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

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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  $Al/Al_2O_3$  NPs in a decamer orientation that are deposited on a SiO<sub>2</sub> 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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#### 1. Introduction

Plasmonic nanoscale structures have extensively been employed in designing various precise and efficient biochemical sensors, immunoassay devices and surfaceenhanced Raman spectroscopy (SERS) [1–4]. It is well

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http://dx.doi.org/10.1016/j.photonics.2014.12.002 1569-4410/© 2014 Elsevier B.V. All rights reserved. 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 crosssectional 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  $(\lambda < 500 \text{ nm})$  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 ( $\lambda > 300$  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 ( $\lambda \sim 100-550$  nm) and visible wavelengths as well [21]. It is verified that compositional arrangement of pure Al particle, oxide cover layer (Al<sub>2</sub>O<sub>3</sub>), and

SiO<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> 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 SiO<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> 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/Al<sub>2</sub>O<sub>3</sub> 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),

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