

The Anomalous Infrared Transmission of Gold Films on Two-Dimensional Colloidal Crystals**

By Peng Zhan, Zhenlin Wang,* Han Dong, Jie Sun, Jun Wu, Hui-Tian Wang, Shining Zhu, Naiben Ming, and Jian Zi

Tailoring optical response using periodic nanostructures is one of the key issues in the current research on functional composite materials.^[1–5] The anomalous light transmission through metallic films that have a regular array of submicrometer holes^[3–6] has stimulated much interest. This interest stems from both the underlying physics and also the perceived potential for applications in nanophotonics,^[7] quantum-information processing,^[8] nanolithography,^[9] and surface-enhanced Raman scattering.^[10]

Extraordinary transmission of light through an optically opaque metal film perforated with a 2D array of subwavelength holes was first reported by Ebbesen et al.^[5] This unusual phenomenon can be understood as a result of diffractive coupling to evanescent surface plasmon polaritons (SPPs) that leads to a strong concentration of light at the metal surface, which then weakly tunnels through the holes in the film, reradiating by the inverse process on the exit side.^[4,11–13] In order to explore the SPP properties of microstructured metal films, extensive efforts have been made to study their spectral response and dependence on geometrical parameters, such as the type of lattice symmetry, metal film thickness, and adjacent dielectric media.^[14] Recent studies show that the hole shape has a significant effect on the optical transmission.^[15–19] Nearly all the metallic films studied have been on a flat substrate and the hole arrays were made using focused ion-beam milling,^[5,15,17,19] and electron-beam lithography^[8] or interferometric lithography combined with reactive ion etching.^[16,18]

Here we use nanosphere lithography^[20] as the sample production technique. This approach has several advantages over

the conventional lithographic and machining techniques, including the relative ease of casting large, high-quality, ordered nanomaterials and the low cost of implementation. Ordered arrays of gold half shells and nanocaps have been constructed by controlled gold vapor deposition with thicknesses less than 20 nm by using a 2D colloidal crystal (CC) as a substrate.^[21,22] Baumberg's group has fabricated metallic nanocavity arrays by electrodeposition within the pores of CC templates and observed the excitation of the SPPs in metallic cavities that led to rich features in reflectivity spectra.^[23] Very recently, Landström et al. have shown that the transmission spectra through a metal film formed on a 2D CC substrate are quite similar to those observed through subwavelength hole arrays in metal films.^[24]

In this communication, we report a study on the infrared transmission properties of gold films patterned on 2D CCs. The fabricated metallodielectric structures have a strong surface corrugation as well as a 2D periodic pore array. We show that the SPPs on these curved surfaces display unusual dispersion properties, compared to those of metal films on flat substrates studied before. The dielectric property of the template spheres is also found to have a substantial effect on the transmission. More importantly, the transmission features vary dramatically as the gold film thickness is increased, with an apparent transition from the excitation of localized SPP resonance to extended SPP propagation at a critical metal film thickness. Our results will be useful for designing and fabricating new optical devices based on SPP excitation and this will stimulate further studies on the optical properties of metallic microstructures deposited on 2D CCs.

The ordered metallic microstructures were prepared by sputtering a thin gold layer onto a monolayer of dielectric microspheres self-assembled onto a quartz chip.^[21] The 2D sphere arrays were crystallized by controlled evaporation from a colloidal solution within a channel formed using two quartz chips.^[25] The microbeads were hemispherically covered with metal and the resulting gold film consists of a hexagonally close-packed (HCP) array of gold half-shells with a size dictated by the template spheres. The diameters of these hemispherical shells can be conveniently controlled from 200 nm to several micrometers by choosing colloidal beads with different sizes.

Figure 1 shows the scanning electron microscopy (SEM) image of a typical sample with a thin gold layer on a 2D silica CC substrate. In the center of the image, there is a vacancy

[*] Prof. Z. L. Wang, Dr. P. Zhan, H. Dong, J. Sun, J. Wu, Prof. H.-T. Wang, Prof. S. N. Zhu, Prof. N. B. Ming
National Laboratory of Solid State Microstructures
Nanjing University
Nanjing 210093 (P.R. China)
E-mail: zlwang@nju.edu.cn

Prof. J. Zi
Surface Physics Laboratory, Fudan University
Shanghai 200433 (P.R. China)

[**] We thank J. R. Sambles for a critical reading of the manuscript. We also thank C. T. Chan, Z. Y. Li, and Y. Y. Zhu for helpful discussions. This work was supported by a grant for the State Key Program for Basic Research of China and by the NSFC under Grant Nos. 10425415, 90501006, and 10534020. Z. L. Wang is grateful to the Distinguished Youth Foundation of the NSFC.

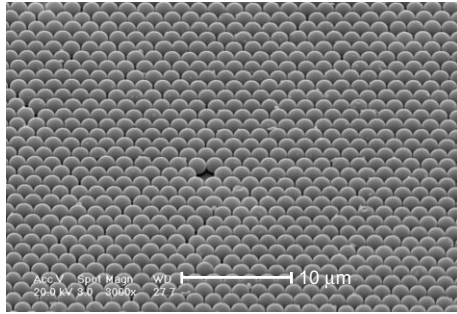


Figure 1. SEM image (tilted view) of a highly corrugated gold film deposited on a 2D CC assembled from 1.58 μm diameter silica spheres on a planar quartz chip. The thickness of the gold shells on top of the spheres is about 30 nm.

through which the monolayer CC substrate can be clearly identified. Since the silica microspheres were densely packed, the gold half-shells on adjacent silica spheres were interconnected after a certain amount of deposition, thus forming a conducting network on the CC surface. In addition, due to the locally curved surface of the CC template, a lateral variation of the metal thickness was created on the spheres, with the thinnest layer at the equator of each sphere. The fabricated metallic microstructure reflects the order of the 2D CC template, whose assembly can be controlled using a variety of self-organization methods.^[26]

The optical response of such metallic microstructures was measured by zero-order Fourier-transform infrared (FTIR) spectroscopy. In all transmission measurements, the optical spot size on the samples was about 0.8 mm. All transmission spectra were normalized to the transmittance of a pure quartz substrate. We first present the transmission spectra of the modulated metallic networks under normal incidence of linearly polarized light.

Figure 2a shows typical experimental results for two corrugated gold films deposited on 2D CC substrates with different dielectric constants. Both films have a nominal thickness $t = 30$ nm.^[27] The CCs are assembled from silica spheres (1.58 μm in diameter) and polystyrene (PS) spheres (1.59 μm in diameter) on a quartz substrate. For the metal film patterned on a silica template (solid line in Fig. 2a), up to four transmission resonances are clearly seen. In particular, a strong, extraordinary transmission peak at 1935 nm is observed, a phenomenon similar to that observed in planar metal films perforated with a regular hole array.^[5–10,13–19] This is compared to the negligible transmission observed for the homogeneous gold film deposited directly on a planar quartz substrate (dotted line in Fig. 2a). The main resonance has a transmittance of about 23 % which is about 2.5 times the projected area (about 9 %) of the pores between the particles in the 2D plane of the structure.^[28] Although the prepared samples have a good local ordering (Fig. 1), the crystal grains are typically tens of micrometers. Since the optical spot size is much larger than the single domain, the measured area is basically a region of multidomains, and as a consequence, the

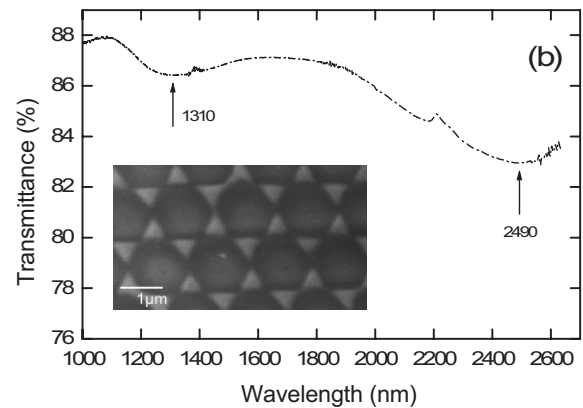
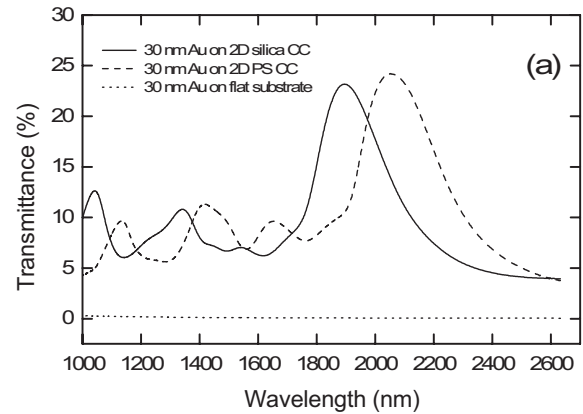


Figure 2. a) Transmission spectra of two textured gold films on different monolayer CCs assembled on a quartz chip. The silica and polystyrene (PS) spheres have nearly identical diameters ($d_{\text{silica}} = 1.58$ μm and $d_{\text{PS}} = 1.59$ μm). The dotted curve is for an unpatterned gold film on a flat quartz chip. b) Transmission spectrum of a gold triangular nanoparticle array obtained by removing the silica spheres ($d_{\text{silica}} = 1.58$ μm) after gold deposition. Inset: SEM image of the gold triangular nanoparticles. All gold layers were deposited under the same conditions with the same thickness $t = 30$ nm.

measured spectra are insensitive to the in-plane orientation of the patterned gold films^[23] (results not shown).

The optical response of ordered assemblies of dielectric spheres partially coated with gold is a superposition of scattering diffraction and light reradiation via the excitations of SPPs on the metal films. It is noted that due to the incomplete shell morphology, the present microstructures allow strong coupling of the SPPs with the CC substrate. Thus, reradiation of SPPs into photons should be affected by the dielectric properties of the colloidal spheres. This is demonstrated in Figure 2a, in which red-shifts of the resonances were observed when a PS CC substrate with a higher refractive index ($n_{\text{PS}} = 1.59$, $n_{\text{silica}} = 1.45$) was used. Since both kinds of spheres chosen have nearly identical sizes (diameters, $d_{\text{silica}} = 1.58$ μm and $d_{\text{PS}} = 1.59$ μm), the wavelength location of the transmission peaks is expected to be in proportion to the refractive index of the template. This is in good agreement with the observations in Figure 2a.

Note that during the sputtering process, gold is inevitably deposited onto the quartz chip through the interstices of the

2D CC, leading to the formation of ordered arrays of discrete triangular gold nanoislands (Fig. 2b, inset). These sharply pointed triangular islands also have strong SPP resonances.^[20,29] In order to reveal their possible contribution to the anomalous transmission resonance, separate measurements of these gold islands have been performed by removing the gold-coated CCs after metal deposition. Figure 2b shows the transmittance spectrum for normal-incident light of an array of triangular gold islands; it was fabricated by removing the silica spheres in the sample shown in Figure 1 via tape stripping. For these uniform gold nanoparticles, the transmittance shows two weak minima at ca. 1310 nm and ca. 2490 nm. The broad band at 2490 nm is due to a dipole resonance of the gold nanoprisms. Such a localized SPP resonance has been observed in silver nanoprisms and have been shown to red-shift linearly with an increase in edge length.^[20,29] The origin of the band at the shorter wavelength is not yet clear, but it is possibly because of a collective light scattering of the particle array. Nevertheless, these bands make a negligible positive contribution to the observed anomalous transmission of the metal film. Indeed, our assumption could be compromised if there exists a strong coupling between the array of the triangular islands and the array of the caps. However, it is understood that a strong near-field coupling happens only when the involved systems are closely located both spectrally and in spatially. Here, such a coupling should be weak as the resonances of the array of triangular islands are located far away from the main resonance of the whole structure (compare Fig. 2a and b), although the spatial separation between the arrays is on a submicrometer level.

To obtain more information about the SPP resonances of the microstructured gold film, we further measured zero-order transmission spectra for off-normal incidence. Angle-resolved measurements were performed using linearly polarized light whose electric field was perpendicular (s polarization) and parallel (p polarization) to the plane of incidence, respectively.

In Figure 3a and b, the acquired transmission spectra are displayed separately for two polarizations. The angle of incidence was varied from $\theta=0^\circ$ to 20° with an interval of 2° . It is seen that the transmission resonances show quite different dispersion behaviors for different resonant modes, which depends on the polarization. For p-polarized incident light, the main SPP resonance initially shows little dispersion for $\theta < 8^\circ$ in conjunction with a steady decrease in its intensity. Further increase in θ leads to the appearance of a small blue-shift ($\Delta\lambda = 30$ nm), although this is actually due to red-shifting of the resonance at ca. 1720 nm across the main resonance, followed by a clear red-shift. The two weak resonances at the blue edge of the main peak also show a decrease in intensity upon increasing the incident angle. For the two resonances with the highest energies in the spectrum at ca. 1050 and

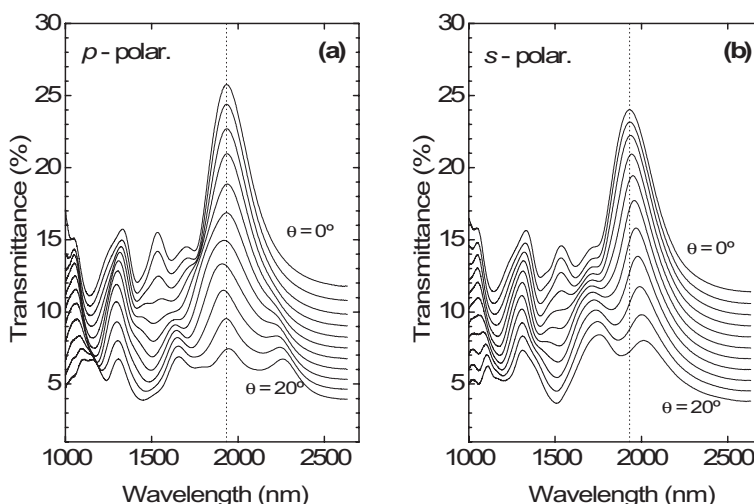


Figure 3. Transmission spectra of a textured gold film ($t=30$ nm) on a 2D silica CC ($d_{\text{silica}} = 1.58 \mu\text{m}$) as a function of incident angle (θ). Spectra were taken for the structure in steps of 2° from 0° to 20° for a) p polarization and b) s polarization. The individual spectra are offset vertically by 3% from one another for clarity. The dotted vertical line indicates the wavelength $\lambda = 1935$ nm of the main SPP resonance at normal incidence.

ca. 1330 nm, quite different dispersion properties are seen. The shorter-wavelength peak displays a red-shift, whereas the longer-wavelength one exhibits a blue-shift for $\theta < 14^\circ$, followed by a red-shift on further increasing θ . It is noted that optically inactive surface modes under normal incidence could be excited under off-normal incidence, leading to new resonances in the spectra. This is confirmed in Figure 3a where new resonances develop as the angle of incidence is changed; the obvious resonance at 2250 nm shows a red-shift with increasing angle.

A different dispersion behavior, however, is observed for the main resonance at 1935 nm when the polarization of the incident light is changed to the s state (Fig. 3b). The main resonance shows a noticeable dispersion even for s-polarized incident light, that is, it shifts steadily towards longer wavelength with decreasing intensity. In addition, in contrast to the case of p-polarization, the mode at ca. 1720 nm at the blue edge of the main resonance becomes more intense as θ increases.

Previous studies have demonstrated that for planar metal films drilled with regular hole arrays, the SPPs exhibit quite different dispersion features for incident light of different polarizations.^[4,8,30,31] For example, the SPPs have been observed to exhibit a direction-independent dispersion in these metal films for s-polarized incident light.^[5,8,30] This was explained as being due to the fact that the SPPs at the interfaces of a planar dielectric/metal interface are mainly longitudinal waves and, as a consequence, the coupling between the SPP and s-polarized light is independent of θ because, in this case, the electric field remained parallel to the planar interface.^[11,12] In contrast, the main SPP resonance in our system has a noticeable dependence on incident angle under s polarization (Fig. 3b).

We have tried to assign the transmission peaks to the reciprocal lattice of the periodic structure. However, there was a large disagreement between the observed peak positions and the calculated values using the formula for labeling the transmittance peaks of planar metal films.^[4,13] Currently, an exact calculation of the transmission and SPP dispersion of the interconnected half-shell arrays is not yet possible. However, a qualitative explanation can be made by considering the unique feature of the metal film (Fig. 4a). Due to the quasi-3D property of the gold film, linearly polarized incident light always has an electric-field component that is somewhere perpendicular to the gold film surface, regardless of its polarization (Fig. 4b). It is expected that the strong corrugation in the metal film could lead to a dramatic modification of the properties of the SPP eigenmodes from those in a flat metal film for both s- and p-polarized incident light. We suggest that sophisticated numerical calculations be implemented to simulate the surface plasmonic properties of this new kind of metal microstructure, by taking into account the 3D distribution of metal on the highly curved CC substrate.

An important issue in the study of plasmonics is the transition from a localized SPP to an extended SPP when the metallic nanoparticles merge to form a periodic hole array.^[32] Here, the conducting metal network on a 2D CC is formed via gold nanobridges at the touching points of neighboring spheres, which can be established only after a certain amount of gold deposition.^[21] In this case, a geometrical transition from isolated hemispherical metal shells to an interconnected periodic metal network occurs. This provides us with a convenient and novel route to study the transition from local SPPs on isolated metal shells and triangular islands to extended SPPs propagating along the metal network. Figure 5 shows the transmission spectra under normal incidence of a series of samples with different gold thicknesses, which were prepared by increasing the amount of gold deposit on a 2D silica CC supported on a quartz substrate. The thickness of the gold layer was varied from 0 (curve A) to 48 nm (curve N).

Curve A in Figure 5 corresponds to a 2D CC of bare silica spheres. The minimum transmittance at 1810 nm is due to the excitation of a surface eigenmode of the 2D dielectric CC.^[33] For a sufficiently low thin metal layer (curve B with $t=5$ nm

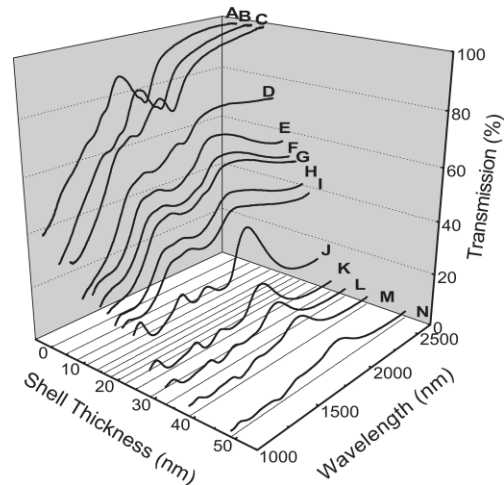


Figure 5. In situ transmission spectra of a series of gold-deposited 2D silica CCs. These samples were prepared by sequentially increasing the gold thickness on a silica CC ($d_{\text{silica}} = 1.58 \mu\text{m}$). The gold-shell thickness was increased from 0 (curve A) up to 48 nm (curve N). The dotted lines in the bottom plane are the corresponding projections of the transmission spectra, whose intersections with the shell-thickness axis show the thickness of the corresponding gold layer.

and curve C with $t=8$ nm), the sputtered gold forms isolated aggregates on the microspheres and in the triangular gaps. In such cases, light scattering by the 2D dielectric periodic structure dominates the transmission spectra, which are similar to that of the bare silica template (curve A).

When the gold deposit is increased from 8 (curve C) to 11 nm (curve D), a large decrease in the overall transmittance is observed over the whole spectrum with the greatest decrease occurring in the long-wavelength region. Electrical-resistance measurements show that the template surface is still non-conducting, which indicates that a metal network has not yet formed. However, a continuous layer (nanocaps) may already be formed on each silica sphere^[21] as well as in the triangular gaps between the spheres. In such cases, localized SPPs can be excited^[32,34] and, as a consequence, the formation of these separated gold particles leads to the first strong redistribution of the photonic modes of the 2D dielectric photonic crystal (see curve E with $t=14$ nm).

When the gold thickness is further increased up to about 25 nm, a conducting metallic network is created on the 2D CC surface. In this case, an abrupt decrease in transmittance in the long wavelength limit is observed and a sharp transmission peak with a high intensity is established simultaneously (compare spectra J and I in Fig. 5). We suggest that, upon the formation of gold nanobridges between touching silica spheres, a transition from localized SPPs to extended SPPs occurs. Large optical electric fields are then estab-

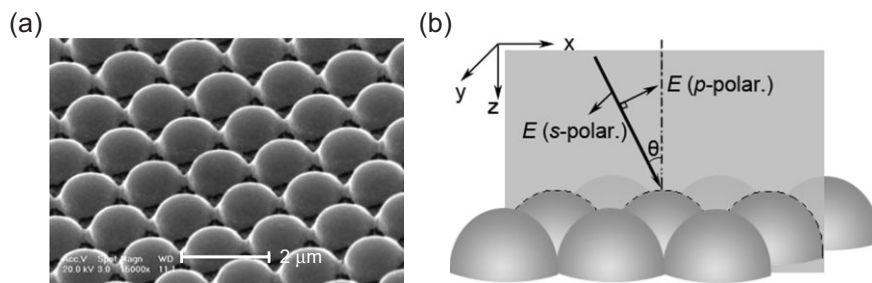


Figure 4. a) SEM image of a textured gold film after removal of the silica cores, showing that the metal film is composed of interconnected metal half shells. b) Representations of p- and s-polarized radiation incident upon the textured gold film at an angle θ .

lished via excitation of SPPs that assist light tunneling through the nanopore array, giving rise to very high transmittance at specific wavelengths.

In summary, we demonstrate a new avenue for tuning SPP properties by depositing metal films on a monolayer CC substrate. Extraordinary transmission resonances through the metal film are demonstrated with unique dispersion properties that depend on both s- and p-polarizations of the incident light. Furthermore, a clear transition from localized SPPs to extended SPPs is observed that leads to a sudden attenuation of transmittance in the low-energy limit. These findings will stimulate further theoretical and experimental efforts in engineering the optical properties of these 2D ordered metallo-dielectric microstructures and exploit their potential applications in the near-infrared spectral region. The relative ease of growing high-quality CCs with a high ordering and large single domain, and the low cost of fabricating such plasmonic crystals with submicrometer periodicity promise applicability in areas ranging from biotechnology to optoelectronics.

Experimental

The monodisperse silica microspheres (size dispersion 1.9%) and PS microspheres (size dispersion 1%) used in the work were purchased from Duke Scientific Corps. The 2D silica and PS CCs were prepared by injecting an aqueous solution of colloidal dispersion with a suitable concentration into a channel that was formed from two parallel quartz slides separated by a U-shaped spacer. The quartz slides had been pretreated to render their surface hydrophilic by soaking in a solution of 30% hydrogen peroxide at 80 °C for 30 min. After drying in air, highly ordered CCs were grown within the channel under capillary force. The prepared 2D CCs acted as a topographic pattern and gold was then sputtered on the top of the microspheres in a vacuum of 5×10^{-6} Torr (1 Torr \approx 133 Pa) at a rate of 1.2 \AA s^{-1} to the desired thickness by an ion-beam coater (IBC Model 682, Gatan Corp.). Through this process, ordered 2D arrays of metallo-dielectric beads with a hemispherical metal coverage were fabricated. The dielectric spheres could be removed, if needed, via suitable chemical etching by using toluene to remove the PS and HF to remove the silica spheres.

Sample structures were characterized by scanning electron microscopy (FEI Philips XL-30). Transmission spectra were obtained using a far-field FTIR spectrometer (Nicolet 5700). The optical spot size of the incident beam on the samples was about 0.8 mm. The numerical aperture set for the transmission was estimated to be less than 0.01.

Received: December 2, 2005
Final version: March 26, 2006
Published online: May 19, 2006

- [1] a) E. Yablonovitch, *Phys. Rev. Lett.* **1987**, *58*, 2059. b) S. John, *Phys. Rev. Lett.* **1987**, *58*, 2486.
- [2] N. B. Ming, *Adv. Mater.* **1999**, *11*, 1079.
- [3] J. B. Pendry, *Phys. Rev. Lett.* **2000**, *85*, 3966.
- [4] W. L. Barnes, A. Dereux, T. W. Ebbesen, *Nature* **2003**, *424*, 824.
- [5] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, P. A. Wolff, *Nature* **1998**, *391*, 667.
- [6] D. E. Grupp, H. J. Lezec, T. Thio, T. W. Ebbesen, *Adv. Mater.* **1999**, *11*, 860.
- [7] H. J. Lezec, A. Degiron, E. Devaux, R. A. Linke, L. Martin-Moreno, F. J. Garcia-Vidal, T. W. Ebbesen, *Science* **2002**, *297*, 820.
- [8] E. Altewischer, M. P. van Exter, J. P. Woerdman, *Nature* **2002**, *418*, 304.
- [9] a) W. Sritravanich, N. Fang, C. Sun, Q. Luo, X. Zhang, *Nano Lett.* **2004**, *4*, 1085. b) Z. W. Liu, Q. H. Wei, X. Zhang, *Nano Lett.* **2005**, *5*, 957.
- [10] a) A. G. Brolo, R. Gordon, B. Leathem, K. L. Kavanagh, *Langmuir* **2004**, *20*, 4813. b) A. G. Brolo, E. Arctander, R. Gordon, B. Leathem, K. L. Kavanagh, *Nano Lett.* **2004**, *4*, 2015.
- [11] H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer, Berlin **1988**.
- [12] J. R. Sambles, G. W. Bradbery, F. Yang, *Contemp. Phys.* **1991**, *32*, 173.
- [13] H. F. Ghaemi, T. Thio, D. E. Grupp, T. W. Ebbesen, H. J. Lezec, *Phys. Rev. B* **1998**, *58*, 6779.
- [14] a) A. Degiron, H. J. Lezec, W. L. Barnes, T. W. Ebbesen, *Appl. Phys. Lett.* **2002**, *81*, 4327. b) T. J. Kim, T. Thio, T. W. Ebbesen, D. E. Grupp, H. J. Lezec, *Opt. Lett.* **1999**, *24*, 256.
- [15] K. J. Klein Koerkamp, S. Enoch, F. B. Segerink, N. F. van Hulst, L. Kuipers, *Phys. Rev. Lett.* **2004**, *92*, 183901.
- [16] W. Fan, S. Zhang, B. Minhas, K. J. Malloy, S. R. J. Brueck, *Phys. Rev. Lett.* **2005**, *94*, 033902.
- [17] J. A. Matteo, D. P. Fromm, Y. Yuen, P. J. Schuck, W. E. Moerner, L. Hesselink, *Appl. Phys. Lett.* **2004**, *85*, 648.
- [18] Y. H. Ye, D. Y. Jeong, Q. M. Zhang, *Appl. Phys. Lett.* **2004**, *85*, 654.
- [19] R. Gordon, A. G. Brolo, A. McKinnon, A. Rajora, B. Leathem, K. L. Kavanagh, *Phys. Rev. Lett.* **2004**, *92*, 037401.
- [20] C. L. Haynes, R. P. van Duyne, *J. Phys. Chem. B* **2001**, *105*, 5599.
- [21] J. C. Love, B. D. Gate, D. B. Wolfe, K. E. Paul, G. M. Whitesides, *Nano Lett.* **2002**, *2*, 891.
- [22] J. Liu, A. I. Maarroof, L. Wiczorek, M. B. Cortie, *Adv. Mater.* **2005**, *17*, 1276.
- [23] a) S. Coyle, M. C. Netti, J. J. Baumberg, M. A. Ghanem, P. R. Birkin, P. N. Bartlett, D. M. Whittaker, *Phys. Rev. Lett.* **2001**, *87*, 176801. b) M. C. Netti, S. Coyle, J. J. Baumberg, M. A. Ghanem, P. R. Birkin, P. N. Bartlett, D. M. Whittaker, *Adv. Mater.* **2001**, *13*, 1368. c) T. A. Kelf, Y. Sugawara, J. J. Baumberg, M. Abdelsalam, P. N. Bartlett, *Phys. Rev. Lett.* **2005**, *95*, 116802.
- [24] L. Landström, D. Brodoceanu, K. Pigmayer, G. Langer, D. Bäuerle, *Appl. Phys. A* **2005**, *81*, 15.
- [25] a) Z. Chen, P. Zhan, Z. L. Wang, J. H. Zhang, W. Y. Zhang, N. B. Ming, C. T. Chan, P. Sheng, *Adv. Mater.* **2004**, *16*, 417. b) P. Zhan, J. B. Liu, W. Dong, H. Dong, Z. Chen, Z. L. Wang, Y. Zhang, S. N. Zhu, N. B. Ming, *Appl. Phys. Lett.* **2005**, *86*, 051108.
- [26] a) P. Jiang, J. F. Bertone, K. S. Hwang, V. L. Colvin, *Chem. Mater.* **1999**, *11*, 2132. b) S. O. Lumsdon, E. W. Kaler, J. P. Williams, O. D. Velev, *Appl. Phys. Lett.* **2003**, *82*, 949. c) N. D. Denkov, O. D. Velev, P. A. Kralchevsky, L. B. Ivanov, H. Yoshimura, K. Nagayama, *Langmuir* **1992**, *8*, 3183. d) R. Micheletto, H. Fukuda, M. Ohtsu, *Langmuir* **1996**, *12*, 333. e) A. S. Dimitrov, K. Nagayama, *Langmuir* **1996**, *12*, 1303. f) Q.-H. Wei, D. M. Cupid, X. L. Wu, *Appl. Phys. Lett.* **2000**, *77*, 1641.
- [27] Here t is defined as the thickness of the metal film on the top area of the template spheres.
- [28] For the 2D CC assembled from $d = 1.58 \text{ \mu m}$ silica spheres, the equilateral triangular gaps between spheres is estimated to have an edge size of 420 nm.
- [29] a) R. C. Jin, Y. C. Cao, E. C. Hao, G. S. Metraux, G. C. Schatz, C. A. Mirkin, *Nature* **2003**, *425*, 487. b) K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B* **2003**, *107*, 668.
- [30] W. L. Barnes, W. A. Murray, J. Dintinger, E. Devaux, T. W. Ebbesen, *Phys. Rev. Lett.* **2004**, *92*, 107401.
- [31] K. L. van der Molen, K. J. Klein Koerkamp, S. Enoch, F. B. Segerink, N. F. van Hulst, L. Kuipers, *Phys. Rev. B* **2005**, *72*, 045421.
- [32] W. A. Murray, S. Astilean, W. L. Barnes, *Phys. Rev. B* **2004**, *69*, 165407.
- [33] H. Miyazaki, H. Miyazaki, K. Ohtaka, T. Sato, *J. Appl. Phys.* **2000**, *87*, 7152.
- [34] C. Charnay, A. Lee, S. Man, C. E. Moran, C. Radloff, R. K. Bradley, N. J. Halas, *J. Phys. Chem. B* **2003**, *107*, 7327.