Efficient confinement of ultraviolet light into a self-assembled, dielectric colloidal monolayer on a flat aluminum film

Seungwoo Lee\textsuperscript{1}\textsuperscript{*} and Juyoung Kim\textsuperscript{2}

\textsuperscript{1}SKKU Advanced Institute of Nanotechnology (SAIN) and School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon 440-746, Republic of Korea
\textsuperscript{2}Department of Neurobiology, Stanford University School of Medicine, Stanford, CA 94305, U.S.A.
E-mail: seungwoo@skku.edu

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Herein, we propose the efficient confinement of ultraviolet (UV) light into a self-assembled dielectric colloidal monolayer on a flat aluminum (Al) film. Using a numerical approach, we analyzed each different resonant mode at the UV wavelengths, including the surface plasmon polariton (SPP) and waveguided (WG) mode. The calculated quality-factors (Q-factors) of each resonant mode were at least one order of magnitude higher than those of the existing Al nanostructures. Finally, we examined the influence of the oxide contamination, induced during the Al deposition, on both the SPP and WG modes in order to develop strategies for a realistic experimental fabrication.

Abstract

\textsuperscript{*}Corresponding author: seungwoo@skku.edu

In contrast to noble metals (e.g., gold and silver), aluminum (Al), owing to its d-band located above its Fermi level, allows us to push the near-infrared (IR)/visible-frequency regime of plasmon to the ultraviolet (UV) regime.\textsuperscript{1,11} In particular, as the relatively high energy level of UV corresponds well to the various electronic transition levels of organic molecules, the development of advanced molecular spectroscopy based on enhanced fluorescence sensing or surface-enhanced Raman scattering (SERS) can be further facilitated by taking advantage of UV wavelength plasmonics. Moreover, aluminum’s natural abundance and its high compatibility with the complementary metal–oxide–semiconductor (CMOS) process make it a highly promising candidate material for other transformative applications in UV plasmonics.\textsuperscript{1,11} This unique ability to instantiate UV plasmonics has driven the creation of Al nanostructures and the exploitation of the relevant plasmonic modes; however, there has been little advancement in rationally designed Al nanophotonic structures capable of a high quality factor (Q-factor) at UV wavelengths.\textsuperscript{2,7,11} Although most Al-mediated UV plasmonics have been exploited mainly by the localized or propagating modes in Al nanostructures, the obtainable Q-factor thus far remains relatively low (generally less than 50).\textsuperscript{2,7,11} This relatively low Q-factor especially limits the availability of UV plasmon-applications; thus, the currently obtainable Q-factor of Al nanophotonic structures must be further increased.

In this study, we achieved an efficient UV light confinement and the resultant high Q-factor by using an Al plasmonic–photonic crystal hybrid that can be developed by the self-assembly of a dielectric (silica) colloidal monolayer on a flat Al film. With respect to the spatial distribution of the electric field intensity (\(|E|^2\)) and E-vector, this system can support both whispering gallery-like resonant waveguided (WG) and surface plasmon polariton (SPP) modes at the UV wavelength. Also, we determined that the Q-factor at each mode can be as high as several hundred; the resonant wavelengths of its WG and SPP modes can be tuned from deep to far UV by the versatile adjustment of the silica nanosphere size. Meanwhile, the Al can be easily contaminated by oxidation (Al\(_2\)O\(_3\)) during the fabrication.\textsuperscript{11} Thus, we systematically analyzed the effect of Al\(_2\)O\(_3\) on each mode in order to develop a general guide for the experimental fabrication and a reproducible exploitation of the relevant optical responses.

The main structural motif studied in this work comprised hexagonally close-packed, 300-nm silica colloidal monolayers, which can be assembled onto a 100-nm-thick flat Al film/Si wafer [Fig. 1(a)]. The size of the silica colloidal nanosphere was varied from 250 to 350 nm: 350-nm silica nanosphere was found to be the upper limit for conceiving the far-UV-wavelength resonant modes, as will be discussed later. Using a numerical approach (finite-difference time-domain, FDTD), the collective set of optical responses, including the reflection spectra, \(|E|^2\) spatial distribution, E-vector, and Q-factor (\(\omega/\Delta\omega\), where \(\omega\) is the resonant frequency and \(\Delta\omega\) is the resonant linewidth)\textsuperscript{12-15} was systematically rationalized: all of the optical responses were obtained by simulating a unit cell [the box highlighted by the blue dotted line, as shown in the inset of Fig. 1(a)] with the periodic boundary conditions. An ultra-fine grid (at least 60 pts per wavelength in x-, y-, z-directions) was employed; the time-transient response was collected for a relatively long time (at least 3 ps). The dielectric constants of the Si wafer, Al\(_2\)O\(_3\), and silica were empirically obtained by an ellipsometric measurement. We used silica nanospheres rather than their polymeric counterparts (e.g., polystyrene) because of the relatively low lossy characteristics of the silica nanosphere at the UV wavelength of interest. The bottom surface of the silica nanospheres was slightly truncated by 6-nm heights in order to avoid unrealistic point contact between the silica nanosphere and a flat Al film. The complex permittivity of Al was characterized using a modified Drude model: \(\varepsilon = \varepsilon_\infty - (\omega_p^2/((\omega^2 + i\gamma \Omega)))\), where \(\varepsilon_\infty\) is the background dielectric constant, \(\omega_p\) is the plasma frequency, and \(\gamma\) is the damping frequency. The adapted Drude model fitting parameters were as follows: \(\varepsilon_\infty = 3.0\) eV, \(\omega_p = 16.3\) eV, and \(\gamma = 0.8\) eV. The employed electric polarization was the x-axis in Fig. 1(a).

Figures 1(b) and 1(c) summarize the optical responses of the 300-nm silica colloidal monolayers on the Al, including the reflection spectra [Fig. 1(b)] and spatial distribution of \(|E|^2\) and the E-vector [Fig. 1(c)]. In this case, the incident light can be coupled to the individual silica nanospheres by the whispering gallery mode.\textsuperscript{16} Also, more importantly, the periodically close-packed silica nanospheres can support both the in-plane waveguided modes (slab guided mode) and the resonant waveguided modes, as with other 2D photonic crystal slabs.\textsuperscript{17} The latter, in turn, results in the coupling of resonant light to the surrounding air or Al substrate (i.e.,...
strate, as revealed by the SPP modes (SPP1, SPP2, and SPP3 modes) and (ii) the resonant modes (WG1, WG2, and WG3 modes) and (bottom panel) at SPP1, SPP2, SPP3, WG1, WG2, and WG3 modes.

Fig. 1. (a) Schematic for close-packed, 300-nm silica colloidal monolayer, assembled onto 100-nm-thick Al/Si wafer. (b) Reflection spectra of close-packed, 300-nm silica colloidal monolayer, assembled onto 100-nm-thick Al/Si wafer and flat Al film with 100-nm thickness. (c) Spatial distribution (x-z plane) of electric field intensity $|E|^2$/Q-factors (upper panel) and E-vector: (i) the purely dielectric resonant modes (WG1, WG2, and WG3 modes) and (ii) the SPP modes (SPP1, SPP2, and SPP3 modes).

The SPP modes can be strongly coupled to the Al substrate, as revealed by the $|E|^2$ and E-vector spatial distributions: the E-vectors of the SPP modes near the surface of the Al are oriented in a vertical or nearly vertical direction (TM-like mode), while $|E|^2$ is mainly concentrated between the silica nanosphere and Al. These efficient confinements of the UV light via strongly coupled SPP lead to high Q-factors (e.g., 101.2 at SPP1 mode). Simultaneously, WG modes with high Q-factors can also be induced, as shown in Fig. 1(c) (e.g., 424.3 at WG1 mode and 426.2 at WG2 mode); these achievable Q-factors of the SPP and WG modes are at least one order of magnitude higher than those of existing Al plasmonic systems.2–7,11) Such conceivable high Q-factors achieved by the versatile self-assembly of a colloidal monolayer onto a flat Al film are one of strengths of this system.

Another strength of this Al plasmonic–photonic crystal hybrid is the ability to tune its resonant wavelength with a high flexibility; this can be achieved simply by varying the size of the silica nanospheres. As shown in Fig. 2(a), changing the size of the silica nanospheres from 250 to 350 nm, for example, enables the complement of the wide UV spectrum (from deep to far UV) of the achievable SPP1 and WG1 modes, even though other modes exhibit a limited range of the tunability owing to the scales law. Further extending size range of the silica nanospheres could allow other resonant modes to obtain a wider UV spectrum, as with the SPP1 and WG1 modes.

Figure 2(b) summarizes the Q-factors at the varied resonant wavelengths; it is important to note that the Q-factor of the WG1 mode can be increased up to 1068 at a resonant wavelength of 280 nm (250-nm silica nanosphere). Also, the Q-factors of both the WG and SPP modes exhibit a dispersive behavior. In particular, even if some fluctuations are clearly visible, the Q-factors of both the WG and SPP modes are reduced, as the resonant wavelengths are increased. The overall trend of the Q-factor variations according to the resonant wavelengths can be associated with the losses in the system.15,18) As the WG modes are supported almost in the dielectric silica nanospheres via total internal refraction, the refractive index contrast between the silica colloidal monolayer and surrounding environments can have a significant influence on their resonant behaviors. Indeed, the lowered refractive index of Al [0.2–0.4; see Fig. 2(c)] than both that of air (1.0) and the effective refractive index of the silica colloidal monolayer (1.33–1.35, average refractive index, calculated by weighting its filling ratio in air) enables the minimized radiative loss, greatly enhancing the Q-factors of the WG modes. The trend of the Q-factors’ evolution of the WG modes according to the resonant wavelengths, which is well matched to both the dispersive behavior of the Al refractive index [Fig. 2(c)] and the refractive index contrast between the silica and Al [Fig. 2(d)], further supports this analysis. Because the $|E|^2$ of the SPP modes can be highly confined in the space between the silica nanospheres and a flat Al film, the ohmic loss of the Al should significantly influence the Q-factors of the SPP modes. Indeed, the Q-factors of the SPP modes are far smaller than those of the WG modes owing to the large ohmic loss of Al. Moreover, the dispersive $k$ of Al [Fig. 2(c)] is well correlated with the trend of the Q-factor variation with respect to the resonant wavelengths.

We next demonstrate the effect of oxide contamination on the optical response of Al plasmonic–photonic crystals, as Al has been shown to be vulnerable to oxide contamination.11)
These studies can contribute toward developing a general guide for a realistic experimental fabrication and reproducible optical characterizations. According to the recent results reported by the Naomi Halas group, two types of Al2O3 contaminations can preferably occur in the Al nanostructures: (i) the Al2O3 encapsulation of the pristine Al nanostructure and (ii) a uniform distribution of Al2O3 within the Al (i.e., Al/Al2O3 composite). First, we investigated the effect of the Al2O3 encapsulation layer on each resonant mode; 300-nm silica colloidal monolayers were assembled on the stacked Al2O3/Al/Si wafer [Fig. 3(a)]. The thickness of the Al2O3 was varied from 1 to 5 nm, as this range of Al2O3 thickness has been generally observed in experimentally developed Al nanostructures. In this case, the effect of the Al2O3 encapsulation layer on each resonant mode can be interpreted according to perturbation theory, whereby the material perturbation of the resonator can give rise to the shift of the resonant wavelengths, as follows:

$$\Delta \lambda_{\text{res}} = -\frac{\iiint dV[(\Delta \varepsilon \cdot H) \cdot H_0^* + (\Delta \varepsilon \cdot E) \cdot E_0^*]}{\iiint dV(|H_0|^2 + \varepsilon |E_0|^2)}.$$  

Here, $\lambda_{\text{res}}$ and $\lambda_0$ indicate the perturbed and unperturbed resonant wavelengths, respectively; both $\Delta \varepsilon$ and $\Delta \mu$ represent the material perturbation by external sources; $H_0$ and $E_0$ represent the unperturbed electromagnetic (EM) wave, whereas $H$ and $E$ correspond to the EM wave under the perturbed status; and their complex conjugates are expressed by $H_0^*$ and $E_0^*$. Thus, the dominator and numerator of the right side of the equation represent the unperturbed total EM energy and the variation of EM energy by material perturbation, respectively. This theory conclusively indicates that the shift in the resonant wavelength can be effectively caused by the overlap between the material perturbation (herein, Al2O3 encapsulation layer) and the $|E|^2$.

Figure 3(b) summarizes the resonant wavelength shifts of the WG and SPP modes (red shift) according to the thickness of the Al2O3 encapsulation layer. The SPP3 mode disappears when the Al2O3 is implemented; thus, we exclude this mode for clarity. The results indicate that the SPP modes are more sensitive to the change in the thickness of the Al2O3 encapsulation layer than the WG modes. This can be explained by the relationship between the $|E|^2$ spatial distribution and the material perturbation (i.e., Al2O3 encapsulation layer). Because SPP modes can strongly confine the UV light between silica nanospheres and a flat Al film, we expect that the overlap between the material perturbation and $|E|^2$ is maximized in the SPP modes. In contrast, for both the WG1 and WG2 modes, most of $|E|^2$ is confined merely within the dielectric silica nanospheres, inducing a relatively small portion of the overlap between the material perturbation and $|E|^2$. Indeed, the red shifts of these pure dielectric resonant wavelengths with respect to the change in the thickness of the Al2O3 encapsulation layer are relatively limited, compared with those of the SPP modes. Interestingly, the WG3 mode, despite its main dielectric resonance, exhibits the red shifts of the resonant wavelengths, comparable to those of the SPP modes, because a certain portion of $|E|^2$ can also be confined in the space between the silica nanospheres and the Al layer [see Fig. 1(c)].

Meanwhile, the obtainable $Q$-factors of the WG and SPP modes are simultaneously reduced as the thickness of the Al2O3 encapsulation layer increases [Figs. 3(c) and 3(d)]. Regarding the WG modes, the insertion of a relatively high-refractive-index Al2O3 (0.78–0.83) into the interface between the silica nanospheres and Al can facilitate their radiative losses, thereby reducing the $Q$-factors. Regarding the SPP modes, the Al2O3 encapsulation layer significantly hinders the intimate coupling between the silica nanosphere and the metallic Al, reducing the efficiency of the Al-mediated plasmonic light confinement [Figs. 3(c) and 3(d)]. These resonant-wavelength red shifts and $Q$-factor changes appear quite sensitive to changes of just a few nanometers to the thickness of the Al2O3 encapsulation layer. These exotic abilities can be used for a reporter of oxide contamination.

Finally, we exploited the effect of another type of oxide contamination (i.e., Al/Al2O3 composite) on the optical responses of the Al plasmonic–photonic crystal hybrid. For this, the thickness of the Al2O3 encapsulation layer was set to 0 nm in order to elucidate the effect of the Al/Al2O3 composite. There is a need to obtain the dielectric properties of the Al/Al2O3 composite with varying oxide ratios; the Bruggeman effective medium approximation allows us to calculate the complex permittivity of the Al/Al2O3 composite, as follows:\(^{(20)}\)

$$n_{\text{al}} \left(\frac{\varepsilon_{\text{Al}} - \varepsilon}{\varepsilon_{\text{Al}} + 2\varepsilon}\right) + n_{\text{oxide}} \left(\frac{\varepsilon_{\text{oxide}} - \varepsilon}{\varepsilon_{\text{oxide}} + 2\varepsilon}\right) = 0.$$  

Here, $n_{\text{al}}$ and $n_{\text{oxide}}$ are the volume ratios of Al and Al2O3, respectively; and $\varepsilon$ is the permittivity of the Al/Al2O3 composite.
with different oxide ratios. As the ratio of $\text{Al}_2\text{O}_3$ to Al increases, three SPP modes weaken and eventually disappear. Also, we clearly see that two higher WG modes (WG2 and WG3) merge together at the high ratio of $\text{Al}_2\text{O}_3$ to Al (40%). In this case, the reduced refractive index contrast between the silica colloidal monolayer and substrate [Fig. 4(d)] due to adding $\text{Al}_2\text{O}_3$ to the pure Al results in the reduction of the $Q$-factors [see Fig. 5(f)]. Nonetheless, the Al/$\text{Al}_2\text{O}_3$ composite with 50% oxide can exhibit a lower refractive index (0.82 at the UV wavelength of interest) than both air and the silica colloidal monolayer and thus can confine a certain portion of the UV light within the dielectric silica nanosphere.

We propose the efficient confinement of UV light into a plasmonic–photonic crystal hybrid, which can be developed by the self-assembly of dielectric colloidal nanospheres onto a flat Al film. Using a numerical approach, we analyzed the modal characteristics of each different resonant mode at the UV wavelengths, including the surface plasmon polariton (SPP) mode and waveguided (WG) mode. The calculated $Q$-factors of each resonant mode were at least one order of magnitude higher than those of the existing Al nanostructures. Finally, we studied how the amount of oxide, which can be generated during the deposition of the Al, can influence both the SPP and WG modes in order to guide strategies for a realistic experimental fabrication.

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Fig. 4. Complex permittivity of $\text{Al}/\text{Al}_2\text{O}_3$ composite with controlled oxide ratio, calculated using Bruggeman model.\(^\text{20}\) (a) Real permittivity. (b) Imaginary permittivity. (c) Refractive index. (d) Refractive index contrast between silica and $\text{Al}/\text{Al}_2\text{O}_3$ composite with respect to oxide ratio.

Fig. 5. Reflection spectra of close-packed, 300-nm silica colloidal monolayer, assembled onto 100-nm-thick $\text{Al}/\text{Al}_2\text{O}_3$ composite with different oxide ratios: (a) 10, (b) 15, (c) 30, (d) 40, and (e) 50%. (f) Spatial distribution ($x$–$z$ plane) of electric field intensity $|E|^2$ and $Q$-factors at WG1 mode with different oxide ratios.

$\varepsilon_{\text{Al}}$ and $\varepsilon_{\text{oxide}}$ were obtained using a modified Drude model and an empirical measurement, respectively. Figures 4(a)–4(d) indicate the calculated complex permittivity [Figs. 4(a) and 4(b)], refractive index [Fig. 4(c)], and refractive index contrast between the silica and $\text{Al}_2\text{O}_3$ [Fig. 4(d)]. With the ratio of $\text{Al}_2\text{O}_3$ to Al, Al becomes less metallic, and the refractive index of the Al/$\text{Al}_2\text{O}_3$ composite intrinsically increases, decreasing the refractive index contrast between the silica nanosphere and Al/$\text{Al}_2\text{O}_3$ composite substrate.

Figures 5(a)–5(e) show the reflection spectra of the 300-nm silica colloidal monolayers on the flat Al/$\text{Al}_2\text{O}_3$ composite with different oxide ratios. As the ratio of $\text{Al}_2\text{O}_3$ to Al increases, three SPP modes weaken and eventually disappear. Also, we clearly see that two higher WG modes (WG2 and WG3) merge together at the high ratio of $\text{Al}_2\text{O}_3$ to Al (40%). In this case, the reduced refractive index contrast between the silica colloidal monolayer and substrate [Fig. 4(d)] due to adding $\text{Al}_2\text{O}_3$ to the pure Al results in the reduction of the $Q$-factors [see Fig. 5(f)]. Nonetheless, the Al/$\text{Al}_2\text{O}_3$ composite with 50% oxide can exhibit a lower refractive index (0.82 at the UV wavelength of interest) than both air and the silica colloidal monolayer and thus can confine a certain portion of the UV light within the dielectric silica nanosphere.

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