Plasmon-resonance-induced enhancement of the reflection band in a one-dimensional metal nanocomposite photonic crystal

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We report the realization of a one-dimensional photonic crystal consisting of alternating layers of metal nanocomposite and polymer layers. The structure shows a large change in the width of the reflection band due to the interplay between the plasmon resonance of the metal nanoparticle and the Bloch modes of the photonic crystal. The width of the reflection band is found to increase by 200% when the photonic band edge approaches the plasmon resonance of the silver nanoparticles. © 2011 Optical Society of America

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The linear and nonlinear optical properties of photonic crystals can be manipulated by control of the electromagnetic field through the modification of their geometry and dielectric properties. This capability has in turn led to a variety of applications of both fundamental and technological importance. More recently metal–dielectric photonic crystals (MDPCs) have received much interest due to their highly dispersive properties and their ability to exploit the optical nonlinearity of metals. Such structures have been realized in one, two, and three dimensions and use a combination of bulk metal and dielectric materials [1–6]. The optical properties in these structures are controlled by their geometry and the plasmon frequency of the bulk metal. It was shown that by engineering these characteristics through careful design, it is possible to exploit the linear and nonlinear optical properties of the metals [7–12].

In the present work we add a new degree of tunability to the optical properties of MDPCs by replacing the metal component of the structure with a composite material containing metal nanoparticles (NPs). Through control of fill factor, size, and shape of metal NPs, one can control the metallicity of the layers and their plasmon resonance, thus providing two additional tuning parameters. Metal NPs have garnered much attention these days due to numerous application areas stemming from local field enhancement effects near the surface plasmon resonance frequency.

Here we demonstrate enhancement in the reflectivity band of a one-dimensional (1D) MDPC embedded with silver NPs when the photonic bandgap approaches the plasmon resonance. This enhancement is attributed to the interaction between the absorption due to plasmon resonance of the metal NPs and the Bragg resonance of the photonic crystal.

Silver NPs embedded in poly (vinyl alcohol) (PVA) were synthesized by the reduction of silver nitrate by PVA [13]. A mixture of PVA and silver nitrate in water is used as the precursor solution that is spin coated on a silicon or glass substrate. The spin coated film is then kept on a hot plate at 95 °C for 90 minutes, where the silver NPs are formed through reduction. The film appears yellowish in color, and the PVA acts as a reducing agent as well as a stabilizer for the silver NPs.

Nanocomposite films with different silver NP fill factors were optically characterized using a spectroscopic variable angle ellipsometer in the reflection mode. The experimental data was fit to a Maxwell–Garnett model to estimate the effective linear optical constants and the fill factor of the composite film [14]. The estimated values of real and imaginary parts of the effective dielectric constant of one such composite film having an estimated metal nanoparticle fill factor of ~7% are shown in Fig. 1. The fill factor of the metal nanoparticles can be varied by changing the concentration of silver nitrate.

Following the optical characterization of the nanocomposite film, we fabricated the 1D MDPC structure. A schematic drawing of the structure is shown in Fig. 2(a). Transfer-matrix-based simulation is used to model the 1D structure where the alternating layers are assigned to be polymethyl methacrylate (PMMA) with a refractive index of 1.489 and the silver nanocomposite, whose index is as determined above. The thicknesses of the layers

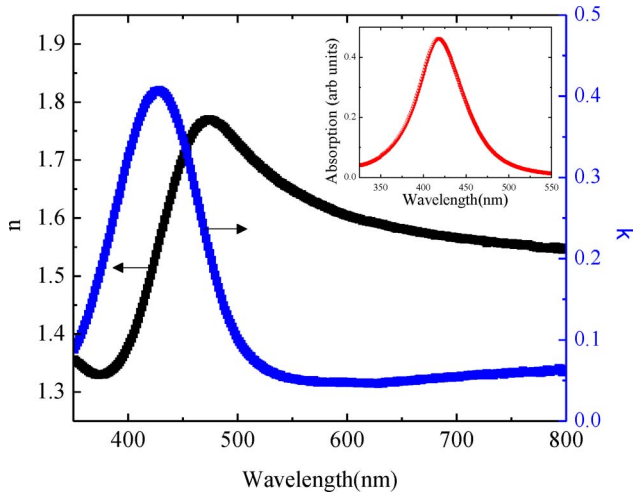

Fig. 1. (Color online) Effective index of silver NPs synthesized using 80 mg of silver nitrate and 60 mg of PVA in 5.7 ml of water. The inset shows the absorbance spectrum of the film, showing the plasmon resonance at 418 nm.

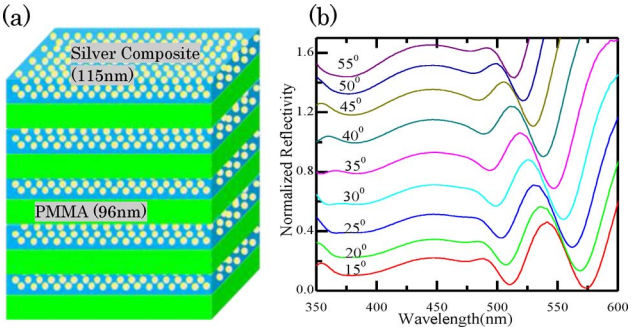

Fig. 2. (Color online) (a) Schematic of 1D metal nanocomposite–dielectric photonic crystal, (b) results of transfer-matrix-based simulations carried out on such a structure consisting of alternating layers of silver nanocomposite and PMMA indicating modification of the reflection band near the plasmon resonance.

($d_{\mathrm{PMMA}} \sim 96\,\mathrm{nm}$ and $d_{\mathrm{AgNC}} \sim 115\,\mathrm{nm}$) are chosen such that the spectral position of the Bragg reflection band can be tuned into the plasmon resonance of the silver nanoparticles. Under this condition we see the modification of the reflection band, which becomes much wider than the Bragg bandgap as seen in Fig. 2(b).

The 1D photonic crystal structure is realized by spin coating alternating layers of PMMA and the silver nanocomposite. Spin coating can be used to realize these structures because PMMA dissolves in nonpolar solvents such as toluene and PVA dissolves polar solvents such as water. This incompatibility of the solvents preserves the integrity of the layers while layers are spin coated on top of each other. A similar technique has been used in the past to realize flexible microcavities [15]. The PMMA solution is prepared by mixing 0.27 g of PMMA with 13.5 ml toluene. The silver nanocomposite prepared using the technique discussed above is spun at 3000 rpm, giving a layer thickness of ~115 nm, while the PMMA layer is spin coated at 7000 rpm to obtain a layer thickness of ~96 nm. The structure consists of five periods. Angle dependent reflectivity measurements are carried out using a white-light source and a CCD-based spectrometer. Results of these measurements are shown in Fig. 3. It can be seen that as the reflectivity peak is tuned in toward the silver plasmon resonance, a modification in the bandgap is observed. The reflectivity peak broadens due to the interaction between the band edge states of the Bragg reflection band and the plasmon resonance of the silver NPs.

Although the absolute maximum reflectivity of the present structure is only ~40%, this can be improved by increasing the number of periods and the refractive index contrast between the layers. The latter can be engineered by controlling the fill factor of the metal NPs.

For a periodic system without absorption, photonic bandgaps are defined as spectral regions with complex valued solutions to the dispersion equations for Bloch wave numbers $kD = \pi m + i\xi(\omega)$, where D is the period of the structure and $m = 0, 1, 2\cdots$. Weak absorption usually makes the real part of the wave vector different from $m\pi$ and weakly dependent on frequency, therefore blurring the boundaries of the bandgaps. In the system under consideration the plasmon-resonance-induced absorption plays a more peculiar role. We analyzed the band structure of our structure using the effective

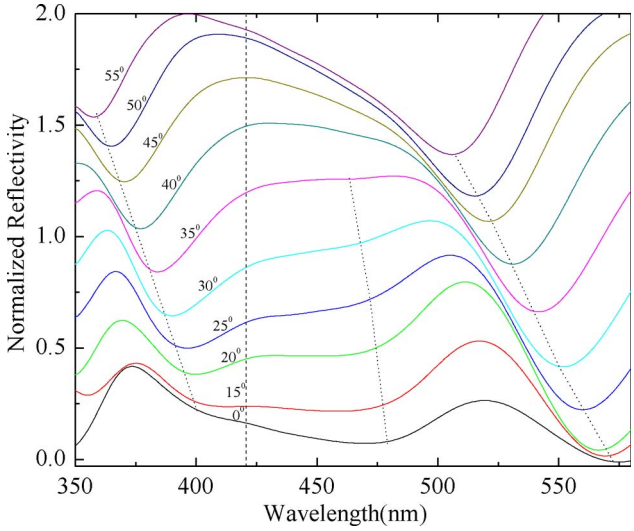

Fig. 3. (Color online) Angle dependent reflectivity on 1D metal–dielectric structure shows significant broadening of the reflection band as the band edge (dotted) of the Bragg peak approaches the plasmon resonance (dashed line).

refractive index based on the Maxwell–Garnett effective medium theory [14], which can be presented in the following form for a polar dielectric:

$$n_c = \sqrt{\varepsilon_{\mathrm{eff}} \frac{\omega^2 + i\gamma\omega - \omega_L^2}{\omega^2 + i\gamma\omega - \omega_T^2}},$$

where

$$\varepsilon_{\mathrm{eff}} = \varepsilon_h \frac{\varepsilon_\infty(1+f) + \varepsilon_h(2-f)}{\varepsilon_\infty(1-f) + \varepsilon_h(2+f)};$$

$$\omega_L^2 = \omega_p^2 \frac{\varepsilon_\infty(1+f)}{\varepsilon_\infty(1+f) + \varepsilon_h(2-f)};$$

$$\omega_T^2 = \omega_p^2 \frac{\varepsilon_\infty(1-f)}{\varepsilon_\infty(1-f) + \varepsilon_h(2+f)}$$

are expressed in terms of bulk plasmon frequency ω_p, fill factor f, dielectric constant of the host material ε_h, and parameters ε_∞ and γ, characterizing the dielectric function of the metal inclusions taken in the Drude model: $\varepsilon_i = \varepsilon_\infty(1 - \omega_p^2/\omega(\omega + i\gamma))$.

In the absence of absorption the structure under consideration would have possessed a polariton band between ω_T and ω_L as well as a set of Bragg related bandgaps, which would accumulate in the vicinity of ω_T [16]. In this spectral region the Bloch phase kD would have experienced increasingly fast changes between 0 and π caused by divergence of the refractive index n_c at ω_T as shown in black (dashed curve) in Fig. 4. Absorption washes out such oscillations, producing a Bloch bandgap adjacent to ω_T, where the real part of the Bloch wave number stays approximately equal to π, followed by the propagating band.

When the Bragg bands move toward the polariton band, the role of absorption becomes much more significant, and it prevents the real part of the Bloch wave number to decrease significantly from π before it starts increasing again due to effects of the polariton band as

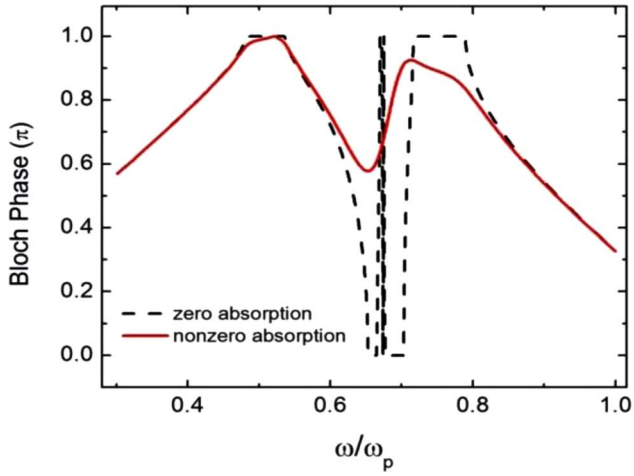

Fig. 4. (Color online) Calculated Bloch phase for the metal nanocomposite–dielectric photonic crystal structure in the presence (red solid) and absence (black dashed) of absorption. With absorption present, the Bloch phase stays in the vicinity of π, explaining the broad reflection band observed experimentally.

shown in red (solid curve) in Fig. 4. As a result the band structure is significantly modified as the Bloch phase remains very close to π over a broad spectral region, which essentially mimics formation of a broad bandgap and is manifested in the observed reflection spectra.

In summary, we have demonstrated the enhancement of the reflectivity band in a 1D photonic crystal consisting of alternating layers of silver nanocomposite and a dielectric. This enhancement is attributed to the interplay between the absorption at the plasmon resonance of the metal NPs and the Bloch modes of the photonic crystal, which causes the Bloch phase to remain close to π over a wider spectral range. This effect should be observable with any type of metal NPs, and the reflectivity can be controlled by changing the refractive index contrast and the number of periods. Such metal-NP-embedded photonic crystals will allow one to realize structures with engineered linear and nonlinear optical properties for applications such as all-optical switches, broadband reflectors, and optical limiters.

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