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Fabrication and Characterisation of an Adaptable Plasmonic Nanorod Array for Solar Energy Conversion

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Abstract. The surface plasmonic modes of a side-by-side aligned gold nanorod array supported on a gold substrate has been characterised by electron energy loss spectroscopy (EELS). Plasmonic coupling within the array splits the nanorods' longitudinal mode into a bright mode (symmetrically aligned dipoles) and a dark mode (anti-symmetrically aligned dipoles). We support this observation by means of finite element modelling (FEM).

1. Introduction

Metallic nanoparticles exhibit fascinating optical properties based on surface plasmon resonances (SPRs) which could aid in the design of advanced metamaterials. The field of plasmonics has received much attention due to the generation of localized electromagnetic fields with enhanced strengths and increased light absorption. With careful design of the geometry, the material and the distance between nanoparticles, a device may be engineered to enable a variety of applications including molecular detection using surface enhanced Raman spectroscopy (SERS) [1] and photocatalysis [2].

Coupling between SPRs of neighbouring nanoparticles is of interest as it can provide large field enhancements localised between the particles and dramatic shifts in resonance energy. Such a coupling-induced spectral shift has been explained theoretically within the plasmon hybridisation model [3]. This is analogous to molecular orbital theory and, for a strongly coupled nanorod dimer, this predicts two possible arrangements of the dipole moments which give rise to two coupled SP dipolar modes. For a symmetric alignment, the modes have a net dipole moment and may be excited by optical means, referred to as "bright modes". For an anti-symmetric alignment, there is a zero net dipole moment, making these modes in effect "invisible" to light and hence denoted as "dark modes". In contrast, electron spectroscopy techniques (such as EELS) are capable of probing both bright and dark modes of a nanorod array and the spatial and energy resolution achievable in modern monochromated aberration-corrected analytical electron microscopes allow the spatial distribution of these modes to be visualized. The aim of this work is both to understand the fundamentals involved in plasmonic coupling between nanorods and to investigate the design of high surface area devices based on nanorod arrays coated with thin semiconductor layers, for efficient solar energy conversion.

2. Methodology

Gold nanorod arrays (figure 1) were fabricated by electrodeposition within porous anodic aluminium oxide (AAO) templates [4]. The AAO templates were initially produced by a 2-step anodisation method whereby 0.5 mm thick aluminium (99.9999% purity) supplied by Alfa Aesar was



anodised in a 0.3M H₂SO₄ electrolyte at a voltage of 25V. This was anodised for 24 hours producing nanoscale pores that gradually ordered into a regular hexagonal arrangement with time. This first alumina layer was then selectively etched using a solution of 6wt% phosphoric acid and 1.5wt% chromium (VI) oxide at a temperature of 65°C for two hours. Although this removed the alumina layer, the remaining aluminium was textured with a highly ordered pattern from the previously grown pores. Performing anodisation a second time selectively starts the pore growth at these sites leading to an ordered array of pores that propagate vertically down through the alumina. Unreacted aluminium was then selectively etched away using a solution of 0.1 M copper (II) chloride and 6M HCl, before then also removing the insulating barrier layer by soaking the AAO in 5wt% phosphoric acid for 20 minutes. This resulted in an AAO template with ordered pores of approximately 30nm in diameter.

The nanorod arrays were grown in these pores by first thermally evaporating a 150 nm thick gold layer on the bottom of the AAO to form a working electrode. This was then placed in a three-electrode cell using a platinum wire as the counter electrode and an Ag/AgCl reference electrode. A gold electrolyte supplied by Technic Inc. (Orotemp 24 RTU) was then added and subsequently electrodeposited within the pores using an applied potential of -0.92 V versus the reference electrode. The charge passed was monitored to control the aspect ratio (AR) of the nanorods.

An electron transparent (<100 nm thick) cross-section sample of the embedded nanorod array and substrate was prepared for STEM-EELS investigations by ion beam thinning in a Gatan PIPS; the AAO template was then partially removed by etching in a 0.5M NaOH solution for 4 minutes. All EELS measurements were performed at the SuperSTEM facility using a Nion UltraSTEM 100MC “Hermes” with Nion Quadrupole-Octupole (QO) aberration corrector and a monochromated electron source. This allowed for a simultaneous sub-Angstrom electron probe size and a high energy resolution on the order of 15 meV. All EEL spectra were acquired at an accelerating voltage of 60 kV, collection and convergence angles of 44 and 31 mrad respectively and an energy dispersion of 0.01 eV per channel.

Three-dimensional finite element modelling (FEM) of optical properties was performed using Comsol Multiphysics v5.2a. A two-step approach was used whereby the solution for a p-polarised plane wave incident on a 150nm thick gold substrate was first determined in the absence of a nanorod according to Fresnel’s equations. Periodic Floquet boundary conditions were applied on each side wall in order to represent the substrate as infinite. This solution was then input as the background solution with the nanoparticle present. To simulate an infinite array of nanorods, the periodic conditions were also applied in the second solution. The refractive index of gold was taken from reference [5].

3. Results

It is well known that an isolated gold nanorod exhibits both a transverse surface plasmon mode with an oscillation over the short axis of the rod and a longitudinal mode with an oscillation over the long axis. FEM of a 30 nm diameter nanorod with aspect ratio (AR) 3 in a vacuum (not shown) predicts that dipolar plasmonic modes occur in the visible region at ca. 500 nm and 600 nm for transverse and longitudinal modes respectively; the exact position of the latter depending on rod-end geometry. FEM modelling also predicts that the position of the transverse mode is relatively insensitive to nanorod diameter, whereas the longitudinal mode is weakly red-shifted with increasing rod diameter and more strongly red-shifted with increasing rod aspect ratio, with the additional appearance of higher order (e.g. quadrupolar) modes for high AR rods at shorter wavelengths. When stood vertically on a gold substrate, coupling between the nanorod and its substrate image in the metallic film induces a strong red-shift of the longitudinal mode, analogous to coupling seen in an end-to-end configuration of nanorods [3].

In addition to the particle-substrate coupling, nanorod dimers have also been shown to couple if the separation is sufficiently small [6]. Based upon plasmon hybridisation theory, this coupling is predicted to result in the splitting of the longitudinal mode into both a bright and dark coupled mode. For side-by-side aligned nanorods, the dark mode is calculated to occur at lower energy and has an anti-symmetric alignment of the dipole moments leading to an attraction of the surface plasmons. On the other hand the bright mode occurs at higher energy and has a symmetrical alignment of the dipole moments and therefore the surface plasmons are expected to repel.

Experimental EEL spectra and corresponding spectrum image (SI) maps for a gold nanorod dimer stood vertically on a 150 nm thick gold substrate are shown in Figure 2. Although only two nanorods are shown, these formed part of a much longer nanorod array. The nanorods have a diameter and aspect ratio (AR) of approximately 30 nm and AR=3 respectively and are separated by approximately one nanorod diameter. As stated above, single unsupported nanorods of an equivalent size would exhibit a longitudinal dipolar plasmonic mode in the visible region (~600 nm). However, EELS measurements show a red-shifted mode occurring at a much higher wavelength of 1348 nm (0.92 eV) owing to both coupling with the substrate and between the nanorods. Analysis of the SI map for this energy range suggest that this mode is indeed related to the dipole mode due to the energy loss being localized towards the end of the nanorod (Figure 2b). Furthermore, the SI map of the nanorod dimer shows that the energy loss is localized towards the dimer gap suggesting that coupling between the nanorods is present and is related to the attractive dark mode. However, according to the plasmon hybridisation theory, splitting of the longitudinal mode should result in an optically bright mode in addition to the dark mode discussed above. Based upon the rod centre-to-centre separation distance, this splitting of the mode would be fairly symmetrical due to dipolar interactions being dominant [7]. This would mean a corresponding blue-shift of the bright mode of a similar magnitude to that seen for the red-shift of the dark mode (with respect to the non-hybridised longitudinal mode). The EEL spectrum in Figure 2a exhibits three peaks at higher energies than the dark mode. The mode at 2.33 eV (~530 nm) is the transverse mode, whereas the peak at 1.41 eV (880 nm) appears to be related to a defect in the right-hand nanorod, where a sharp gap is formed. The mode at 1.96 eV (~630 nm) however is distributed towards the base of the nanorods, as shown in Figure 2c. Although the 1.96 eV (~630 nm) mode has a similar field distribution to that of a quadrupolar longitudinal mode, FEM simulations detailed below suggest that this relates to the bright mode of the supported array.

FEM was performed for both individual and infinite arrays of gold nanorods supported on an Au substrate and excited by a p-polarised plane wave (exciting longitudinal bright modes). Modelling individual nanorods in the array when supported on a substrate but without any inter-rod coupling, the resonant energy of the longitudinal mode is predicted to occur at ca. 1000nm. As the dark mode seen with EELS actually occurs at 1348nm, symmetrical splitting of the two coupled modes suggests that the bright mode would then be expected to occur at ca. 650nm, in agreement with experimental observations. Additionally, modelling the nanorods within an infinite array shows a redistribution of the electric field from the ends of the nanorod to a localisation of the bright mode towards the base of the nanorod (Figure 3a). This occurs as the inter-particle spacing is reduced (coupling strength increased) and is concurrent with a blue-shift and reduction in intensity of the plasmon mode (Figure 3b). These results support the conclusion that both the bright and dark modes arising from coupling within a supported nanorod array have been characterized and visualized at high spatial resolution by EELS, providing insight that can aid in the development of efficient solar device applications. Ongoing FEM modelling includes the incorporation of excitation by an electron probe rather than a plane wave, allowing simulation of both bright and dark modes.

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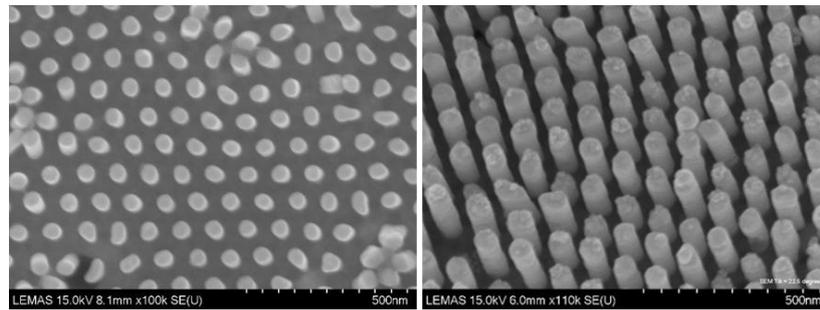


Figure 1. SEM images of a gold nanorod array grown via electrodeposition within AAO templates for a top down view (left) and tilted view (right).

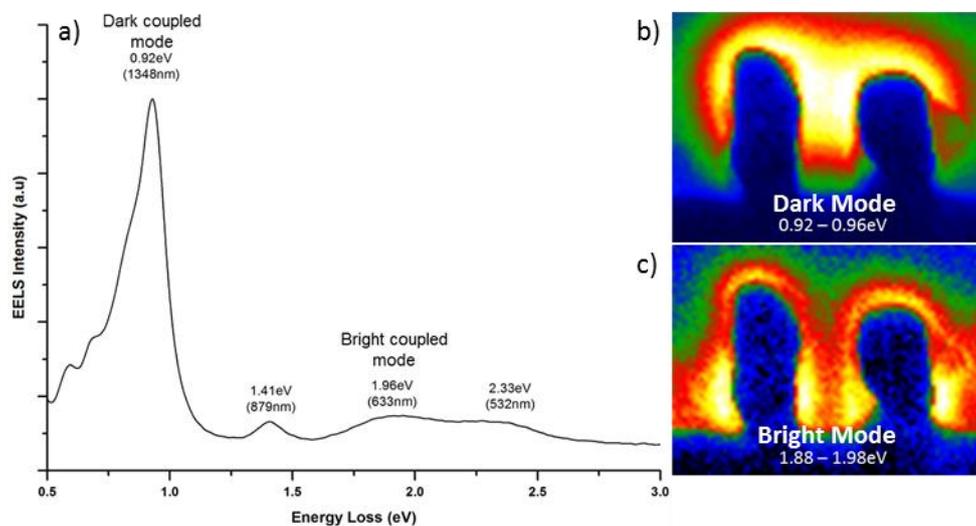


Figure 2. a) EELS spectrum for an Au nanorod dimer obtained from integrating over all the pixels in the corresponding SI. b) SI map of the dark and c) bright mode over stated energy windows.

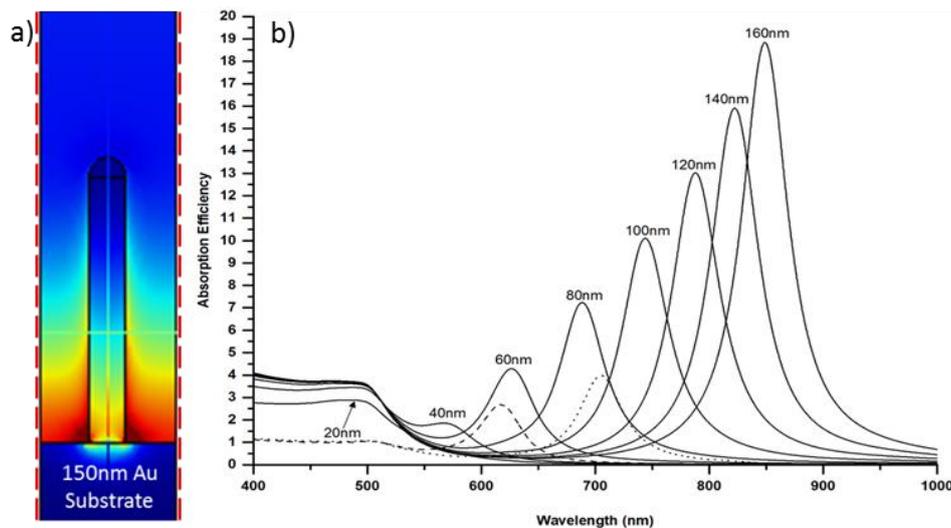


Figure 3. a) Simulated electric field distribution for the bright mode of a supported Au nanorod array (AR=7). Red-dashed lines indicate periodic boundary conditions. b) Blue-shift and reduced absorption efficiency of the bright mode with decreasing inter-rod spacing for an AR=3 supported nanorod array; dashed (AR=3) & dotted (AR=4) lines show results for single unsupported nanorods.