Fano resonances in plasmonic aluminum nanoparticle clusters for precise gas detection: Ultra-sensitivity to the minor environmental refractive index perturbations

Arash AhmadiVand a,*, Saeed Golmohammadi b, Nezih Pala a

a Department of Electrical and Computer Engineering, Florida International University, 10555W Flagler St., Miami, FL 33174, USA
b School of Engineering-Emerging Technologies, University of Tabriz, Tabriz 516664761, Iran

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Abstract

In this study, a compositional molecular cluster of aluminum (Al) nanoparticles (NPs) has been proposed and examined numerically to design efficient and applicable nanoscale plasmonic sensors. Considering the scattering spectral profile of Al/Al2O3 NPs in a decamer orientation that are deposited on a SiO2 substrate with the determined geometrical dimensions, we detected pronounced Fano resonance dip in the UV spectrum. The position and narrowness of the Fano minima in the declared wavelength region have been evaluated for various structural sizes with different oxide layer thicknesses to enhance its quality. Finding the appropriate nanocluster dimensions, we exposed the structure to the presence of various gases with extremely minor differences in refractive indices. The position of Fano minima in the UV spectrum and its depth yields an ability to extremely precise localized surface plasmon resonance (LSPR) sensing in the mentioned spectrum for the subtle environmental variations. Measuring the accuracy of the compositional Al-based decamer, we quantified the corresponding figure of merit (FoM) as 15.24, while the refractive index of the surrounding medium was a variant factor. Ultimately, we proved that the examined structure has a strong potential to exploit in designing precise, CMOS-compatible, and efficient plasmonic subwavelength sensors that are able to detect extremely small perturbations of the ambient. Finite-difference time-domain (FDTD) method is utilized as a numerical method to extract the optical properties of the examined plasmonic subwavelength cluster.
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Keywords: Aluminum nanoparticles; Compositional cluster; Ultraviolet spectrum; Fano resonance; Plasmonic sensors; FDTD method

1. Introduction

Plasmonic nanoscale structures have extensively been employed in designing various precise and efficient biochemical sensors, immunoassay devices and surface-enhanced Raman spectroscopy (SERS) [1–4]. It is well accepted that surface plasmon resonances (SPRs) yield an ability to confine the electromagnetic (EM) fields in subwavelength structures and below the diffraction limit [5,6]. Sensitivity of localized surface plasmon resonances (LSPRs) to the subtle or minor perturbations in the environmental condition provides a facility to design plasmonic sensors that are able to recognize a single molecule or DNA [2,7]. To this end, diverse methods based on plasmonic components have been proposed and applied theoretically and experimentally to provide
maximum possible accuracy and preciseness in detection of substances and analytes in molecular levels by optical sensors [3,4]. On the other hand, closely packed nanoclusters composed of noble metallic (e.g. Au and Ag) nanodisks, rings, shells, cubes, pyramids, and wires have broadly been employed in designing of several resonance sensing and SERS devices [8,9]. For instance, NPs clusters in two- and three-dimensional orientations have been tailored to support strong EM plasmon and Fano resonances (FRs) in nanoscale dimensions. Quadrumers, heptamers, hexamers, octamers, tetramers, decamers, oligomers, and necklaces are some of the regular and common nanoclusters that are able to support strong plasmon and Fano resonances [10–15]. It is well known that the behavior of Fano dip can be employed to detect the reflection and response of the structure to the surrounding medium perturbations such as refractive index variations in the dielectric medium in various systems such as transient and constant regimes [16]. To characterize the plasmonic behavior of these closely spaced NPs in a certain cluster, plasmon hybridization theory has been proposed as a key method to analyze these resonance interactions [17]. Considering plasmon hybridization model, appeared robust and deep Fano minima can be characterized by the scattering cross-sectional profile related to these structures from the visible to the near infrared region (NIR). From the technical viewpoint, the spectral response of a symmetric plasmonic cluster includes a superradiant bright mode and a subradiant dark mode corresponding to the dipolar and quadrupolar resonant modes during excitation of surface plasmon polaritons (SPPs). Overlapping of these modes and destructive interference between them give rise to arising of FRs in strong and weak regimes through the scattering cross-sectional profile [18]. Studies have demonstrated that FR position and performance could be affected dramatically by symmetry breaking in the NP cluster [16,19]. On the other hand, generation of strong FRs in the UV spectrum is challenging due to the effective operating region of Au and Ag substances. Knight et al. [20] verified and demonstrated that Au material shows highly lossy behavior at short wavelengths (λ < 500 nm) due to the interband transitions which cause the appearance of dissipative channels. In contrast, Ag is able to support robust resonances in the shorter wavelengths (λ > 300 nm), but the plasmonic characteristics of this material in short wavelengths are poor due to the rapid oxidation. Newly, aluminum (Al) has been introduced as an alternative material to utilize in the UV spectrum (λ ∼ 100–550 nm) and visible wavelengths as well [21]. It is verified that compositional arrangement of pure Al particle, oxide cover layer (Al2O3), and SiO2 substrate can be employed to generate dipolar and quadrupolar plasmon resonances in the short spectra efficiently [20–22]. For instance, Golmohammadi et al. [23] have proved that Al/Al2O3 NP clusters are able to support sharp and narrow Fano dips in the UV spectrum that can be utilized in designing bio/chemical sensors. In this recent work, complex and antisymmetric octamer cluster has been employed to detect subtle variations in the surrounding ambience.

In this study, we demonstrate that Al NPs with a measured thickness of oxide layer that are deposited on a SiO2 substrate in a decamer orientation can be tailored to support strong FRs in the UV spectrum. Investigating the optical properties of a molecular decamer composed of Al/Al2O3 NPs, the behavior and quality of FR minima are enhanced and shown numerically. We proved that proposed complex molecular decamer can be employed to design precise sensors that are highly sensitive to the extremely minor environmental perturbations. Exposing the proposed nanostructure to the various gases with different refractive indices, we measured the sensitivity of the LSPR by plotting the corresponding linear figure of merit (FoM) and also these parameters have been quantified numerically using FDTD method.

2. Observation of FR in Al-based decamer

The plasmon response of a pure aluminum nanodisk has been investigated numerically and experimentally by Knight and Martin et al. [20,22]. Herein, we designed a nanosize cluster (decamer) composed of the compositional Al/Al2O3 NPs that are suited in a close proximity to each other with a same offset distance as a gap spot. Fig. 1(a) exhibits a schematic diagram of the proposed complex decamer composed of a central nanodisk and nine adjacent peripheral nanodisks that surrounded the middle particle in a ring shape orientation. Seeking for the narrow and deep Fano minima, we modified the geometrical sizes of the employed NPs in the decamer cluster. Fig. 1(b) shows numerically calculated scattering cross-sectional profile for the proposed decamer based on pure Al NPs without the presence of oxide layer with the geometrical sizes that are listed in Table 2. Accordingly, the radius of the central particle is larger than peripheral NPs radii due to provide required symmetry cancelation, which needs for appearing of dark modes. Then, we examined the influence of each one of geometrical parameters on the plasmon response of the structure individually. The height (H) of the NPs has been set as an infinite parameter and the oxide layer thickness is an increasing parameter in the range of 1–45%. Noticing in Fig. 1(b),
Fig. 1. (a) A three-dimensional schematic diagram of a decamer cluster composed of Al/Al₂O₃ nanodisks in two- and three-dimensional views, (b) scattering cross-sectional diagram for the examined decamer based on the pure Al NPs without the presence of oxide layer under excitation by an incident transverse ($\Phi = 0^\circ$) and longitudinal ($\Phi = 90^\circ$) polarization mode, (c) the effect of geometrical modifications on the position and quality of FR are illustrated, where the place and wavelength of the Fano dip are indicated for each one of the regimes, separately.
Table 1

<table>
<thead>
<tr>
<th>Parameter descriptions</th>
<th>Settings</th>
</tr>
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<tbody>
<tr>
<td>Spatial cell sizes</td>
<td>1 nm</td>
</tr>
<tr>
<td>Number of cells</td>
<td>150,000</td>
</tr>
<tr>
<td>Number of time steps</td>
<td>9000</td>
</tr>
<tr>
<td>Simulation time</td>
<td>3500 fs</td>
</tr>
<tr>
<td>Number of snapshots</td>
<td>19,874</td>
</tr>
<tr>
<td>Boundary conditions ((x, y, z))-axis</td>
<td>Perfectly matched layers (PML) with 12 layers</td>
</tr>
<tr>
<td>Background refractive index</td>
<td>(n = 1)</td>
</tr>
<tr>
<td>Plane wave source amplitude</td>
<td>1.5854e−20</td>
</tr>
<tr>
<td>Pulse length</td>
<td>2.6533 fs</td>
</tr>
</tbody>
</table>

we compared an initial response of the structure to illuminating by an incident light source in transverse \((\Phi = 0^\circ)\) and longitudinal \((\Phi = 90^\circ)\) electric (TE and LE) polarization mode excitations. Accordingly, strong dipole resonance extremes appeared at \(\lambda \sim 260\) nm and 290 nm, and quadrupole resonance peaks were observed at \(\lambda \sim 135\) nm and 160 nm, for transverse and longitudinal polarization modes, respectively. Obviously, detected quadrupolar shoulders are significantly weak and cannot couple efficiently to dipole modes to provide acceptable FR dip based on the destructive interference of dark and bright modes. It is shown that illuminating a compositional arrangement of Al/Al\(_2\)O\(_3\) NPs on a SiO\(_2\) substrate directly leads to generating of dipolar and quadrupolar plasmon resonance modes in strong regime in the UV spectrum [21]. To compute and measure the dielectric response of the employed Al NPs as a complex nanostructure to the various depositions and material embellishments (e.g. Al\(_2\)O\(_3\) cover layer and SiO\(_2\) substrate), two-dimensional FDTD method is utilized, where Table 1 contains all of the required settings and parameter descriptions for the FDTD model. To this end, an incident linear light source (plane wave) with transverse and longitudinal polarization modes with the angles of \(\Phi = 0^\circ–90^\circ\) and the bandwidths of \(\lambda = 150–800\) nm is employed. To determine and measure the appropriate geometrical dimensions for the proposed decamer, we draw Fig. 1(c) which includes the scattering intensity over the wavelength variations for variable NPs sizes, while the offset gap distance is constant (14 nm) and also, the thickness of a homogenous oxide layer is fixed to 9 nm. In this regime, the antisymmetric nature of the proposed decamers remains unchanged and we increased the radii of all of the NPs by 10 nm. Noticing in this comparative diagram, the Fano dip appeared around the \(\lambda \sim (245 \pm \Lambda)\) nm, where \(\Lambda\) is the wavelength tolerance around the central spectrum. We verified that Al NPs with the geometrical sizes as \(R_c = 85\) nm and \(R_p = 65\) nm in a decamer orientation provide a pronounced Fano minima at \(\lambda \sim 258\) nm. The effect of oxide layer deposition in the presence of dielectric substrate on the plasmon resonance and Fano minima would be interesting. In this regime, the dielectric function of the Al/Al\(_2\)O\(_3\) NPs for each one of the employed materials can be derived from the ellipsometric data considering a bilayer multiplex of a narrow dielectric oxide layer covering an infinite thick Al layer which is specified by modified Drude model as below [22–24]:

\[
\varepsilon_{Al} = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}
\]

where \(\omega_p\) is the bulk plasmon frequency, \(\gamma\) is the damping constant, and \(\varepsilon_\infty\) is the frequency response. In this simulation model the thickness of the Al\(_2\)O\(_3\) layer is completely matching with each other and considered in the range of 5–10 nm, \(\varepsilon_\infty\) is \(\sim 2.5–4.5\), and the Drude damping constant is in the range of \(\gamma = 0.5–1.8\) eV. It has already been proved that utilizing Bruggeman model allows for calculation of the dielectric function of a compositional arrangement such as the proposed nanostructure of this study (Al/Al\(_2\)O\(_3\)/SiO\(_2\)). Considering the calculated and formulated values for the pure Al and Al\(_2\)O\(_3\) based on presented data in Refs. [20,23], using this method, we would be able to measure the effect of oxide (Al\(_2\)O\(_3\)) layer increment around the NPs of the proposed decamer and in the presence of dielectric substrate (SiO\(_2\)) on the spectral response of the compositional nanostructure numerically. To perform demanded FR minima in the UV spectrum, we grew an oxide layer (Al\(_2\)O\(_3\)) with certain thickness around the NPs of the complex cluster homogeneously. Fig. 2(a) exhibits the scattering cross-sectional profile for the investigated Al-based decamer, wherein the thickness of the oxide layer of the NPs is increasing. In addition, it should be noted that the examined cluster is deposited on a SiO\(_2\) substrate as a dielectric host. Noticing in this diagram, the desired Fano dip is generated by increasing the ratio of the oxide layer, while the intensity of the dipolar resonance mode is increased dramatically. Accordingly, for a decamer based on the geometrical parameters that are listed in Table 1, with the 12% oxide layer thickness a strong and deep Fano minimum appeared at \(\lambda \sim 256\) nm (see Fig. 2(a)). Next, increasing the percentage of the oxide layer, the dark mode becomes stronger and generated Fano dip is red-shifted to the longer wavelengths, but this movement is subtle and limited to a few nanometers. For the cluster with the oxide layer thickness of 25%, the pronounced Fano dip became narrower and
Fig. 2. (a) This profile demonstrates the scattering cross-sectional diagram for the Al-based decamer, while the thickness of the oxide layer of the NPs is variant under transverse electric polarization mode. Inset shows the place and deposition of Fano minima for three different regimes with details, (b) charge density distribution direction between adjacent Al/Al₂O₃ NPs in the examined decamer is illustrated by arrows for the transverse polarization mode excitation for dark and bright modes, respectively.

deeper in comparison to the earlier examination, while a strong coupling between subradiant and superradiant modes is performed. In this regime, the FR position is exactly in the \( \lambda \sim 264 \) nm and as a result, we encountered with a delicate red-shift in its position (see Fig. 2(a)). For the final investigation, we increased the oxide layer thickness to the possible maximum ratio as 39%. This cross-sectional profile also shows the scattering spectra for the proposed later regime, and therefore, the Fano dip becomes broader, its depth increases, and the Fano position red-shifts to the longer wavelengths (\( \lambda \sim 275 \) nm). This subtle movement in the position of the Fano minima would be useful to design a device that is able to sense trivial perturbations in the environmental condition, such as refractive index variations. In this regime, two relevant modes for the interference of FR are the bounding bright mode, which is associated to the dipolar resonance oscillation with a same dipolar momentum direction with the peripheral Al/Al₂O₃ NPs, and in contrast, the other resonant mode is the antibonding dark mode that has an opposite direction of dipolar resonance oscillation (dipole moment) in comparison with the surrounding proximal particles. Fig. 2(b) shows the charge density distribution direction between proximal Al/Al₂O₃ NPs in the examined cluster for dark and bright modes (at \( \lambda = 190 \) nm and 360 nm), respectively under transverse electric polarization excitation. Fig. 3(a) and (b) illustrates two-dimensional snapshots of the plasmon resonance excitation under transverse and longitudinal polarization modes and resonance coupling inside the examined Al-based decamer, where the effect of oxide layer thickness increasing on the plasmon resonance
excitation inside the cluster is shown by an arrow. In this regime, increasing the thickness of the oxide layer, we detected strong hybridization of plasmon resonances inside the cluster.

3. \textbf{Al/Al}_2\text{O}_3 \text{ decamer for sensing based on FR minima position}

It is well accepted that plasmonic nanostructures that are able to sense the gas analytes operate based on refractive index adsorption-dependent mechanism [25–27]. Jackšič et al. [27] calculated the performance of the plasmonic sensors that are able to sense the environmental refractive index perturbations based on adsorption concept. Considering the refractive index fluctuations through the surrounding medium of the structure, thus, the refractive index alterations are pertinent to the number of adsorbed molecules.

Table 2

Herein, we try to present a simpler and effective method to sense the subtle refractive index variations based on FR topic. To this end, the ability of appearing FR minima in the UV spectrum is exploited to sensing delicate variations in the refractive index of the ambient
perturbations, while the dielectric substances are gases, such as nitrogen (N2), oxygen (O2), carbon dioxide (CO2), argon (Ar), helium (He), and xenon (Xe). The major challenging issue here is the very small differences between the refractive indices of these gas materials which makes the diagnosis of these elements highly difficult. We listed all of the effective refractive indices of the mentioned gases in Table 3, based on the measured values in the range of λ ~ 200–500 nm [28–32]. Considering listed parameters in this table, to sense some of these gases, we have to yield Fano minima in the UV spectrum based on a plasmonic structure. Therefore, illuminating the examined Al/Al2O3/SiO2 decamer by an incident plane wave source (with the transverse polarization mode), and exposing the structure by each one of the gases, we are able to calculate and draw the scattering spectral profile numerically based on FDTD method as exhibited in Fig. 5. To provide more clear and definitive results, we illustrated each one of the diagrams separately for two different gases with exact diagrams that illustrate the delicate

Fig. 4. Numerically calculated scattering spectral responses for the final Al/Al2O3/SiO2 for transverse mode excitation, while the refractive index of the environmental medium is variant, (a) the position of the FRs to the presence of N2 and O2 are evaluated, (b) the position of the FRs for the presence of Ar and CO2 is determined, (c) the position of the FRs for the presence of He and Xe is drawn.

Table 2
Final geometrical sizes for the examined compositional decamer and utilized sizes for investigations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Size</th>
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<tr>
<td>Rc</td>
<td>Central NP radii</td>
<td>85 nm</td>
</tr>
<tr>
<td>Rp</td>
<td>Peripheral NPs radii</td>
<td>65 nm</td>
</tr>
<tr>
<td>H</td>
<td>Height of the NPs</td>
<td>Infinite</td>
</tr>
<tr>
<td>D9h</td>
<td>Gap distance of peripheral NPs</td>
<td>14 nm</td>
</tr>
<tr>
<td>t</td>
<td>Al2O3 thickness</td>
<td>Variable</td>
</tr>
</tbody>
</table>

Table 3
Effective refractive index (n) of various gases with the considered wavelength bandwidth for determination.

<table>
<thead>
<tr>
<th>Element (gas)</th>
<th>Effective refractive index (n)</th>
<th>Wavelength range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N2)</td>
<td>n = 1.00030</td>
<td>λ = 200–400 nm</td>
</tr>
<tr>
<td>Oxygen (O2)</td>
<td>n = 1.00025</td>
<td>λ = 200–400 nm</td>
</tr>
<tr>
<td>Carbon dioxide (CO2)</td>
<td>n = 1.00045</td>
<td>λ = 200–400 nm</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>n = 1.00028</td>
<td>λ = 200–600 nm</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>n = 1.000035</td>
<td>λ = 200–5000 nm</td>
</tr>
<tr>
<td>Xenon (Xe)</td>
<td>n = 1.00083</td>
<td>λ = 150–400 nm</td>
</tr>
</tbody>
</table>
movements in the Fano minima and its quality as well. Fig. 4(a) demonstrates appearance of pronounced Fano minima at $\lambda \sim 281$ nm and 275 nm for the presence of N$_2$ and O$_2$, respectively. It is obvious that minor differences between the refractive indices of declared gases cause difference in the position of FRs and also their depth. Accordingly, corresponding Fano dip for N$_2$ with higher refractive index is deeper and red-shifted to the longer wavelengths. Next, we compared the spectral response of the Al/Al$_2$O$_3$/SiO$_2$ decamer in presence of two other gases (CO$_2$ and Ar) that have pronounced differences in refractive indices. Fig. 4(b) illustrates calculated scattering cross-section for the assumed regime under transverse electric polarization mode numerically. Noticing in this picture, we detected two Fano minima at $\lambda \sim 284$ nm and 320 nm for the presence of Ar and CO$_2$, respectively. The noteworthy point here is the dramatic depth of the FR for CO$_2$ (Fig. 4(b)) in comparison to N$_2$ (see Fig. 4(a)). As a result, increasing the refractive index directly yields deeper Fano minima which provide precise detection at the different surrounding ambient. For the last examination, we evaluated the spectral response of the nanostructure to the presentment of the He and Xe in Fig. 4(c). Here, two different gases with a big gap between refractive index measures are considered which verifies the subtle modifications around the decamer. As we expected, the Fano minima for the He with the smallest refractive index occurred at $\lambda \sim 192$ nm and for the Xe the Fano position red-shifted to the $\lambda \sim 280$ nm. For the final verification of the structure to utilize in sensing of LSPR in the UV spectrum, we quantified corresponding sensitivity and figure of merit (FoM) by plotting the linear diagrams for each one. For sensitivity determination, we plotted energy peaks positions over the refractive index variations, where for FoM definition the energy deviations over the refractive index variations are computed and depicted. Fig. 5(a) depicts the sensitivity diagram for the examined decamer during exposing by various gases which is quantified as $S = 329$ nm RIU$^{-1}$. In addition, we computed the plasmon resonance energy shifts over the refractive index variations as a linear plot. Technically, dividing the plasmon energy shifts per refractive index variations of the ambient by the width of scattering peak helps to realize the required FoM numerically. For the obtained asymmetric FRs in the UV spectrum, the resonance energy is defined as the middle point between the plasmon energy (eV) of the minimum and maximum peaks. Fig. 5(b) depicts the linear plot of FoM determination and accordingly, the FoM is measured as 15.24 which proves the preciseness of the designed complex plasmonic nanostructure in sensing the minor alterations in the refractive index of environmental gas substances.

4. Conclusions

In this study, we investigated the optical properties and plasmon response of an Al-based NPs cluster which are designed in a decamer orientation. Utilizing Al oxide layer (Al$_2$O$_3$) with controlled thickness size and SiO$_2$ as a substrate material, we calculated the spectral response of the proposed decamer to the incident transverse and longitudinal polarization modes numerically. With formation of FR dip in the UV spectrum, we exploited this opportunity to design a plasmonic subwavelength structure to detect presence of various gases in the surrounding ambience with trivial differences in the associated refractive indices. We proved that examined nanostructure is able to detect extremely subtle perturbations in the refractive index of surrounding medium precisely. In this method, the behavior and position of FR dip in the UV spectrum helped us to detect various gases that can be defined at this bandwidth. Ultimately, quantifying and plotting linear sensitivity and FoM diagrams for the studied configuration, we proved its remarkable accuracy in sensing purposes. Proposed decamer composed of Al/Al$_2$O$_3$/SiO$_2$ is a strong
candidate to exploit in designing plasmon nanosensors with easy fabrication processes, high accuracy, and CMOS compatible opportunities.

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