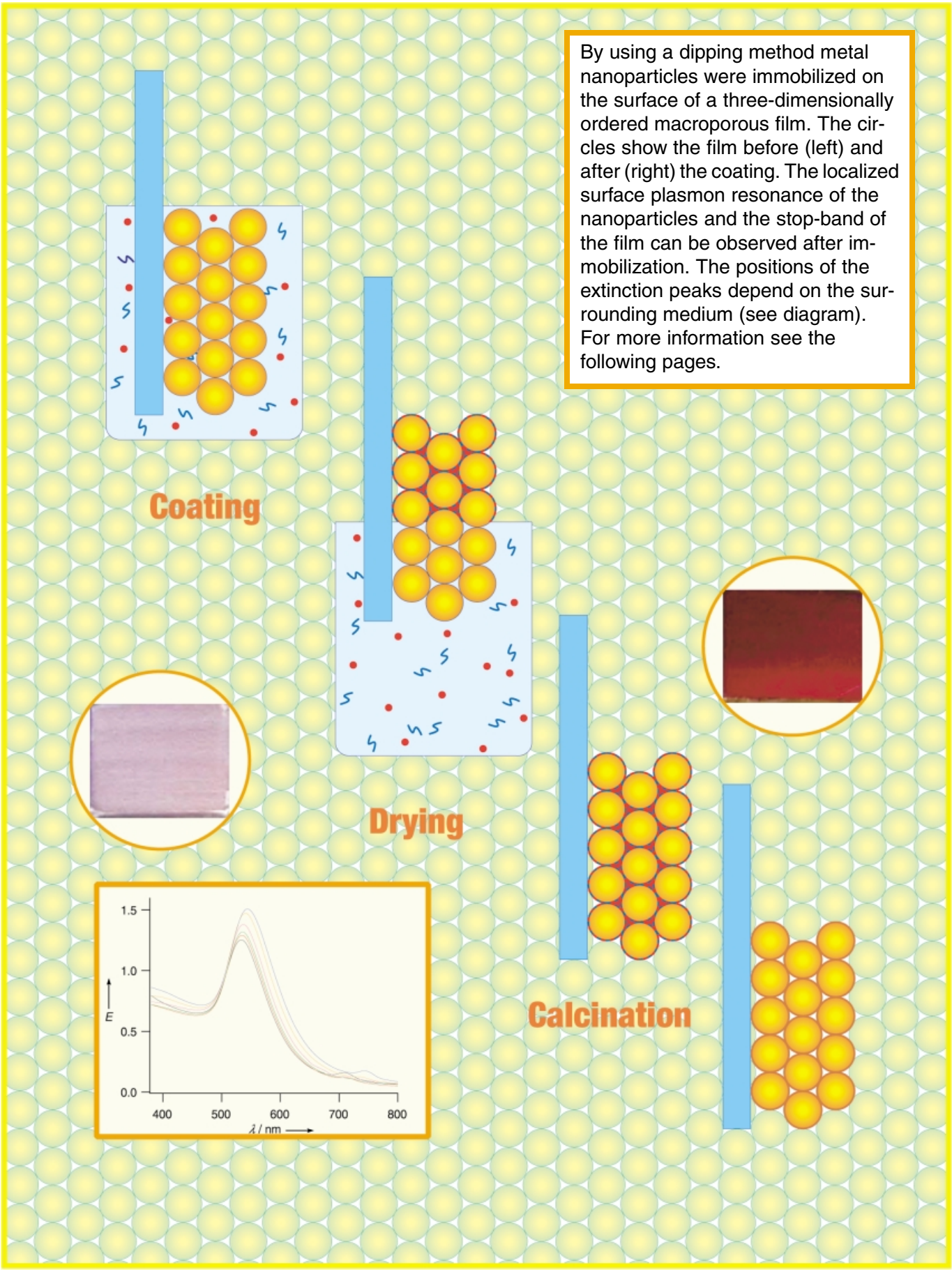
By using a dipping method metal nanoparticles were immobilized on the surface of a three-dimensionally ordered macroporous film. The circles show the film before (left) and after (right) the coating. The localized surface plasmon resonance of the nanoparticles and the stop-band of the film can be observed after immobilization. The positions of the extinction peaks depend on the surrounding medium (see diagram). For more information see the following pages.



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Fabrication of a Metal-Coated Three-Dimensionally Ordered Macroporous Film and its Application as a Refractive Index Sensor**

Zhong-Ze Gu, Rumiko Horie, Shoichi Kubo, Yasuhiro Yamada, Akira Fujishima, and Osamu Sato*

Nanoparticles are of interest because of their unique optical, magnetic, and electronic properties, which are different from those of bulk materials.[1–5] They are expected to have wide applications in optical devices and catalysis, and as chemical and biological sensors. Nanoparticles of noble metals such as gold and silver are attractive because of their so-called localized surface plasmon resonance (LSPR), which manifests itself as an absorption band when the incident photon frequency is resonant with the collective oscillation of the conduction electrons.[6, 7] The LSPR frequency of the nanoparticles is a function of their shape and of the surrounding medium. Under the isolated approximation, their relationship can be expressed by Equation (1),[8] where κ is the absorption coefficient, N is the numerical density of the nanoparticles, ε_1 and ε_2 are the real and imaginary parts of the dielectric constants of nanoparticles, and ε_m is the dielectric constant of the surrounding medium. From Equation (1), the LSPR absorption depends on the dielectric constant of the surrounding medium. By exploiting this property, metal nanoparticles have been used to construct chemical and biological sensors for detecting the surrounding medium.

$$\kappa = \frac{8\pi}{27} N R^3 \frac{\varepsilon_m^{3/2}\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2} \quad (1)$$

Much work has been devoted to developing sensors from silver and gold nanoparticles suspended in solution.[9, 10] In some cases, it is necessary to immobilize the nanoparticles on a substrate because immobilized nanoparticles are more stable. The most common method for silver and gold nanoparticles is chemical immobilization with compounds such as alkanethiols.[11, 12] Recently, it was shown that physical immobilization can also be effective. Nanoparticles were immobilized on a substrate by evaporating a metal through a mask to give two-dimensional nanoparticle arrays[13, 14] that act as efficient sensors for detecting the surrounding medium. Here we report a colloidal approach to immobilizing nanoparticles on a substrate by exploiting the structural properties of a three-dimensionally ordered macroporous (3DOM) film. Use of the nanoparticle-modified 3DOM film as a refractive-index sensor is demonstrated.

The fabrication of gold-coated 3DOM films is depicted in Figure 1. First, 3DOM films were fabricated on a glass substrate by vertical deposition[15, 16] of silica spheres with diameters of 195 or 300 nm in ethanol. The substrates were

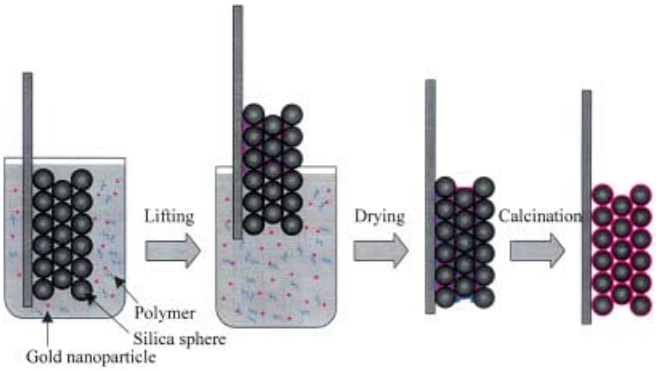

Figure 1. Outline of the fabrication of the gold-coated 3DOM film.

dried in air before use. To coat the 3DOM film, the substrate was immersed in ethanol containing gold nanoparticles with an average diameter of 10 nm. To prevent complete filling of the voids in the 3DOM films by metal nanoparticles, polymer additives were added to the solution (metal/polymer 3/1 w/w). Then the substrate was lifted out of the solution at a speed of 2 mm min^{-1}. During the lifting process, both the nanoparticles and the polymer additives infiltrated into the voids in the 3DOM film simultaneously. Then the films were dried in air and calcined at 300 °C to remove the polymer filling the voids and to immobilize the nanoparticles on the surfaces of the silica spheres.

Figure 2 shows the 3DOM film before and after gold coating. The uniform color of the films over a large area indicates that the gold was uniformly distributed, and the color after coating depends on the size of the spheres in the 3DOM film. The UV/Vis spectra of the films (Figure 3) show two peaks. The peak around 527 nm, assigned to the LSPR of gold, is in almost the same position as that of the gold colloid and indicates that the nanoparticles themselves were immobilized. After gold coating, the yellow color of a bulk gold film was only observed in the areas without the 3DOM film (at the bottom of the coated substrates in Figure 2). This indicates that the gold nanoparticles aggregate without the 3DOM film. The prevention of aggregation in the 3DOM film can be ascribed to the unique structural properties of the 3DOM film, in which the largest voids for infiltration of gold nanoparticles and polymers are only 45% of the size of the silica spheres.[17] The other UV/Vis peak of the gold-coated 3DOM film depends on the size of silica spheres. It appears at 426 nm for 195-nm silica spheres, and at 639 nm for the 300-nm spheres. These peaks arise from the stop-band of the 3DOM, which originates from the diffraction of the three-

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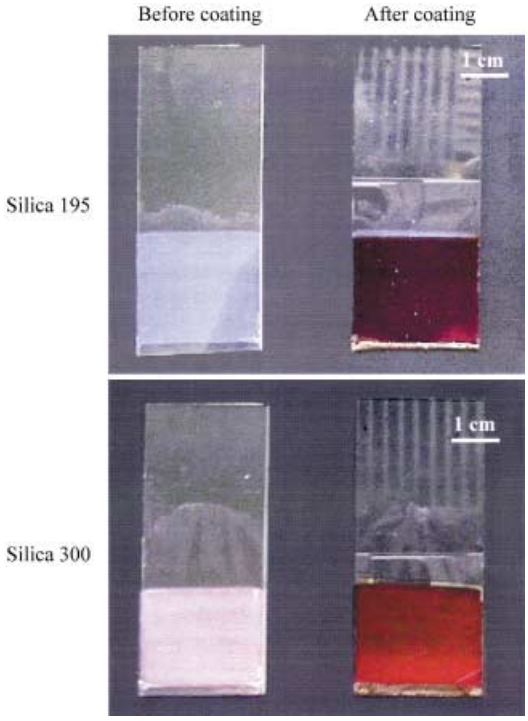

Figure 2. 3DOM films on glass substrates before and after gold coating.

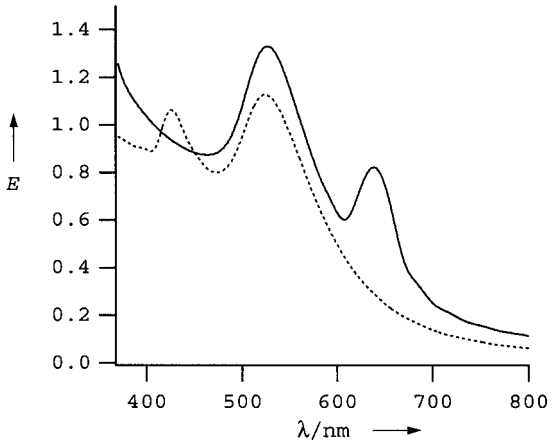

Figure 3. Transmission spectra of the gold-coated 3DOM films composed of silica spheres with a diameter of 300 (——) or 195 nm (- - - -).

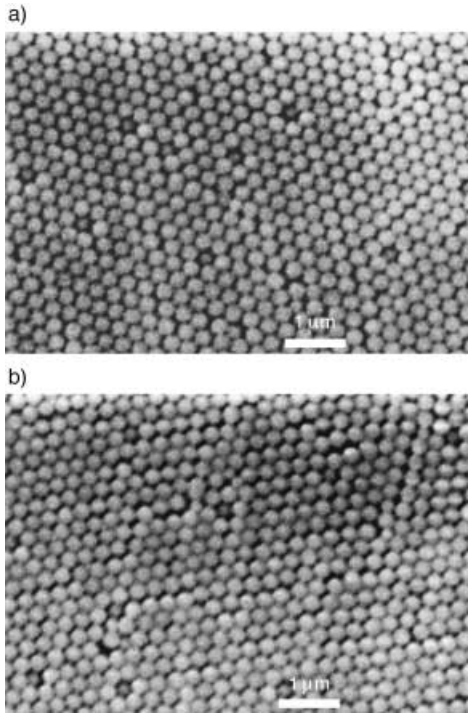

Figure 4. SEM images of the 3DOM film before (a) and after (b) gold coating. Scale bar = 1 μm.

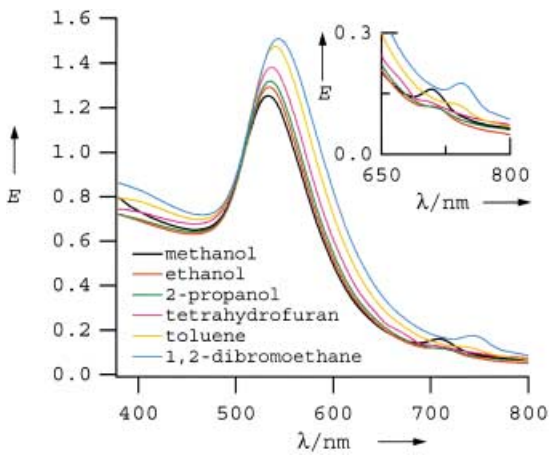

Figure 5. Spectra of the gold-coated 3DOM film composed of 300 nm silica spheres in different solvents. The inset shows an enlarged plot of the region between 650 and 800 nm to illustrate the change in the stop-band.

dimensionally ordered structures.[18] This indicates that the ordered structure of the 3DOM film was maintained after gold coating. This conclusion is supported by scanning electron microscopy (SEM) images (Figure 4), which show that the hexagonally ordered structure can be observed both before and after coating.

The suitability of the gold-coated 3DOM film as a refractive index sensor was investigated by immersion in solvents with different refractive indices: methanol ($n = 1.329$), ethanol ($n = 1.360$), 2-propanol ($n = 1.377$), THF ($n = 1.407$), DMF ($n = 1.431$), toluene ($n = 1.496$) and 1,2-dibromoethane ($n = 1.538$). The normal transmission spectra of the substrate in these solvents are shown in Figure 5. Both the LSPR peak and the 3DOM stop-band depend on the solvent. The LSPR peak shifts by 23 nm from 520 nm to 543 nm when the refractive index increases from 1 to 1.538 (Figure 6), while the stop-band of opal shifted by 84 nm from 660 nm to 744 nm. Because the origins of the two peaks are completely different, their responses to changes in the surrounding medium are dissimilar. The larger shift of the stop-band (see Figure 6) compared to that of the LSPR indicates that the former is more sensitive to changes in the surrounding medium than the latter. Therefore, the stop-band is more suitable for the precise measurement of the change in refractive index of the surrounding medium. The intensity of the stop-band peak is also sensitive to the refractive index of the medium. It decreases significantly when the refractive index is near to that of silica, and disappears at around 1.45. Therefore, it is difficult to measure the refractive index of the surrounding medium in this region. On the other hand, the peak originat-

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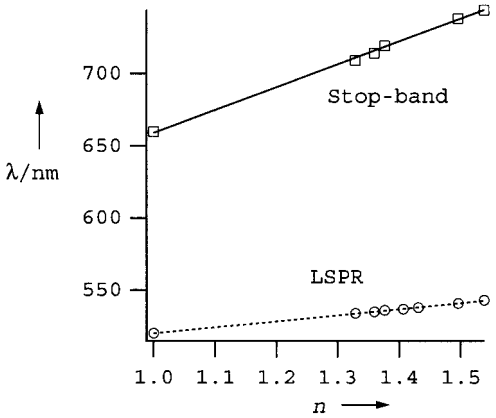

Figure 6. Dependence of the peaks originating from the LSPR (○) and the stop-band (□) on the refractive index. The dotted and solid lines were fitted by using linear functions.

ing from the LSPR can be clearly observed when the refractive index of the surrounding medium changes from 1 to 1.538. Hence, the LSPR can be used to determine any refractive index in this range. In summary, there are both merits and drawbacks to using the LSPR or stop-band peak alone to detect the surrounding medium, while a combination of the two peaks can give a more correct and precise result.

In conclusion, a high-quality metal-coated 3DOM was fabricated by a dipping method, and its application as a refractive index sensor was demonstrated. Both the LSPR and the stop-band can be used to measure the changes in the refractive index, and a combination of the two allows precise measurement of the refractive index of the surrounding medium over a wide range. Potential applications of this kind of film are as a biological sensor and as a vapor sensor. In addition, such a material may also have applications in surface-enhanced Raman scattering (SERS) and metal optical crystals.

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A One-Dimensional BaI_2 Chain with Five- and Six-Coordination, Formed within a Single-Walled Carbon Nanotube**

Jeremy Sloan,* Sara J. Grosvenor, Steffi Friedrichs, Angus I. Kirkland, John L. Hutchison, and Malcolm L. H. Green

Single-walled carbon nanotubes (SWNTs)[1] are cylindrical sheets of sp^2 graphene carbon that, when formed by laser ablation[2] or arc vaporization,[3] form capillaries with diameters predominantly within the range of 1 to 2 nm. We have recently reported that one-dimensional (1D) crystals of rock-salt KI formed within these narrow capillaries exhibit a partial or total reduction in coordination.[4, 5] For example, a 1D KI crystal of 2×2 atomic layers formed within SWNTs 1.4 nm in diameter exhibits a total reduction from 6:6 (i.e., cation:anion) to 4:4 coordination.[4] Similarly, a 1D KI crystal of 3×3 atomic layers observed within wider SWNTs (1.6 nm in diameter) exhibits three separate coordinations of 6:6, 5:5, and 4:4 along central, face, and edge -I-K-I-K- rows, respectively.[5] Binary halides derived from layered or 3D polyhedral framework structures inserted into SWNTs form 1D polyhedral chain structures[6] that also exhibit reduced cation and anion coordination. For example, six-coordinate

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