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Optical Properties of $Al@Al_2O_3$ Nanorod as a UV and Visible Wavelengths Plasmonic Nanostructure

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Abstract

Aluminum as a new plasmonic material shows deep ultraviolet plasmon resonances which are broadly tunable. The use of aluminum plasmonic nanostructures offers new approaches, such as access high energy regions of the spectrum, low-cost and sustainable material. Therefore, aluminum is capable of being alternative plasmonic material compared to conventional gold and silver nanostructures. In this research, surface plasmon resonance properties of $Al@Al_2O_3$ core@shell nanorods in different dielectric environments were investigated. Using boundary element method and MNPBEM simulation package the sensitivity of aluminum plasmon resonance to the presence of Al_2O_3 layer, different aspect ratios and different dielectric mediums were studied. Results show that in Al nanorods with diameter of 3 nm increasing length from 3 to 7 nm plasmon longitudinal peak wavelength monotonously increase from 138 nm to 213 nm. In $Al@Al_2O_3$ nanorods with the same size and presence of 0.5 nm Al_2O_3 oxide layer the peak wavelengths dramatically shift to higher values from 307 nm to 514 nm in the middle of visible region. Plasmon resonance sensitivity to medium refractive index was also investigated. Both aluminum and $Al@Al_2O_3$ nanorods exhibit red shift of longitudinal plasmon resonance wavelength by increasing refractive index from 1 to 2. Furthermore, red shift of plasmon peak wavelength by refractive index is linear in both cases. Finally results show that plasmonic response of $Al@Al_2O_3$ nanorods depend sensitively on presence of oxide layer, size and dielectric medium. As a new plasmonic material, $Al@Al_2O_3$ nanorods are capable for tremendous application due to wide ranges of plasmon resonances from deep UV to the middle of visible region.

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Keywords: Al@Al2O3 Nanorod; plasmonic; boundary element method.

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1. Introduction

Surface plasmon resonances (SPR) is a collective oscillation of free electrons in metallic nanostructures excited by an external electromagnetic field. Strong resonant optical absorption as well as near-field and scattering enhancements are due to plasmon resonances. The optical and plasmonic properties of conventional noble metal such as Ag and Au nanoparticles have been thoroughly studied and reported, Fan et al. (2014), but less information is available concerning new plasmonic metamaterials. The use of aluminum for plasmonic nanostructures opens up new possibilities, such as access to short-wavelength regions of the spectrum, the possibility of low-cost, sustainability and mass producible plasmonic materials. Optical techniques based on Al plasmonic nanostructures have been shown to be successful for biosensing applications, Canalejas-Tejero et al. (2013), nanoantennas, Castro-Lopez et al. (2011), enhanced UV fluorescence, and energy harvesting structures. Aluminum has been known as a deep ultra-violet plasmonic material, but it is also capable of to be assigned as a new visible-plasmonic material. Aluminum plasmon properties sensitively depends on shape, surface oxidation and surrounding dielectric of nanostructures. In this research plasmon properties of $Al@Al_2O_3$ nanorods were investigated as a candidate of UV and visible new plasmonic material. Simulations are needed for precise Al plasmonic nanostructure design for a variety of applications. Furthermore, they are helpful for fundamental understanding of plasmonic properties and exploring the optical response of Al nanostructures. Simulation of nanostructures plasmons involves solution of Maxwell's equations for metallic nanoparticles embedded in a dielectric environment. Among different available approaches for solving Maxwell's equations, boundary element method (BEM) was used in this research. This calculation method have been widely used for the simulation of optical properties of plasmonic particles, Trügler et al. (2011), Trugler et al. (2008), Koller et al. (2010), Jacab et al. (2011), Hohenester et al. (2009). In boundary element method a dielectric environment contains homogeneous and isotropic dielectric functions which are separated by abrupt interfaces, rather than allowing for a general inhomogeneous dielectric environment. In this research first, simulation technique for investigating optical and plasmonic properties of $Al@Al_2O_3$ nanorods was discussed. Then, different parameters that effect on plasmon properties of the nanorods such as aspect ratio, presence and thickness of alumina shell and different surrounding media were investigated. Finally, $Al@Al_2O_3$ nanorods are introduced as a new adjustable UV and especially visible plasmonic material that can be used widely in biosensors, nanoantennas and other plasmonic devices.

2. Simulation

Boundary element method is a numerical computational method that have been used to solve Maxwell's equations for simulation of plasmonic nanoparticles, Hohenester et al. (2012). The boundary element method attempts to use the given boundary conditions to fit boundary values into the integral equation, rather than values throughout the space defined by a partial differential equation. In boundary element method, discretization is done on interfaces between dielectrics to solve the maxwell's equations using the Green function. In this research, MNPBEM14, a Matlab toolbox, was used for simulation of the electromagnetic properties of plasmonic nanoparticles with the aim of boundary element method. All calculations were done using Palik dielectric function, Palik (1998) for Al and Al_2O_3 and dielectric function of the environment was assumed to be constant. Nanorod shape structures with different sizes were designated to investigate how much the absorption plasmon peak is capable of red-shifting to visible region of the spectrum. Oxidation of aluminum highly effect on its SPR properties therefor, influence of Al_2O_3 skin layer with different widths were studied. As a result scattering and absorption (extinction cross-section) of $Al@Al_2O_3$ nanorods with different sizes, Al_2O_3 shell thicknesses and dielectric surroundings were obtained and compared.

3. Results and discussion

3.1. Effect of aspect ratio on plasmon properties of $Al@Al_2O_3$ nanorods

First, aluminum nanorods with 3 nm diameter and different lengths without oxide layer were investigated. As shown in Fig. 1 plasmon longitudinal peak wavelength of Al nanorods with the same diameter increase monotonously from 138 nm to 213 nm with increasing the length of nanorods. When incident electromagnetic wave propagate in a direction perpendicular to nanorod axis there would be two resonance mode therefore, it is two resonance peaks for each nanorod. Longitudinal dipoles oscillate with higher wavelength than transverse ones also, the wavelength increase with rod length because dipoles are separated more distant in that case. $Al@Al_2O_3$ core-shell nanorods consist of metallic cores with 3 nm diameter and 0.5 nm Al_2O_3 oxide layer and different lengths same as Al nanorods. Likewise, in $Al@Al_2O_3$ core-shell nanorods longitudinal peak wavelength increase monotonously with the rod length.

In comparison with Al nanorods, plasmon peak wavelengths dramatically red shifted to visible region of the spectrum in core-shell structures. Plasmon peak wavelength is 307 nm for the smallest core-shell nanorod and increase to 514 nm for the largest one. Fig.2 shows extinction cross section of $Al@Al_2O_3$ core-shell nanorods. Calculations were based on the assumption that nanorods are in vacuum and dielectric functions are homogenous and isotropic.

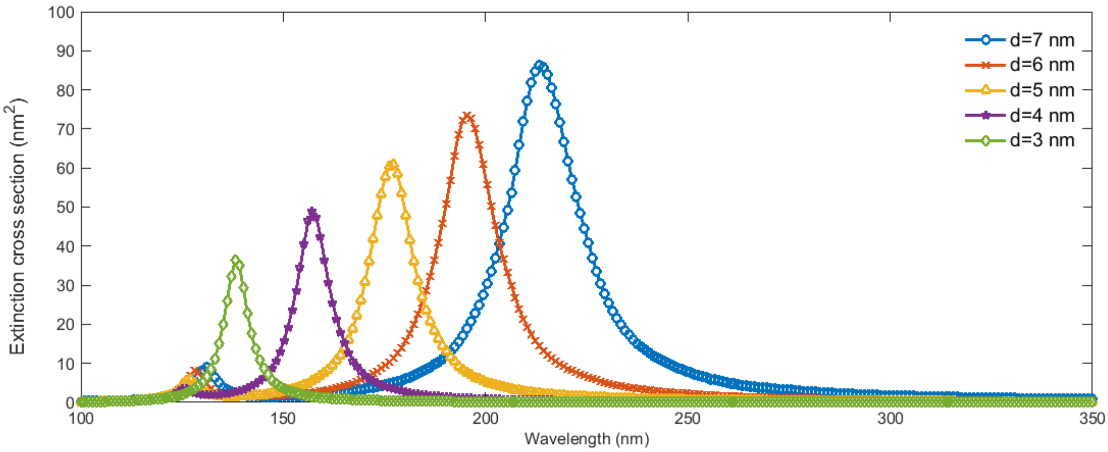

Fig. 1. Extinction cross section of Al nanorods with different diameter.

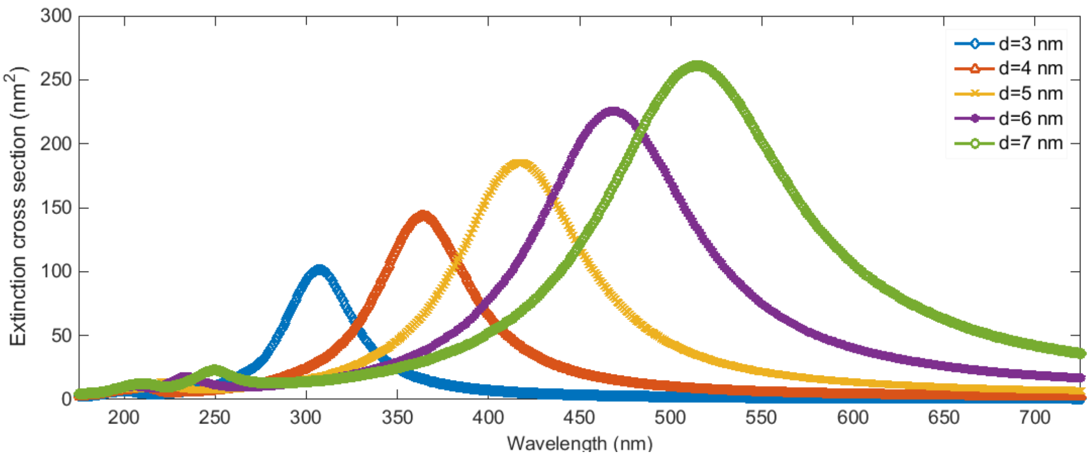

Fig. 2. Extinction cross section of $Al@Al_2O_3$ nanorods with different diameter.

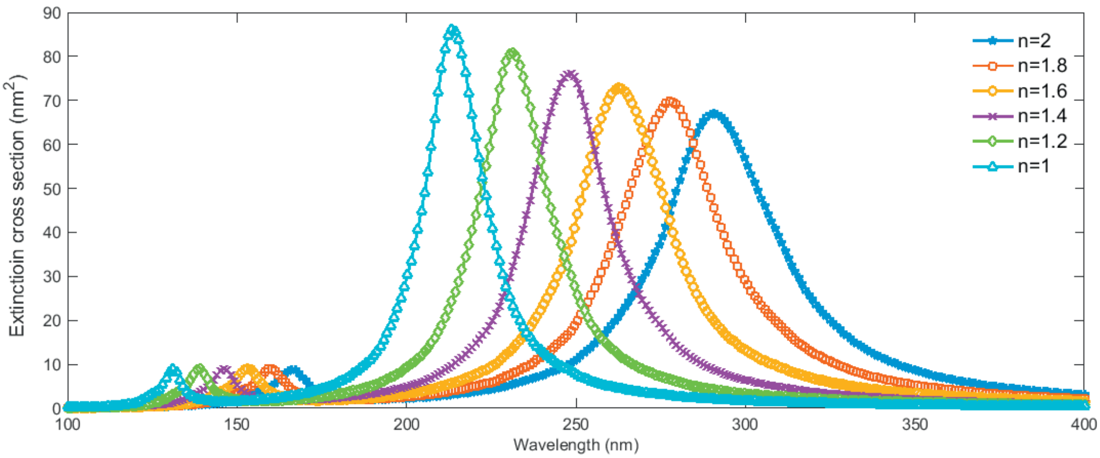

Fig. 3. Extinction cross section of Al nanorod in different dielectric media.

3.2. Effects of dielectric environment and Al_2O_3 layer

Like previous section Al nanorods were considered with and without oxide layer. To investigate the effect of medium the largest nanorod was assumed to be in environments with different refractive indexes. Fig. 3 demonstrates that in Al nanorod with 3 nm diameter and 7 nm length plasmon longitudinal peak shift to larger wavelengths with increasing the refractive index. Existence of oxide layer along with increasing refractive index causes unexpected red-shift of the peak wavelength to visible region. Fig.4 shows that peak positions increase from 510 nm to 660 nm with increasing refractive index from 1 to 2.

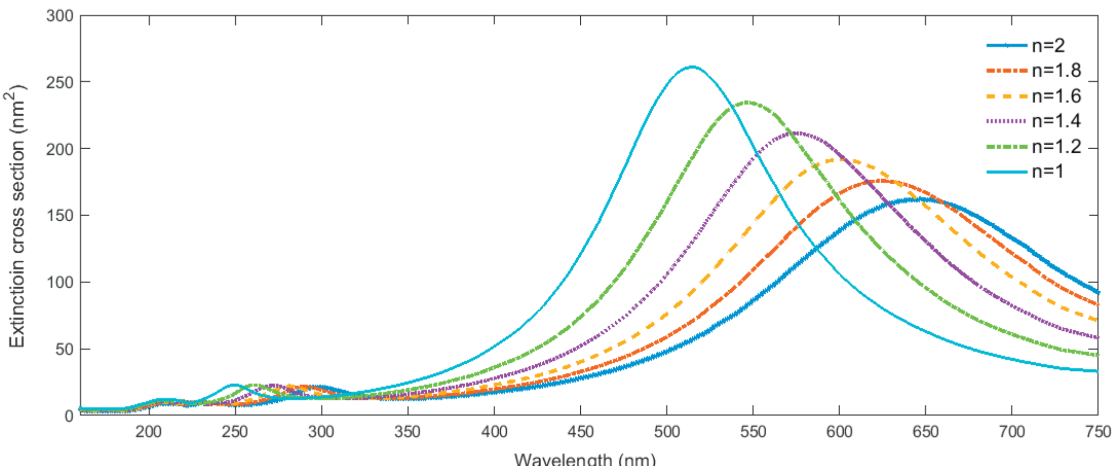

Fig. 4. Extinction cross section of Al@Al_2O_3 nanorod in different dielectric media.

Finally we investigate the effect of oxide layer thickness. Fig. 5 illustrates the result, peak wavelength red-shifted and slightly damped with increasing thickness of oxide layer. The results are for Al@Al2O3 nanorod with 3 nm metallic core, 7 nm length and different shell thicknesses. In this case resonance peaks are completely in visible region.

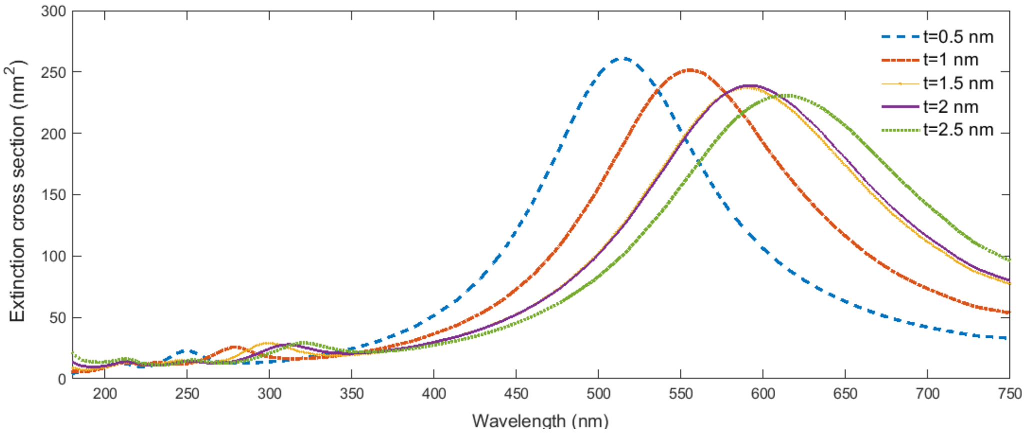

Fig. 5. Extinction cross section of Al@Al_2O_3 nanorods with different shell thicknesses.

4. Conclusion

In this research plasmon resonance properties of Al@Al_2O_3 nanorods were investigated. Effects of aspect ratio, dielectric environment and oxide layer were studied. In comparison with Ag and Au as well-known plasmonic materials Al plasmon resonance peak is much more tunable. With increasing refractive index and oxide shell thickness resonance peak wavelength red-shifted to visible region. This precise tunability of plasmonic properties in term of wavelength, low cost and abundance of aluminum enables many commercial applications of aluminum nanostructures. In addition as a new plasmonic material aluminum is capable of being suitable replacement of silver and gold nanostructures.

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