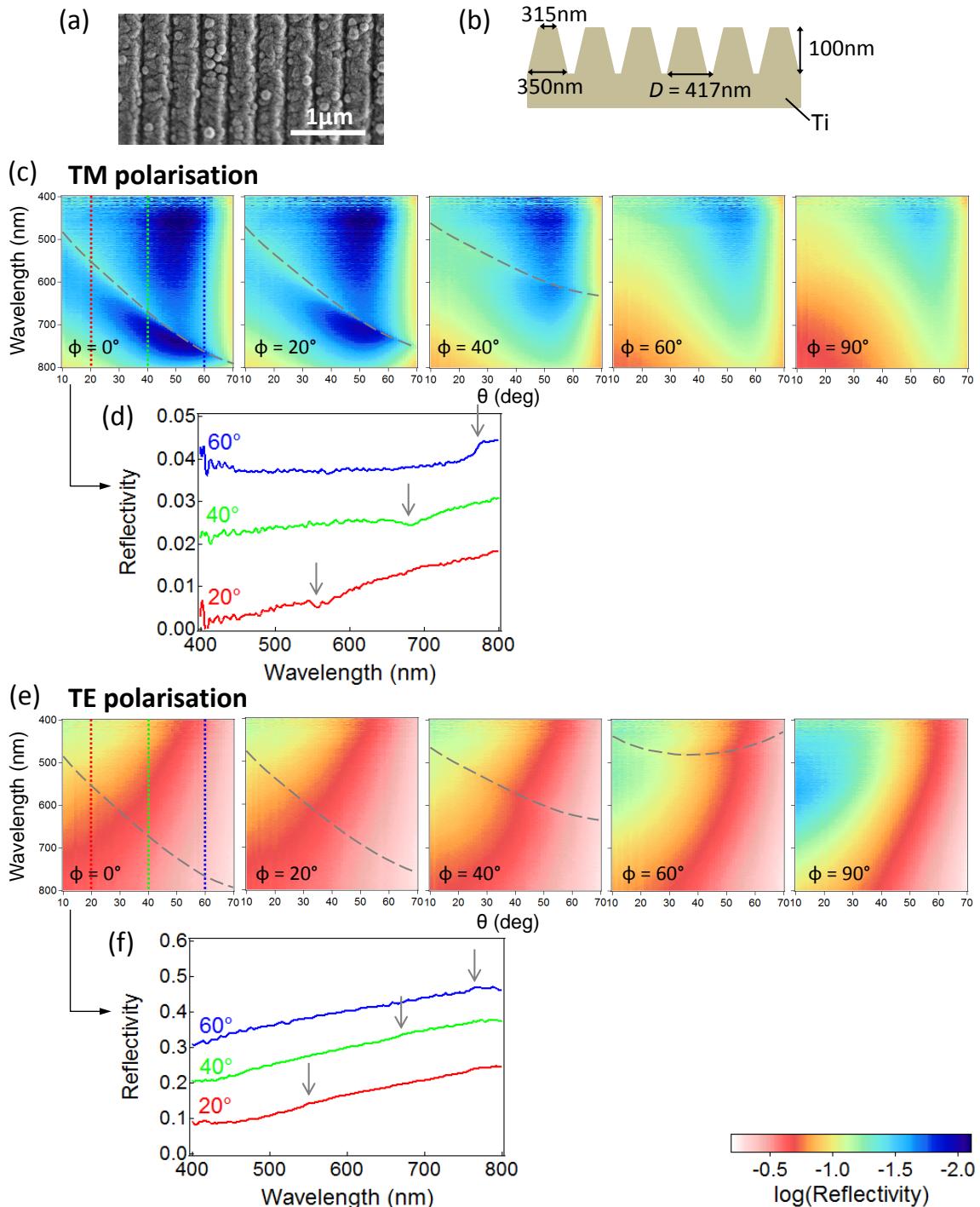


Fig. 7.4 (a) SEM image and (b) schematic structure of  $D = 417\text{ nm}$  Ti grating. (c) TM polarised reflectivity scans of Ti grating, and (d) reflectivity spectra for  $\phi = 0^\circ$ . Spectra are offset for clarity. (e,f) Same as above for TE polarisation. Photonic grating modes are indicated by grey lines/arrows on reflectivity scans/spectra.

### 7.3.2 CHPI-coated Ti gratings

Polarised reflectivity spectra of CHPI-coated planar Ti film [Fig. 7.5] show the appearance of an exciton resonance at 505 nm, indicating the excitons are unaffected by the metal film below. The experimental data fits well to transfer matrix simulations of 70 nm CHPI-coated 120 nm Ti film, and the differences observed can be attributed to non-uniformity and roughness in both the CHPI and Ti films.

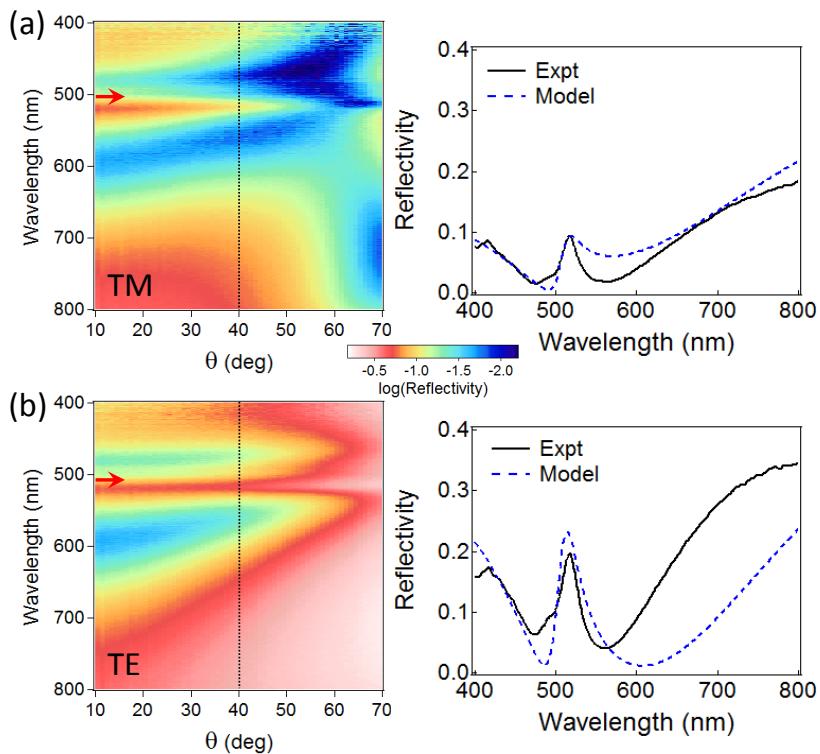


Fig. 7.5 Specular reflectivity scans of 70 nm CHPI film on 120 nm planar Ti film (left) with (a) TM and (b) TE polarised light. Excitons are marked by red arrows. Spectra at  $\theta = 40^\circ$  are plotted with those predicted by transfer matrix simulations (right).

AFM measurements show the metal grating is completely immersed in a non-uniform coating for  $D = 417$  nm CHPI-coated Ti grating [Figs. 7.6(a,b)]. As with CHPI-coated ETFE gratings, the exciton resonance at 505 nm dominates reflectivity spectra for both polarisations [Figs. 7.6(c,e)]. Although very weak dips can be seen to indicate diffractive  $m = -1$  grating modes in TM polarisation [Fig. 7.6(d)], coupling of TE-polarised light to grating modes is so weak that spectra appear almost identical to that of a CHPI-coated planar Ti film [Fig. 7.6(f)]. In both cases there are no interactions between CHPI excitons and modes of the Ti grating.

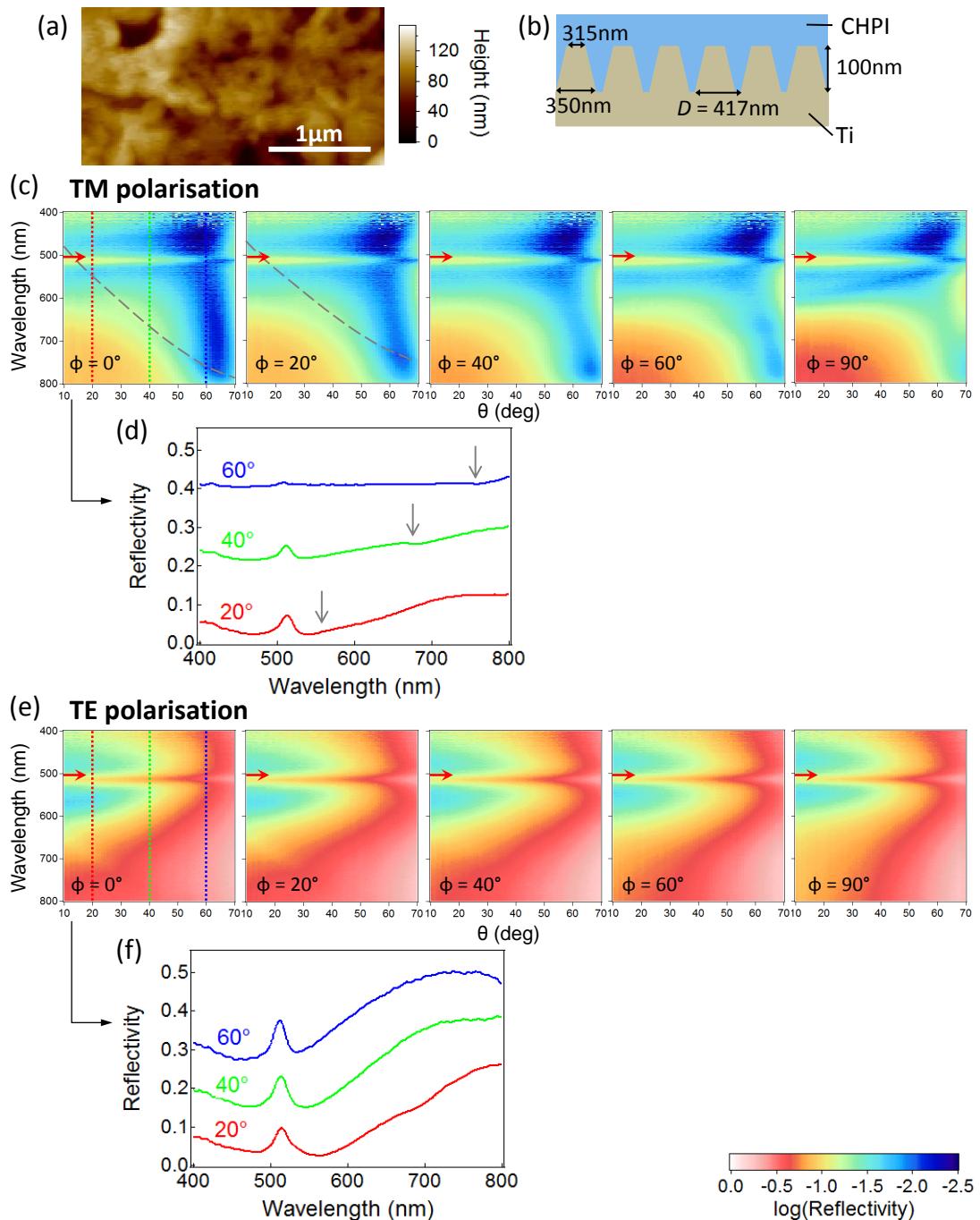


Fig. 7.6 (a) AFM image and (b) schematic structure of  $D = 417$  nm CHPI-coated Ti grating. (c) TM polarised reflectivity scans of  $D = 417$  nm CHPI-coated Ti grating, and (d) reflectivity spectra for  $\phi = 0^\circ$ . Spectra are offset for clarity. (e,f) Same as above for TE polarisation. Photonic grating modes are indicated by grey lines/arrows on reflectivity scans/spectra, and excitons by red arrows.

## 7.4 Plasmonic metal gratings

### 7.4.1 Ag gratings

Fig. 7.7 shows reflectivity scans for Ag gratings,  $D = 556, 417$  and  $278$  nm. The spectra for all three gratings show the same features: in TM polarisation a sharp threshold anomaly whose dispersion follows Eq. 3.11 for  $m = \pm 1$  (grey dashed lines), and a redshifted dip for the resonance anomaly indicating the presence of excited SPPs (black dashed lines). In TE polarisation we don't observe any anomaly features due to the inability to excite SPPs, instead we see the  $m = \pm 1$  photonic modes.

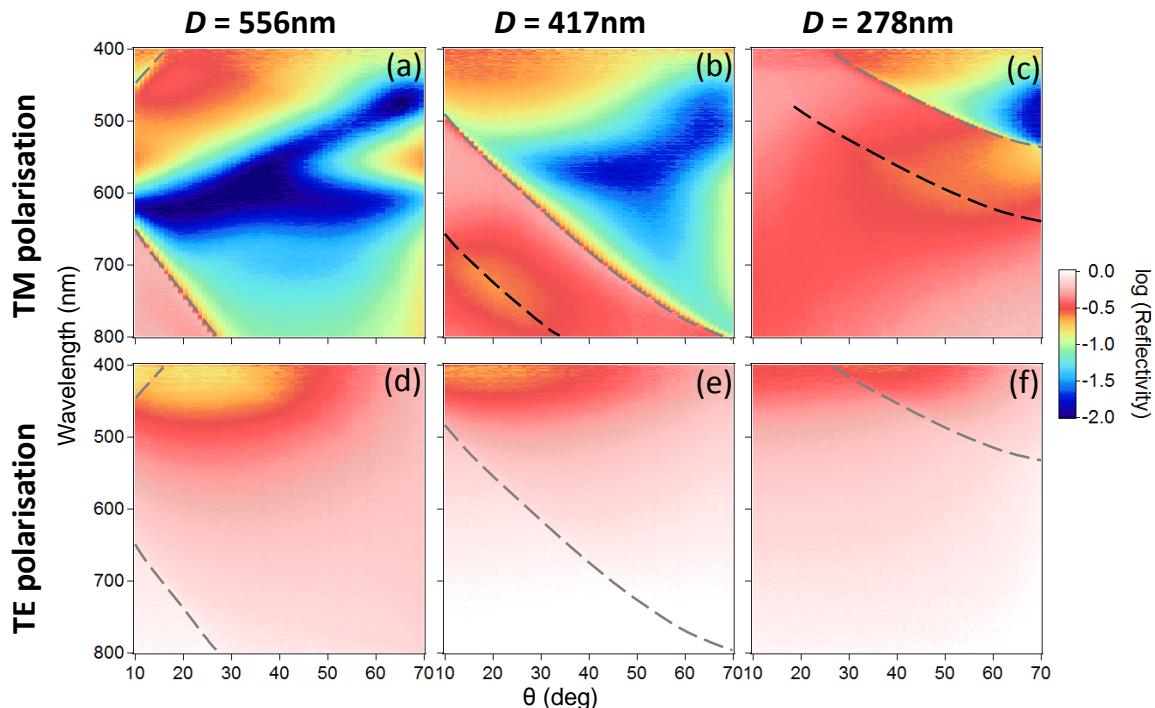


Fig. 7.7 Specular reflectivity scans of uncoated Ag gratings with periodicity  $D$  and polarisation of light as labelled. Photonic grating modes (threshold anomalies) are marked by grey dashed lines, and plasmonic grating modes (resonance anomalies) are marked by black dashed lines.

Concentrating on the  $D = 417$  nm grating, we see that the sputtered Ag film on ETFE shows some roughness [Fig. 7.8(a)], and AFM measurements indicate a square-wave grating with depth 140 nm and slit width 130 nm [Fig. 7.8(b)]. In reflectivity the threshold anomalies (grey dashed lines) shift as expected according to Eq. 3.11 in TM polarisation [Fig. 7.8(c)], and appear as sharp changes in the intensity [Fig. 7.8(d)]. The redshifted resonance anomalies (black dashed lines) become weaker with increasing  $\phi$  and is no longer observed when

$\phi > 60^\circ$  as it becomes harder for photons to couple to SPPs. For the same reason no anomalies are observed in TE polarisation at low  $\phi$ , where the photonic modes appear weakly in spectra [Fig. 7.8(f)]. We would expect to observe anomalies at  $\phi = 90^\circ$  in TE polarisation, however the energy of the mode is too high for our measurement range here. The broad dip seen at  $\phi = 60^\circ$  in both polarisations and  $\phi = 90^\circ$  in TE polarisation is assigned to the Fabry-Perot interference mode of light reflected from the top and bottom surfaces of the grating. This mode doesn't change in position with  $\phi$  and extrapolates to  $\sim 600$  nm at  $\theta = 0^\circ$ , which fits the height of the gratings as seen in AFM measurements.

We use the finite element method (FEM) to model the electromagnetic nearfield of grating modes in order to understand their behaviour. The modelled spectrum for  $\phi = 0^\circ \lambda = 600$  nm agrees very well with the features of the experimental data [Fig. 7.9(a)], but has a larger reflectivity overall as the model does not take into account the Ag film roughness. Low efficiency of the specularly reflected grating order gives rise to the low reflection region seen at high  $\theta$ , instead the coupling is strongest to the  $-1$  diffracted order as shown in Fig. 7.9(b). The modelled  $H_z$  field component for the resonance anomaly shows that it does indeed behave like SPP travelling on the surface of the metal [Fig. 7.9(c)].

The position of the threshold anomaly is fixed by the periodicity of the structure, however as the resonance anomaly is caused by the interference between diffracted light and SPPs we expect the position of this to be much more sensitive to the geometry of the grating. Fig. 7.10 shows the structures and TM reflectivity scans at  $\phi = 0^\circ$  of three different grating profiles, ranging from square-wave [Fig. 7.10(a)] to approximately sinusoidal [Fig. 7.10(b,c)]. The sharp threshold anomalies (grey dashed lines) remain in the same position for all three gratings, barring small changes in  $D$  as a result of the sputtering process. However the widths and positions of the resonance anomalies vary greatly with geometry, and the sharpest resonances are produced by sinusoidal gratings. We also observe a dispersionless mode at  $\sim 450$  nm in Figs. 7.10(b,c) that may be due to the presence of channel plasmons, which require a narrowing of the grating slit as seen in the sinusoidal gratings.

#### 7.4.2 PS-coated Ag gratings

From the AFM image of  $D = 417$  nm PS-coated grating [Fig. 7.11(a)] we see that the Ag grating is almost submerged beneath the non-uniform PS layer, resulting in a shallow sinusoidal grating with an average height of 5 nm [Fig. 7.11(b)]. The presence of the PS overcoating increases the complexity of the reflectivity spectra by allowing access to more modes. In both TM and TE polarisation, photonic (grey dashed lines) and redshifted

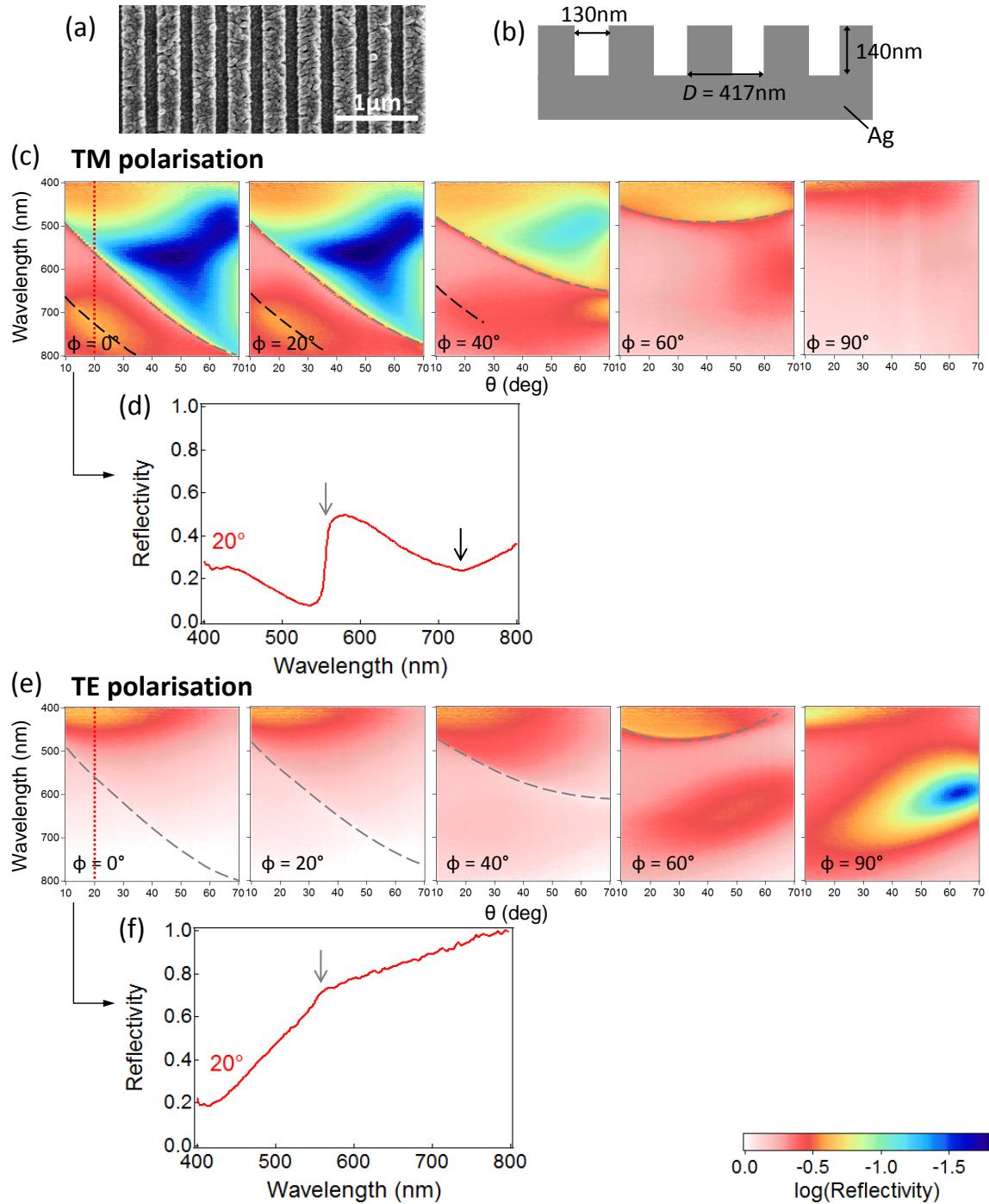


Fig. 7.8 (a) SEM image and (b) schematic structure of  $D = 417\text{ nm}$  Ag grating. (c) TM polarised reflectivity scans of  $D = 417\text{ nm}$  Ag grating, and (d) reflectivity spectra for  $\phi = 0^\circ$ . (e,f) Same as above for TE polarisation. Photonic grating modes (threshold anomalies) are indicated by grey lines/arrows on reflectivity scans/spectra, and plasmonic gratings modes (resonance anomalies) by black lines/arrows.

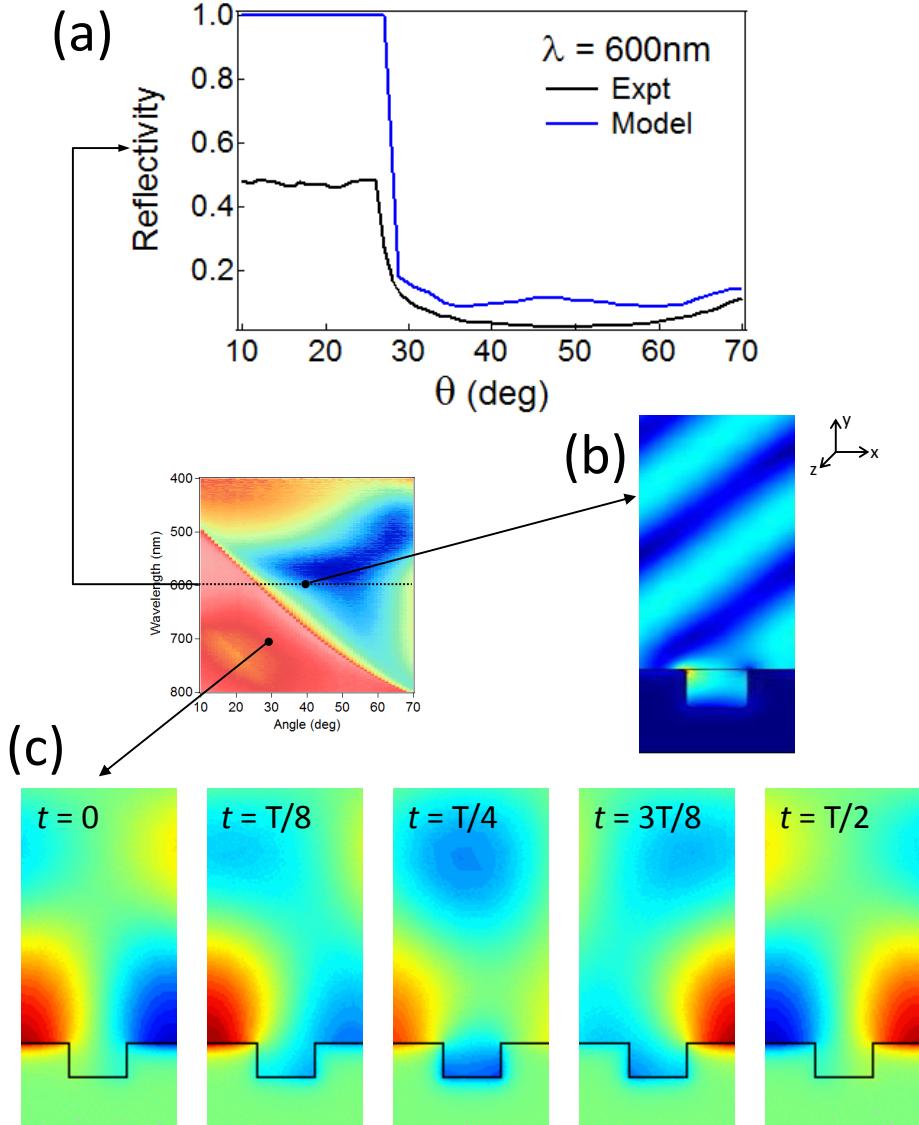


Fig. 7.9 (a) Experimental and modelled TM reflectivity spectra of  $D = 417$  nm Ag grating for  $\phi = 0^\circ$   $\lambda = 600$  nm. (b) Time averaged  $\vec{E}$  field intensity ( $\vec{E} \cdot \vec{E}$ ) profile for  $\lambda = 600$  nm  $\theta = 40^\circ$ . (c)  $H_z$  nearfield profile at time  $t$  of the optical cycle  $T$  for  $\lambda = 700$  nm  $\theta = 30^\circ$ .

plasmonic modes (black dashed lines) can be observed [Fig. 7.11(c,e)], however the photonic mode is much weaker in TE polarisation. At high  $\phi$  in TM polarisation, a second set of plasmonic modes can be seen (black dot-dashed lines), likely due to the differing PS thickness at the top and bottom surface of the grating. We also see a broader mode at  $\sim 560$  nm for  $\phi = 0^\circ$   $\theta = 10^\circ$  in both polarisations, which remains in roughly the same position for all  $\phi$  (purple dashed line).

Using FEM, we observe two types of modes at  $\phi = 90^\circ$  in TM polarisation. A mode

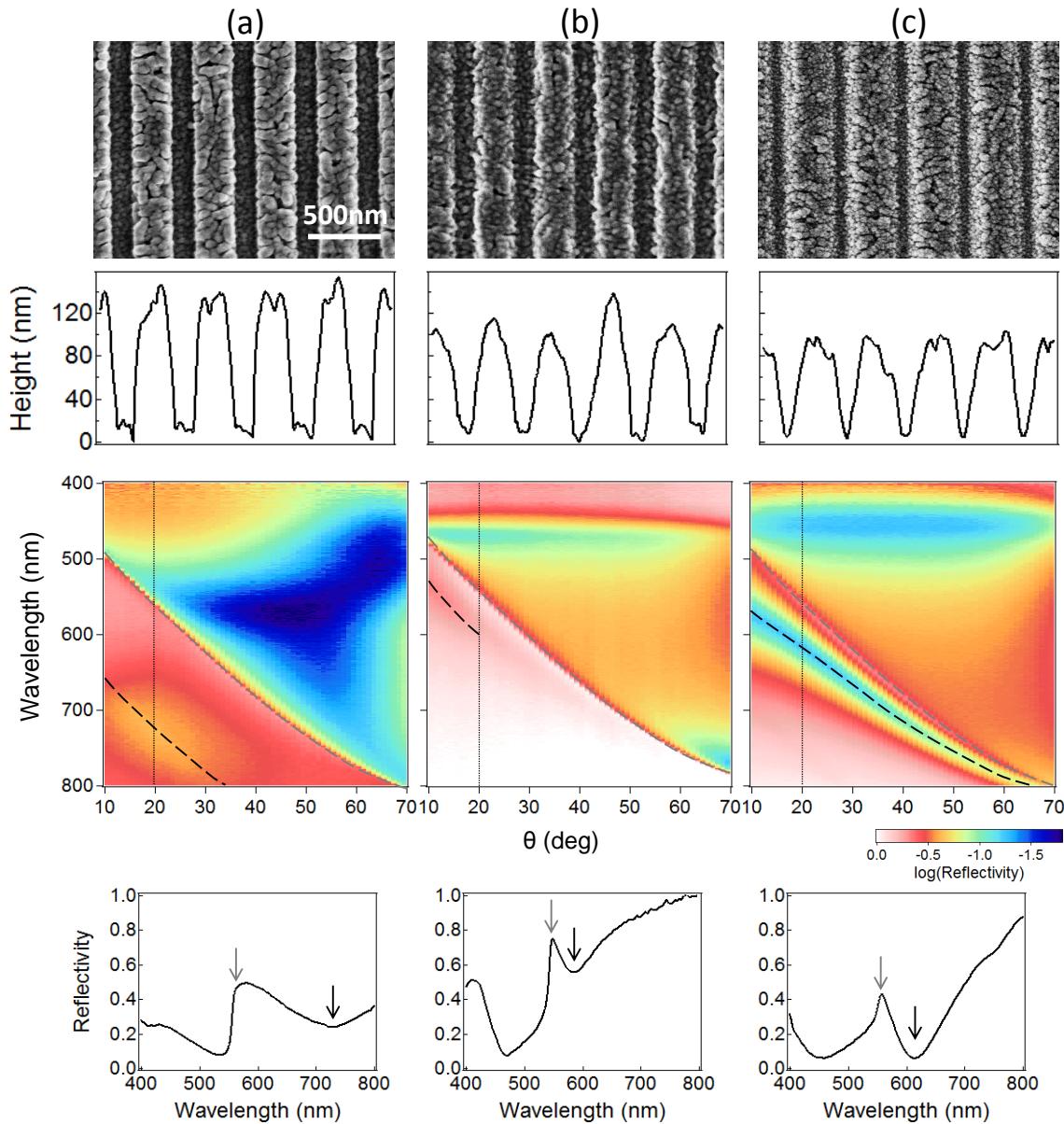


Fig. 7.10 (From top) SEM image, AFM profile, TM specular reflectivity scans at  $\phi = 0^\circ$ , and reflectivity spectra at  $\phi = 0^\circ \theta = 20^\circ$  for three  $D = 417$  nm Ag gratings. Photonic grating modes (threshold anomalies) are marked by grey dashed lines/arrows, and plasmonic grating modes (resonance anomalies) by black dashed lines/arrows on reflectivity scans/spectra.

at higher energy has field intensity concentrated at the top surface of the grating, and evanescently decays from the Ag surface [Fig. 7.12(a)]. Taking snapshots throughout the optical cycle, the mode appears to be a quasiparticle travelling along the top surface of the grating [Fig. 7.12(b)]. By varying the geometry of the grating, we find the mode decreases in energy as  $D$  increases, increases in energy with the slit width, and is unaffected by grating

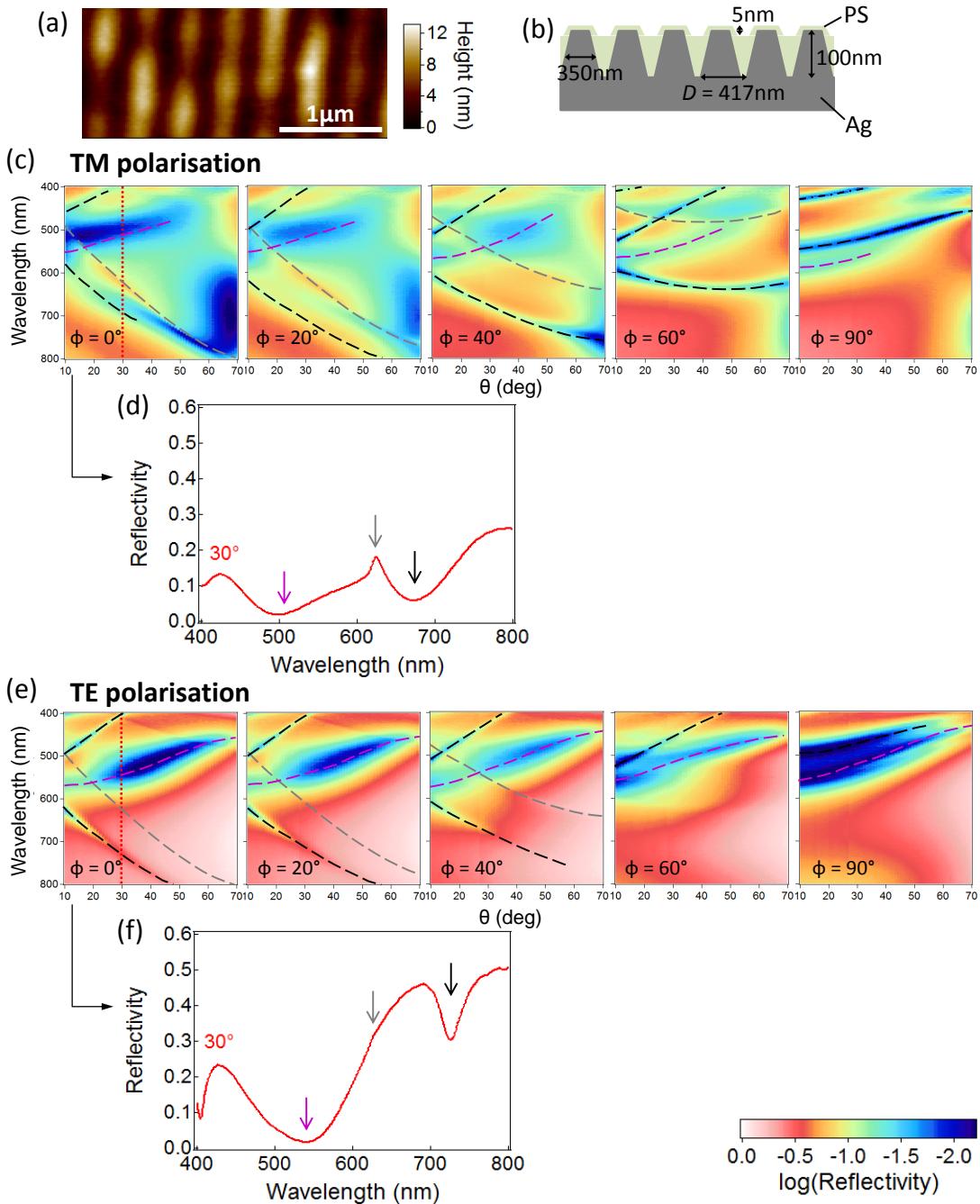


Fig. 7.11 (a) AFM image and (b) schematic structure of  $D = 417\text{ nm}$  PS-coated Ag grating. (c) TM polarised reflectivity scans of PS-coated Ag grating, and (d) reflectivity spectra for  $\phi = 40^\circ$ . (e) Same as above for TE polarisation, and (f) reflectivity spectra at indicated  $\theta$  value for  $\phi = 0^\circ$ . Photonic grating modes are indicated by grey lines/arrows on reflectivity scans/spectra, plasmonic gratings modes by black lines/arrows, and waveguide modes by purple lines/arrows.

height, thus showing the behaviour expected for an SPP mode. On the other hand, the field intensity of the lower energy mode is mainly concentrated in the slit of the grating [Fig. 7.12(c)], and appears to travel along the slit [Fig. 7.12(d)]. The energy of the mode is unaffected by  $D$  or the grating height, and decreases as the slit width increases, the behaviour of a mode waveguided by the grating slit. According to Eq. 3.13 the dispersion fits that of a  $\text{TE}_{10}$  mode.

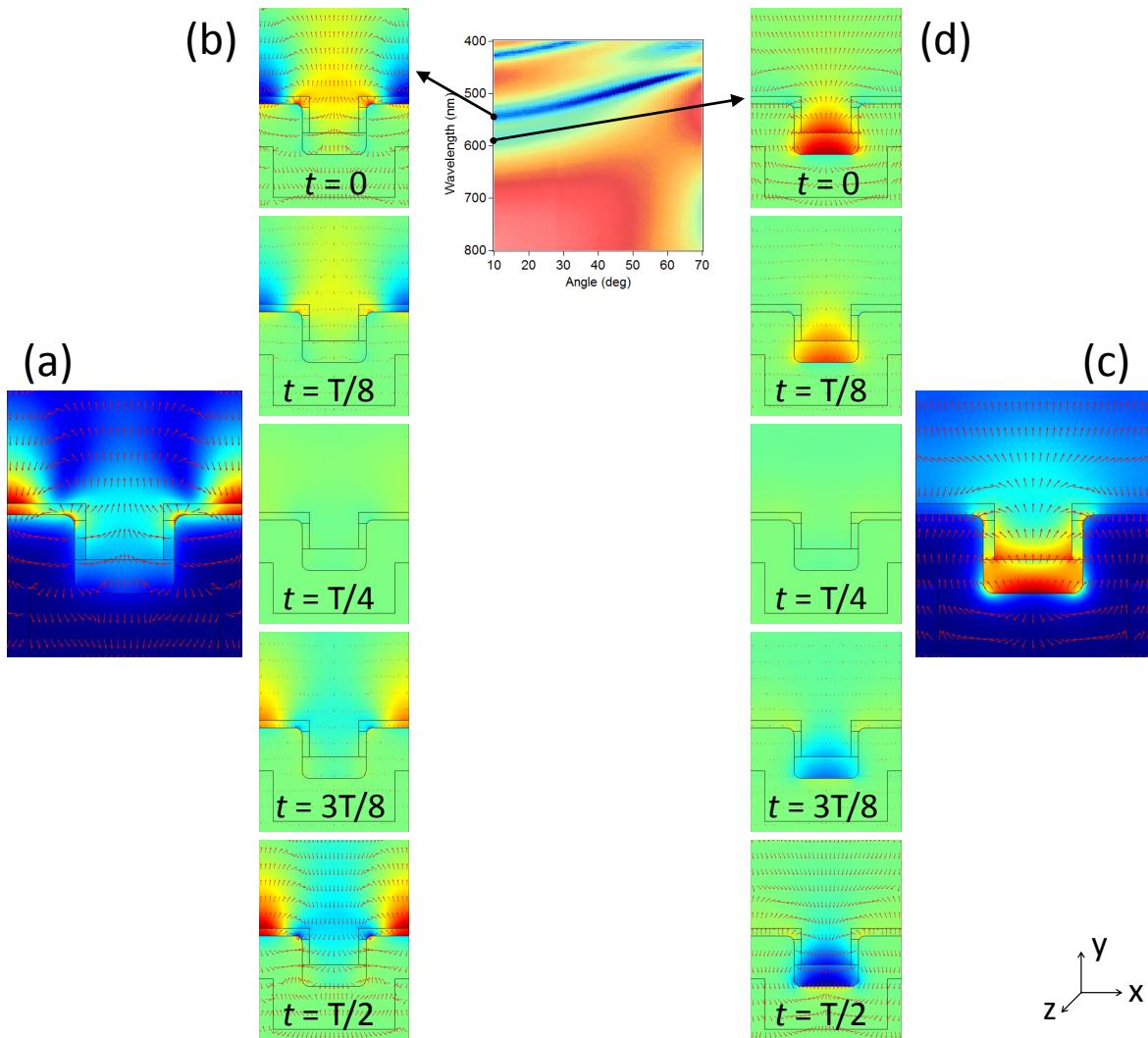


Fig. 7.12 (a) Time averaged and (b) snapshots at time  $t$  in the optical cycle  $T$  of the  $E_y$  nearfield intensity for the higher energy (plasmonic) mode at  $\phi = 90^\circ \theta = 10^\circ$ . (c,d) Same as above for the lower energy (waveguide) mode. Arrows represent the size and direction of the  $\vec{E}$  field vector.

Both SPP and waveguided modes are very sensitive to the dielectric environment as shown by Eqs. 3.11 and 3.13, and Fig. 7.13 shows the change in these modes with increasing PS

thickness. Both the narrower SPP resonances (black dashed lines) and broader waveguided modes (purple dashed lines) redshift with increasing PS coverage as expected. For the structure in Fig. 7.13(c) these two modes actually overlap, although no interactions occur.

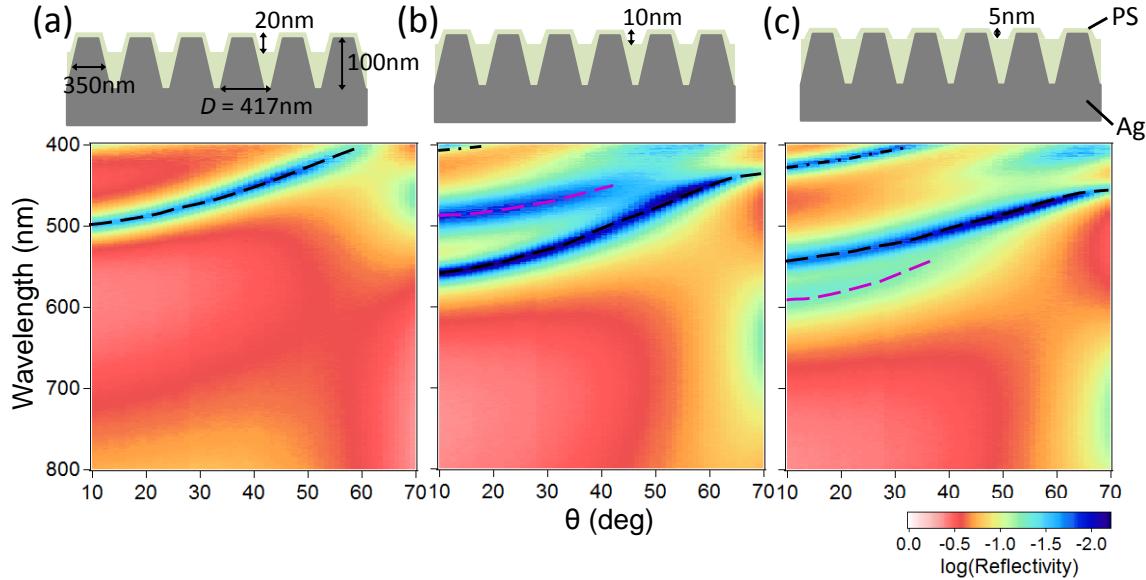


Fig. 7.13 Schematic structure of PS-coated  $D = 417$  nm Ag gratings (top), and TM polarised reflectivity scans at  $\phi = 90^\circ$  (bottom). PS thickness increases from (a) → (c). Plasmonic modes are indicated by black lines, and waveguide modes by purple lines.

### 7.4.3 CHPI-coated Ag gratings

Fig. 7.14 shows TM reflectivity scans for CHPI-coated Ag gratings,  $D = 556, 417$  and  $278$  nm at  $\phi = 0$  and  $90^\circ$ . The spectra for  $D = 556$  and  $417$  nm are very similar, showing two exciton modes (red arrows) that strongly couple to an SPP grating mode (black dashed line) as the oscillations become resonant at  $\phi = 90^\circ$ . Two excitons can also be observed for  $D = 278$  nm, however the SPP mode is at a higher energy and thus the coupling occurs at  $\phi = 0^\circ$ .

TM polarised reflectivity scans of  $D = 417$  nm CHPI-coated Ag grating at  $\phi = 0^\circ$  [Fig. 7.15(a)] show two dispersionless exciton modes at 480 and 500 nm (marked by arrows) far off resonance with grating modes. The persistent presence of a second exciton is only detected when SPPs can be excited, i. e. in TM polarisation [Fig. 7.15(a)] but not TE [Fig. 7.15(b)], nor in CHPI-coated planar Ag films [Fig. 7.15(c)]. It is also not observed for CHPI-coated non-plasmonic gratings [Figs. 7.3 and 7.6], thus from Fig. 7.15 we deduce that SPP excitation leads to the observation of an additional redshifted exciton with a splitting of 100 meV. Its appearance only when SPPs are present rules out any influence from modified

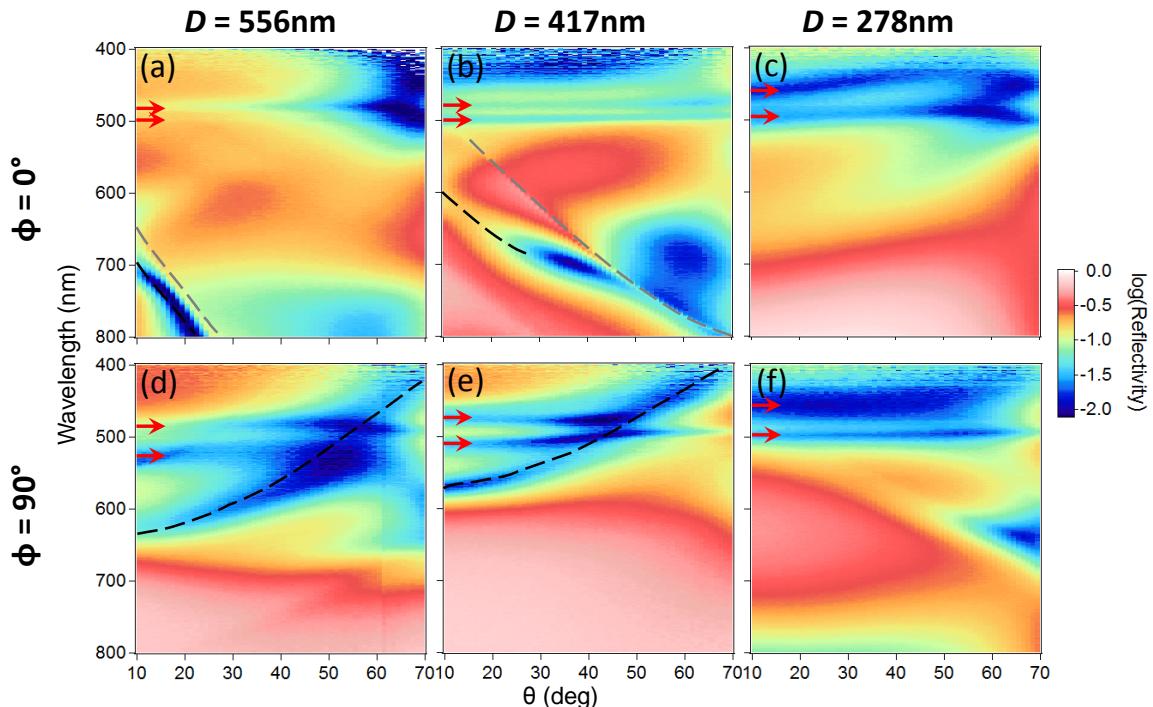


Fig. 7.14 TM specular reflectivity scans of CHPI-coated Ag gratings with  $D$  and  $\phi$  as labelled. Photonic grating modes are marked by grey dashed lines, plasmonic grating modes by black dashed lines, and excitons indicated by red arrows.

CHPI assembly in the grooves, which are in any case hundreds of times larger than the PbI layer spacing. In addition the exciton diffusion length in 2D perovskites is of order 10 nm<sup>92</sup>, therefore we do not expect any limiting effects due to the grating geometry. We note slight changes in the CHPI coverage alter the positions and intensities of dispersive grating modes [*cf* Fig. 7.17(c), with a thinner CHPI coating], however the exciton modes remain essentially unchanged.

It is well known that the emitted energy of a dipole (exciton) is lowered when placed in front of a metallic surface due to interactions between the dipole and the reflected electromagnetic field<sup>201–206</sup>. Using the method of images, we can replace the metal and describe instead the coupling between an exciton in the CHPI ( $\epsilon_1$ ) and its image exciton in the metal ( $\epsilon_2$ ), modified by their respective dielectric environments. Chance *et al.*<sup>204</sup> showed the redshift in the emitted energy of an exciton ( $\Delta E_{ex}$ ) oriented parallel to the interface can be approximated by

$$\Delta E_{ex} \sim \left( \frac{1}{k_1 l} \right)^3 \text{Re} \left\{ \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right\} \Gamma_0, \quad (7.1)$$

where  $l$  is the distance between the exciton and a metal surface,  $k_1$  is the wavenumber of

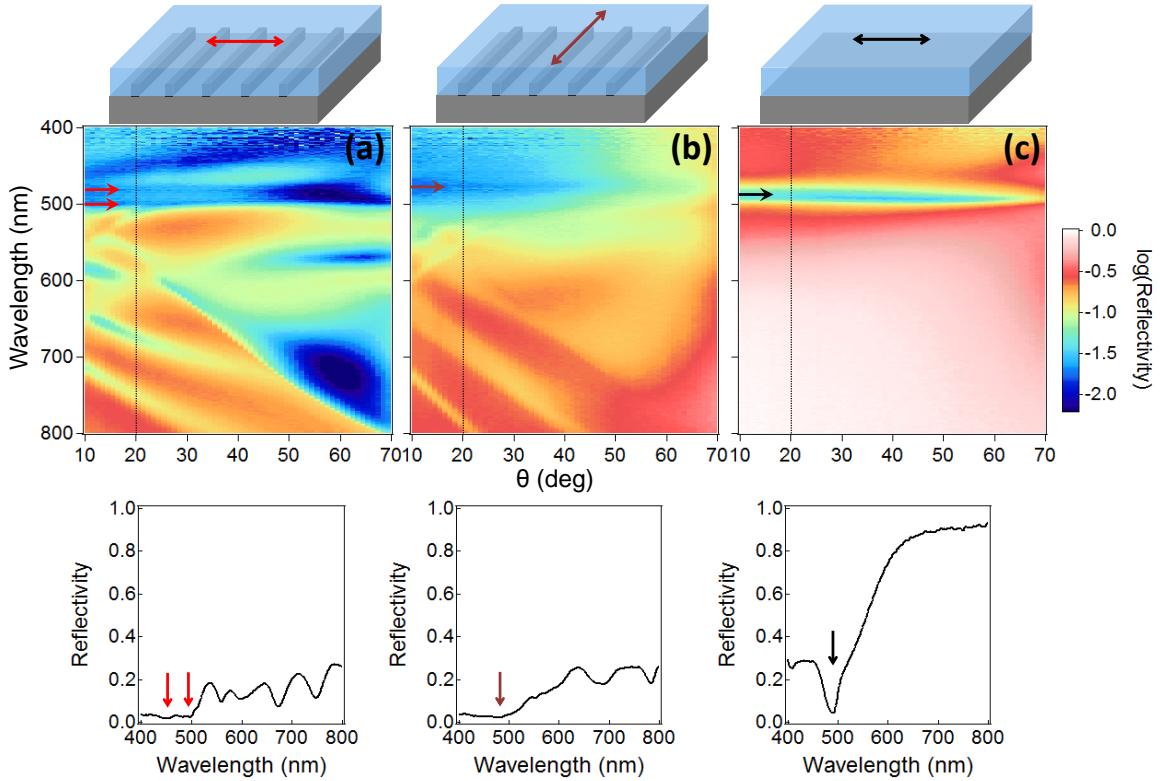


Fig. 7.15 Specular reflectivity scans at  $\phi = 0^\circ$ : CHPI-coated Ag grating with (a) TM and (b) TE polarised light, and (c) CHPI-coated 120 nm planar Ag film with TM polarised light. The electric field orientation is shown above each scan, the reflectivity spectra at  $\theta = 20^\circ$  below, and positions of exciton modes are indicated by arrows.

light in CHPI,  $q$  is the quantum yield of CHPI excitons (taken here to be 1), and  $\Gamma_0$  is the inverse exciton radiative lifetime without the metal. Similar to the appearance of excitons in the spectra, we expect to observe such coupled ‘image-biexcitons’ as minima in the reflectivity, at a wavelength that differs from the uncoupled exciton according to Eq. 7.1. The strength of coupling between the exciton and reflected electromagnetic field depends on the exciton dipole moment, which is controlled by the term  $q\Gamma_0$ . From this we can see the  $l^{-3}$  dependence of the redshift as shown in Fig. 7.16(a), where the experimentally observed  $\Delta E_{ex} \sim 100$  meV corresponds to  $l \sim 22$  nm, close to the experimentally-determined CHPI thickness. Clearly  $\Delta E_{ex}$  is also affected by the dielectric response of CHPI and Ag, and from Eq. 7.1 we see that  $\Delta E_{ex}$  is maximised if  $\epsilon_2 + \epsilon_1 \rightarrow 0$ , i. e. when emission is resonant with an SPP on the metal-dielectric interface. The linewidth of the exciton is also affected by interactions with image charges in the metal, however in our perovskite system this effect is not dominant due to tight planar confinement of excitons. We expect larger effects in systems that are less perfectly 2D, such as semiconductor heterostructures and J-aggregate systems,

where surface charges play a much larger role.

The role of the SPP in this case is to outcouple the signal of the redshifted exciton. There are three main decay channels for dipole emission near a metal surface: direct emission to photons, emission to SPPs, and nonradiative processes such as the excitation of electron-hole pairs and lossy surface waves on the metal. Other nonradiative paths via defects or phonons are independent of  $l$  and will be ignored in this analysis. Emission into SPPs provides an extra radiative decay channel as this signal can be extracted to the far field via the periodic nanostructure, and this mechanism has been used to improve the luminescence efficiency of light emitting devices<sup>207,208</sup>. The relative decay probability for each process is calculated as a function of  $l$ <sup>206</sup> and shown in Fig. 7.16(a). Although these calculations are intended for SPPs propagating on planar metal surfaces, we can use them as approximations for our grating system, although we note such estimates are indeed expected to become less accurate with increasing structure depth. Up to a CHPI thickness of 25 nm, SPP mediated emission is the most important radiative decay channel with a maximum emission probability at 22 nm, matching the experimentally observed  $\Delta E_{ex}$ . Even for thicker CHPI films we expect the exciton modes to remain at the same positions, because SPP emission becomes weak at large  $l$  where  $\Delta E_{ex}$  is negligible.

In our MQW perovskite system, localised excitons in periodically-spaced nearby QWs are optically coupled together to form collective exciton-polariton states an average distance  $l$  from the Ag surface<sup>209–212</sup>. Therefore in CHPI-coated Ag gratings we observe both in-plane exciton-polaritons, and out-of-plane interactions that lead to ‘image-biexcitons’, which are outcoupled via SPP emission with a binding energy of 100 meV at room temperature [Fig. 7.16(b)]. For our grating system, the exciton and SPP modes become closer in energy with increasing  $\phi$  [see below and Fig. 7.17(c)], and as a result splitting between the exciton modes (indicated by arrows in Fig. 7.17(c)) increases to around 185 meV at  $\phi = 90^\circ$ . The azimuthal dependence of the exciton splitting reflects the tuneable modification of the Coulomb interaction in this geometry, but however requires further theoretical development.

AFM image of a  $D = 417$  nm CHPI-coated Ag grating shows a clear grating structure despite the roughness of CHPI coating [Fig. 7.17(a)]. Using AFM measurements, we find CHPI forms a conformal coating around the Ag grating with thickness  $\sim 25$  nm [Fig. 7.17(c)]. In TE polarisation, we only observe the presence of one exciton without the signature of any grating modes, similar to the CHPI-coated Ti gratings. In TM polarised reflectivity scans, as well as strong excitons (red arrows) we also observe  $m = \pm 1$  photonic and plasmonic grating modes [Fig. 7.17(c)]. As the SPP modes become resonant with the exciton and image exciton, the light-matter modes strongly couple and produce an anticrossing in the reflectivity

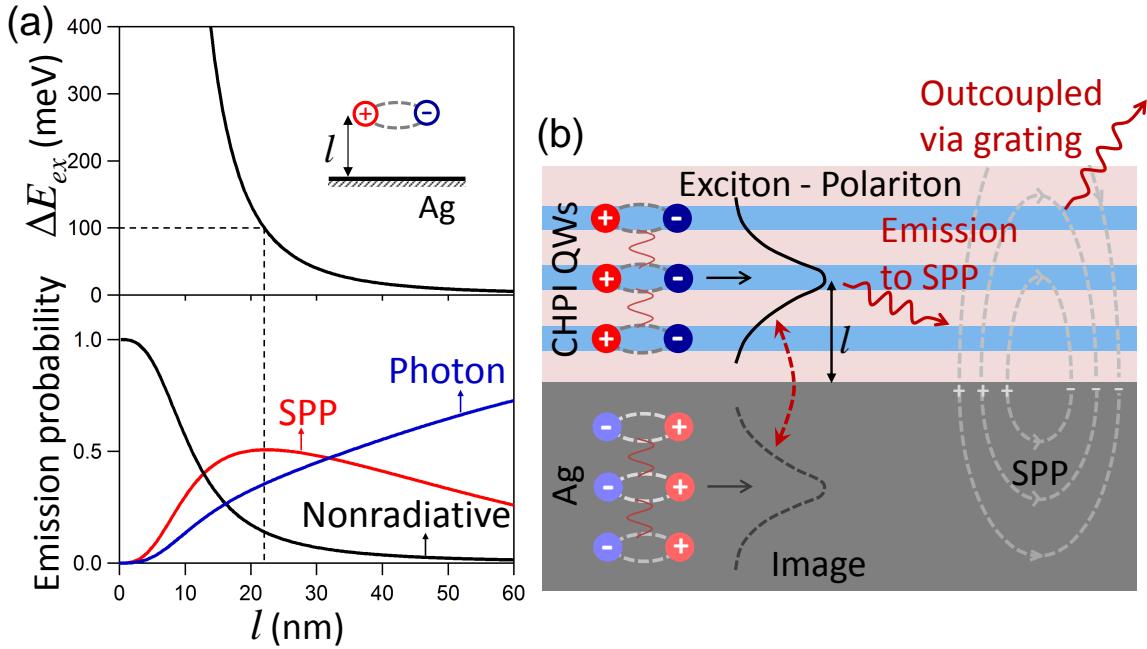


Fig. 7.16 (a) Change in emitted energy (top) and relative decay probabilities (bottom) of an exciton with energy 2.6 eV placed distance  $l$  from the Ag surface. The dashed line indicates the experimentally measured redshift. (b) Schematic mechanism for SPP-mediated emission of image-biexciton.

of 0.25 eV. Extracting the mode positions from the  $\phi = 90^\circ$  scan [Fig. 7.17(c)] allows them to be fit to a three oscillator model using the Hamiltonian

$$\hat{H} = \begin{pmatrix} E_{ex} & 0 & \Omega_{ex}/2 \\ 0 & E_{bx} & \Omega_{bx}/2 \\ \Omega_{ex}/2 & \Omega_{bx}/2 & E_{pl} \end{pmatrix}, \quad (7.2)$$

where  $E_{ex}$ ,  $E_{bx}$  and  $E_{pl}$  are the energies of the exciton-polariton, image-biexciton and plasmonic grating modes respectively, while  $\Omega_{ex}$  and  $\Omega_{bx}$  represent the interaction between the SPP and exciton/image-biexciton. From this we find Rabi splittings of  $\Omega_{ex} = 150$  meV and  $\Omega_{bx} = 125$  meV. These are greatly enhanced because of the large confinement of the plasmonic optical field in the thin PbI QW layers. The Rabi splitting is given by  $\Omega \propto \sqrt{f_{osc}N_{QW}/V}$ , where the oscillator strength ( $f_{osc}$ ) of the CHPI is assumed to be similar for coupling to photons or plasmons, the number of QWs ( $N_{QW}$ ) is proportional to the CHPI thickness, and the mode volume ( $V$ ) is here proportional to the optical mode size. Comparing to Fabry-Perot planar CHPI microcavities in strong coupling<sup>43</sup> which have CHPI thickness of 72 nm, cavity length of 407 nm, and a Rabi frequency of  $\Omega_{FP} = 65$  meV, the simple scaling

above predicts  $\Omega_{SPP} \sim \Omega_{FP} \sqrt{(22/72) \cdot (407/22)} = 156$  meV, in excellent agreement with our measurements. Using SPPs to strongly couple to the excitons thus dramatically reduces the cavity length, thus enhancing the light-matter coupling.

We calculate the full eigenstates of the system using FEM simulations. These confirm the anticrossings observed, and provide the optical field profiles. In the case of strong coupling at  $\phi = 90^\circ$ , the time-averaged near-field shows strongest intensity inside the CHPI which coats the bottom surface of the grating, with a rapid evanescent decay away from the interface [Figs. 7.18(b,c)]. The mode is thus both laterally confined by the grating as well as being trapped inside the surface layers where it couples to the excitons.

The SPP  $\vec{E}$  field direction is primarily perpendicular to the metal-dielectric interface, while excitons in CHPI QWs are polarised parallel to this interface<sup>43,66</sup>. Simulated  $\phi = 90^\circ$  spectra for in- and out-of-plane exciton dipoles are shown in Figs. 7.18(d,e) respectively. While strong coupling is seen for both dipole orientations, the bare exciton is only seen for the in-plane dipole. It thus appears that the coupling between the excitons and their images are responsible for mixing the dipole orientations, enabling the strong coupling with the SPP mode. Far-field light is directly coupled into the layered perovskite system, where the excitons mediate SPP interactions. The polariton states mix excitons within the perovskite which are delocalised across many PbI monolayers, with SPPs which are tightly confined to the CHPI layer above the Ag grating and laterally localised in the grating slits by the coupling of standing waves. Such light-matter polaritonic quasiparticles thus combine organic, inorganic and plasmonic components in an unusual fashion.

## 7.5 Conclusions

Simple plasmonic periodic structures give rise to a wide range of grating modes: photonic modes due to the interference of light, excitement of SPPs on the surface of the metal, or laterally localised modes such as channel plasmons or waveguide modes. The positions and efficiencies of many of these modes depends sensitively on the geometry of the grating and the dielectric environment provided by any overcoating materials.

In CHPI-coated Ag gratings, we observe evidence of image-biexcitons with binding energy 100 meV at room temperature. Such quasiparticles arise from the interaction between excitons and their images in the metal, and are outcoupled from the grating structure via SPP emission. These out-of-plane biexciton states mediate coupling between in-plane QW excitons and out-of-plane SPP grating modes. This enables the observation of strong coupling at room temperature with Rabi splittings of 150 and 125 meV for the exciton and image-

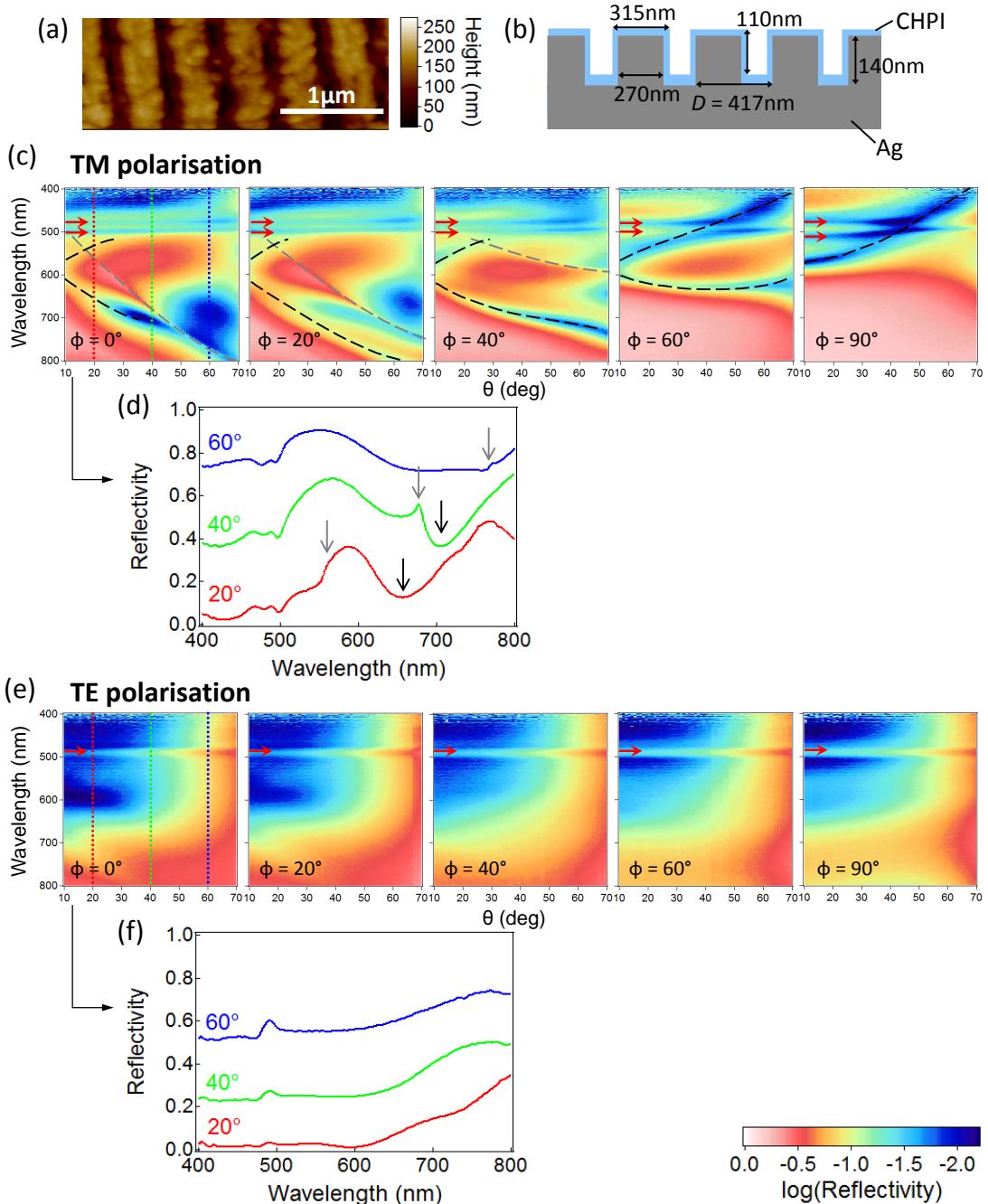


Fig. 7.17 (a) AFM image and (b) schematic structure of  $D = 417 \text{ nm}$  CHPI-coated Ag grating. (c) TM polarised reflectivity scans of  $D = 417 \text{ nm}$  Ag grating, and (d) reflectivity spectra for  $\phi = 0^\circ$ . Spectra are offset for clarity. (e,f) Same as above for TE polarisation. Photonic grating modes are indicated by grey lines/arrows on reflectivity scans/spectra, plasmonic gratings modes by black lines/arrows, and excitons by red arrows.

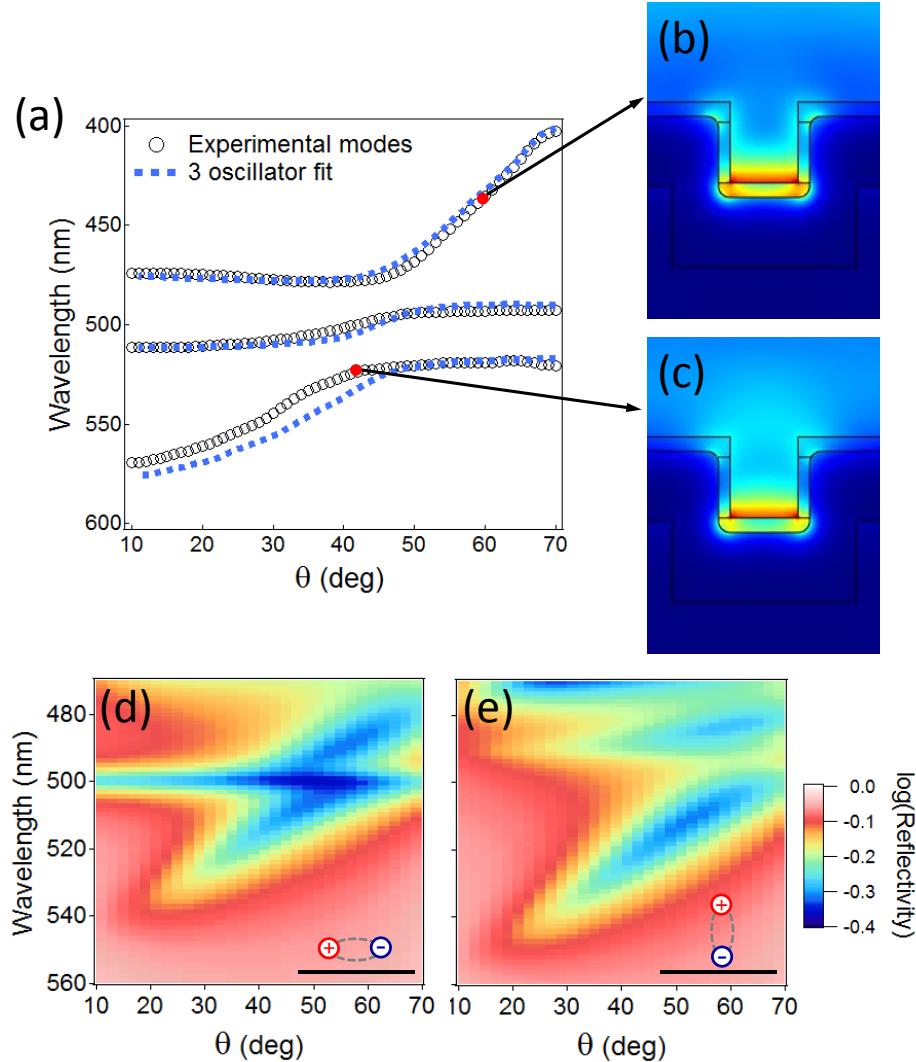


Fig. 7.18 (a) Extracted spectral mode positions for  $\phi = 90^\circ$  reflection dips (open circles), and fit from three oscillator coupling model (dashed lines). (b,c) Time-averaged  $\vec{E}$  field intensity profiles ( $\vec{E} \cdot \vec{E}$ ) as indicated. (d,e) Simulated reflection spectra for (d) in-plane and (e) out-of-plane exciton dipoles.

biexciton respectively. Both the biexciton binding energy and strong coupling Rabi splitting is tunable by small changes in the structure of the coated gratings.

Strong coupling has previously been observed between inorganic or organic excitons and Au nanoslit gratings at low temperature. The coupling constants in these systems are much smaller compared to CHPI at room temperature: 55 meV for 50 nm J-aggregate films at 77 K<sup>213</sup>, and 8 meV for 10 nm GaAs QWs at 10 K<sup>214</sup>. One key difference is that for the III-V semiconductors the QWs have to be spaced at least 20 nm from the metal surface to

maintain their optical quality. In contrast our 25 nm thick CHPI film is prepared directly on the metal, and still gives strongly radiative exciton modes because the organic sandwich protects the PbI QW layers. Theoretically Fig. 7.16(a) shows that excitons remain radiative via SPP coupling for film thickness above 10 nm. Hence the perovskite system is well suited to manipulate light-matter interactions. Such modification of exciton behaviour is of great interest for other layered van der Waals semiconductors such as derivatives of graphene and transition metal dichalcogenides, particularly for future optoelectronic devices that demand large field enhancements by coupling to SPPs.



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