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Enhanced Sensitivity of Delocalized Plasmonic Nanostructures

Madu N. Mendis, Himadri S. Mandal, and David H. Waldeck*

Department of Chemistry, University of Pittsburgh, 219 Parkman Street, Pittsburgh PA 15260, USA

Abstract

This work reports on the observation of a delocalized surface plasmon resonance (DSPR) phenomenon in linear chains of square-shaped silver nanoparticles (NP) as a function of the chain length and the distance between the nanoparticles in the chain. Transmission spectra of the silver nanoparticle chains reveal the emergence of new, red-shifted extinction peaks that depend strongly on the spacing between the nanoparticles and the polarization of the exciting light with respect to the chain axis. As the spacing between the nanoparticles in the linear chain decreases and the number of nanoparticles in the linear chain increases, the strength of the new extinction features increase strongly. These changes can be described by a tight-binding model for the coupled chain, which indicates that the origin of the phenomenon is consistent with an increased coupling between the nanoparticles. FDTD calculations reveal that the electric field is strongly enhanced between the nanoparticles in the chain. The DSPR response is found to be much more sensitive to dielectric changes than the localized surface plasmon resonance (LSPR).

Keywords

Nanoparticle Chains; Plasmon; FDTD; LSPR; Nanoparticle Coupling

1.0 INTRODUCTION

Nanoparticle (NP) based plasmonic sensors offer great promise for deploying miniature, multiplexed, and label free detection platforms.^{1–3} The general working principle for this particular class of sensors is a shift in the localized surface plasmon resonance (LSPR) peak upon a change in the dielectric properties of the surrounding medium, for example, the adsorption of molecules on the surface of the NP.^{1–3} Over the past decade, numerous reports have described different strategies for improving the sensitivity of these sensors by changing the size^{4,5}, shape^{4,6–15}, aspect ratio^{5,12,16}, and material composition⁴ of the NP. Despite these efforts, the molecular sensitivity is still generally limited to a few nm peak shifts.^{1,14,17–22} Even though recent developments^{23–26} in the field have contributed to improved sensitivity of these sensors, the search still continues for novel platforms based on

*Corresponding Author: dave@pitt.edu.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors.

SUPPORTING INFORMATION

The Supporting information provides 1) a schematic of the EBL fabrication procedure for the square nanoparticle chains (Figure S1), 2) a comparison of the experimental and FDTD calculated transmission spectra for an Ag square nanoparticle array (Figure S2), 3) a distance dependence of the DSPR peak area (Figure S3), 4) the FDTD calculated electric field intensity around nanoparticles under transverse polarization (Figure S4), 5) the distance dependence of the coupling constant A that results from FDTD calculated transmission spectra of square nanoparticle chains (Figure S5), and 6) the ellipsometric thickness of alkanethiol self-assembled monolayers on Ag films (Figure S6). This information is available free of charge via the Internet at <http://pubs.acs.org>

these plasmonic NPs that exploit their exceptional sensitivity to perturbations in local environment for the detection of molecular and/or biomolecular events.

Clusters of NPs in close proximity exhibit a unique set of collective plasmon modes, which can be described through a superposition of plasmon modes excited on individual NPs in the assembly.^{27–31} This topic has gained much interest in recent years because of the rich phenomena that these coupled oscillators can display, such as electromagnetic transparency and Fano resonances.^{30,32,33} The dependence of the optical response of these coupled structures on local perturbations, such as a change in the local dielectric constant and symmetry-breaking, has spurred new promise for their use in applications, as compared to uncoupled systems.

Linear chains of NPs provide a useful platform for exploring the coupling of plasmonic metal NPs, and one dimensional NP chains have been studied for their use as waveguides in nanoscale energy transfer.^{27,29,34–37} In addition, NP dimers (or nanoparticle junctions) have been used to demonstrate single molecule sensitivity for SERS applications.^{38,39} Many studies have taken a top-down fabrication approach with precise size and gap control of the NP pairs/chains.^{27,40–49} Computational studies and far-field spectroscopic studies on one-dimensional metal NP chains show that the resonance wavelength of the longitudinal mode increases with the increasing chain length in comparison to that of a single NP, and this resonance wavelength shift plateaus with the increasing number of NPs in the chain.^{40,41,50–53} The optical properties of metal NP chains are not only dependent on the particle size⁵⁴, shape⁵⁵, and material composition⁴⁶ but also on the inter-NP distance^{29,43,47,48,50–52} and the number of NPs^{35,41,46,50–52} in a given chain. As we discuss, these phenomena indicate that the plasmon modes delocalize along the NP chain.

Despite the body of work regarding the coupling between NPs in linear chains, the use of their coupled resonances for sensing dielectric changes is largely unexplored. In this work we systematically investigate the generation of collective plasmon resonances of one-dimensional square NP chains, termed a delocalized surface plasmon resonance (DSPR), and examine its sensitivity to dielectric changes. A simple tight-binding model is applied to the experimental data for the DSPR energy as a function of chain length, and it is used to extract a coupling constant between the NPs in the chain and examine its dependence on the inter-particle spacing. The inter-particle distance dependence of the plasmonic interaction of these NP chains and its sensitivity to the environment's dielectric constant are examined. These latter findings show that it is possible to use the coupled modes to obtain resonance peak wavelength shifts from molecular adsorbates that are much larger than the shifts observed for individual NPs.

2.0 EXPERIMENTAL

Fabrication of Square NP chains

Electron beam lithography (EBL, Raith e-Line) was used for the fabrication of square Ag NP ($170 \times 170 \text{ nm}^2$, and 50 nm thick) arrays ($30 \times 30 \mu\text{m}^2$). The steps involved with the fabrication are summarized in Figure S1 in the supporting information section. Conductive indium tin oxide coated glass slides (ITO) (Delta's Technologies) were used as the substrates to minimize charging during the fabrication. ITO substrates were rinsed using three solvents: acetone, methanol and iso-propanol; ultrasonication was performed in each solvent for 5 min. The ITO substrates were then rinsed with deionized water and dried with a N_2 gas stream. These substrates were baked at 180°C for 2 min to remove any moisture from the surface. Poly-methyl-methacrylate (950k A4 PMMA, MicroChem) was spun on the substrate at a speed of 1500 rpm for 40 s using a spin processor (Laurell WS-400-6NPP-LITE) and baked on a hot plate at 180°C for 5 min. E-beam writing was performed at an

acceleration voltage of 20 keV and with an exposure dose of $300 \mu\text{C}/\text{cm}^2$ using a $7.5 \mu\text{m}$ aperture to write the NP chain pattern on PMMA. The sample was then developed for 90 s in a developing solvent consisting of methyl isobutyl ketone and isopropanol in a 3:1 ratio to dissolve the exposed PMMA. Then silver (Ag) was evaporated onto this sample to a thickness of 50 nm, along with 3 nm of titanium to help the Ag to better adhere to the substrate. The rate of evaporation was maintained at $0.2 \text{ \AA}/\text{s}$ to allow smooth deposition of the metal. After the metal deposition, the samples were kept overnight in acetone to remove the remaining PMMA resist.

Sample Characterization

Sample imaging was done using an SEM in the EBL system. The acceleration voltage was chosen to be 4 keV. Spectral characterization of the square NP chains was carried out using a microspectrophotometer (Craic QDI 2010). A linear broadband polarizer (Glan-Taylor) which was placed in between the sample and the condensor (Figure 1) was used to polarize the light for excitation of transverse and longitudinal LSPR modes. Spectra were collected using a $15\times$ objective in a $20 \mu\text{m} \times 20 \mu\text{m}$ square aperture and a plane $20 \mu\text{m} \times 20 \mu\text{m}$ area of the ITO substrate was used as the reference

Self-assembled Monolayers Formation

1-pentanethiol (C5), 1-octanethiol (C8), 1-decanethiol (C10), 1-dodecanethiol (C12), 1-hexadecanethiol (C16), and 1-octadecanethiol (C18) were obtained from Sigma Aldrich and used for the experiment without further purification. Self-assembly of the alkanethiol monolayer was carried out in a 1 mM solution of alkanethiol in absolute ethanol. The chips were thoroughly washed with copious amounts of ethanol to remove any impurities. Samples were incubated in each alkanethiol solution overnight to form a well-packed SAM. Transmission spectra of the square NP chain arrays were recorded before and after SAM preparation using the microspectrophotometer to determine the peak shifts.

Finite-difference time-domain (FDTD) simulations

Simulations were conducted using the FDTD method (Lumerical Solutions, Inc.). A three-dimensional (3D) FDTD method was used to accurately calculate the light transmission, electric field intensity profiles, and charge distribution profiles of the silver NP chain arrays. The NP chains consist of $170 \text{ nm} \times 170 \text{ nm}$ square NPs with a thickness of 50 nm. Edge rounding of the square NPs was done with a 5 nm radius cylinder so that they better resemble the experimentally realizable NPs. The NP clusters were simulated on an infinite substrate represented by dielectric constants extracted from Palik data for silicon dioxide.⁵⁶ In all the simulations, a uniform mesh with 1 nm in all directions was used for the silver NPs and a non-uniform mesh was used elsewhere. The boundary conditions in the plane of the structures (i.e. the x and y direction) were chosen to represent an infinite square array. The boundary in the z direction was set to contain a perfectly matched layer absorbing boundary condition. The structure was illuminated using a normally incident broadband plane wave source from the substrate side, with the polarization direction either parallel or perpendicular to the chain axis to excite longitudinal or transverse plasmon modes, respectively. A 2D monitor was used to collect and record the transmission data whereas 3D monitors placed around the NPs were used to collect field profiles. The permittivity of silver was modeled using data from Palik.⁵⁶ The edge-to-edge separations between two nearest neighbor NP chain clusters were maintained to be 1000 nm both in the x and the y directions.

3.0 OPTICAL RESPONSE OF NANOPARTICLE CHAINS

This section discusses the dependence of the observed transmission spectra on the nanoparticle chain properties and compares these experimental findings to the FDTD

simulation results for linear NP chains. In addition an analytical formula based on a tight binding model is used to describe the dependence of the DSPR on the chain length and to extract an interparticle coupling strength.

Dependence on Distance between NPs in Chain

Square NP chains were fabricated by changing the interparticle distance (d) systematically from 130 nm to ~30 nm ($d = 830$ nm, 130 nm, 105 nm, 80 nm, 75 nm, 58 nm, 47 nm, and 36 nm). Figure 2 shows transmission spectra for a square NP tetramer chain as a function of the inter-particle spacing, d , under longitudinal polarization of the incident light. All the spectra are normalized to the number of NPs in the field of view under the aperture to remove any effect from a change in the NP density.

When isolated by a large interparticle separation (the case of $d = 830$ nm, edge to edge, in Figure 2), the NP chain shows an extinction spectrum that has a main LSPR peak, λ_{LSPR} , at ~ 811 nm, a less intense peak around ~ 450 nm, and no peak in the near IR region. The FDTD calculated transmission spectrum (see supporting information Figure S2 (a)) of an isolated nanoparticle also exhibits two distinct peaks, with peak positions slightly to the blue as compared to the experimental transmission spectrum. The difference between the experiment and the calculation may arise from the underlying ITO film in the samples as well as fabrication defects. The FDTD results (see supporting information; Figure S2 (b)), show that the ~ 811 nm peak has its electric field intensity concentrated towards the substrate side and the ~ 450 nm peak has its electric field intensity predominantly on the vacuum side. As discussed elsewhere for nanocubes, these modes likely result from a mixing of dipolar and quadrupolar modes of the silver NPs and the symmetry breaking induced by the substrate.^{11,57,58} Note that the additional small features in the transmission spectrum of the NPs may arise from diffractive coupling mediated through the substrate and air media, however the discussion of these is beyond the scope of the current study. As the interparticle separation is reduced from 830 nm to 80 nm along the polarization direction of the excitation light, the growth of a shoulder on the extinction peak appears; the magnitude of this shoulder increases with a further reduction of the interparticle separation to 58 nm. At separation 36 nm, this shoulder has evolved into a well-defined peak of its own. It is this new red-shifted spectral feature that we refer to as the DSPR. In connection with the growth of the DSPR peak, the LSPR peak of the individual NPs decreases in amplitude. Note that the peak area under the LSPR peak reduces and the area under the DSPR peak grows rapidly with decreasing inter-particle distance. This observation reveals a shift in the oscillator strength of the plasmon resonance of the NPs from the LSPR to the DSPR as the NP spacing decreases. (The peak area under the DSPR plotted against the inter-particle distance for a four NP chain is shown in Figure S3, supporting information.)

Dependence on the Number of NPs in the Chain

The strength and position of the DSPR extinction feature also depends on the number of NPs in the chain. Figure 3(b) and 3(c) show transmission spectra for NP chains ($d \sim 36$ nm) comprised of 2, 3, 4, 5, and 7 NPs for two different light polarizations, longitudinal and transverse, with respect to the chain axis. The raw spectra again have been normalized by the number of NPs in the field of view. As the number of NPs in a linear chain increases, the DSPR peak that is observed under longitudinal polarization shifts to longer wavelength. Figure 3(d) plots the wavelength at which the DSPR extinction is a maximum, λ_{DSPR} , as a function of the number of NPs in the chain. The λ_{DSPR} was determined by first subtracting the transmission spectrum of an isolated NP from that of the NP chain, and then assigning the peak maximum.

From Figure 3(b) it can be observed that under longitudinal polarization the maximum of the extinction shifts strongly to the red with an increase in the number of NPs in the chain. However, this shift attenuates as the chain length grows and is nearly saturated for chains of six or more NPs. A similar observation has been reported for strongly coupled linear chains of spherical NPs.⁵⁰ These spectra also reveal that the DSPR absorbance width broadens as the number of NPs in the chain increases. Broadening of the resonance peak when strong near field coupling occurs has been reported previously and has been attributed to increased radiative damping and excitation of dipole-like modes.^{50,53}

Figure 3(c) show the corresponding transmission spectra under transverse polarization. These spectra show only an LSPR signal, and no significant shift for chains of two or more NPs. Note that a small blue shift as compared to the case of isolated NP is indicated; see Figure 4(c) and (d). According to the dipole coupling model, a blue shift of the resonance wavelength arises from repulsion between the induced surface charges on neighboring NPs under the transverse polarization conditions, and this behavior has been reported previously.^{27,50} Also note the large drop in peak area on proceeding from one NP to two NPs, which is consistent with a dipole-dipole coupling picture for this excitation geometry.⁵⁹ For transverse polarization, the NP chains exhibit no significant changes in the resonance wavelength with changing interparticle spacing. It should be noted that defects during fabrication give rise to slight differences in the width and the length of the square NP (ie., the NPs are not perfectly square), and this causes differences in resonance wavelengths for a single NP when the polarization direction is changed; see the case of a single NP in Figure 3(d).

Overall, the extinction per NP is higher in the chains than for isolated NPs under longitudinal polarization. To clearly observe this trend the area under the DSPR peak, which was integrated over energy (eV) and normalized per number of NPs in the field of view, was calculated for NP chains at a 36 nm inter-NP distance and is plotted in Figure 3(e). The area under an extinction peak is proportional to the oscillator strength for the particular transition(s); hence the plot in 3(e) shows how the oscillator strength of the visible and near-IR modes change for plasmonic NP chains of different length. From Figure 3(e) it is evident that the peak area per NP increases systematically as the chain length increases and then saturates as the number of NPs in the chain reaches about six. This chain length coincides with the length for which the DSPR resonance wavelength shift saturates. These observations suggest that the delocalization length of the DSPR excitation is about six NPs for the chains with 36 nm interparticle distance.

FDTD Simulations of NP Tetramers

To gain more insight into the origin of the spectral features, finite-difference time-domain (FDTD) simulations were conducted on a tetramer chain of square NPs to extract the electric field intensity enhancement ($|E|^2/|E_0|^2$) profile at the DSPR excitation wavelength for the case of light polarized along the NP chain. These simulations show that both the intensity and extension of the electric field between the NPs increases as the inter-NP separation decreases; see Figure 4(a). The electric field intensity in the middle of the gap between the NPs is plotted in Figure 4(b). These findings are consistent with those reported for NPs in close proximity^{60,61} for which the field strength is enhanced between the NPs. However, under transverse polarization the FDTD calculations indicate that no significant electric field enhancement occurs in the gap region between the NPs. (see Figure S4 in supporting information). These observations suggest a correspondence between the enhanced electric field in the inter-particle areas and the experimentally observed DSPR peak for the NP chain. The enhanced electric field in the region between the NPs enhances the coupling among the individual NPs and points to a coherent/collective plasmonic oscillation (with a

macro-dipole) extended through the NP chain; i.e., a delocalized surface plasmon resonance (DSPR).

Tight-Binding Model for NP Chain

A simple tight-binding approach (or Hückel model) can be used to rationalize the observations and to provide a semi-quantitative understanding of the coupled NP system.⁶² In this model, only nearest neighbor coupling between the NPs is considered and the coupling strength is described by a parameter A . Using this approach for N NPs in a chain, one finds that the eigenenergies E are given by

$$E = E_0 + 2A \cos\left(\frac{m\pi}{N+1}\right) \quad \text{Eqn(1)}$$

In Eqn 1, E_0 is considered to be the resonance energy of a single NP and m is a mode number. For a fixed value of A , the resonance energy E of the NP chain decreases, and it asymptotically approaches a value of $E = E_0 + 2A$ for an infinitely long NP chain ($N \rightarrow \infty$). This behavior is consistent with the spectral observations for a chain of square NPs under longitudinal polarization; the resonance wavelength of the DSPR peak systematically red shifts towards a limiting value as the number of NPs in the chain increases. Equation 1 also predicts that the resonance energy E should decrease, as the coupling constant A increase at a fixed value of N . This prediction is consistent with the systematic red shift that is observed for the DSPR as the inter-particle distance is reduced at a fixed number of NPs in the chain (see Figure 2(a)).

The plots in Figure 5 for the NP chains with a 36 nm spacing show that Equation 1 describes the experimentally obtained data well. Figure 5 shows the experimentally determined DSPR peak energy as a function of the number of NPs in the chain. The value of E_0 is taken to be the resonance energy of the single NP array, in which the NPs are separated by 830 nm. The red line indicates the best fit by Equation 1 which yields a coupling constant of -0.25 eV under longitudinal excitation of the NPs. In the fit, the mode number m was assumed to be one which indicates an in-phase excitation of all NPs in the chain. Other mode numbers correspond to different resonances in the system, which may or may not be excited by direct light illumination, but they would be higher in energy than the $m=1$ mode. When light is transverse polarized, no DSPR peak is observed. If one fits the resonance energy of the main transmission dip by Equation 1, a small coupling constant of $+0.016$ eV is extracted (Figure 5). These parameters indicate that the NP chains exhibit significant coupling under the longitudinal polarization, but a negligible coupling under transverse polarization.

Distance Dependence of the NP Coupling

Two different regimes of coupling and its distance dependence have been distinguished for arrays of NPs. For the inter-NP distances on the order of the wavelength of light, far field diffractive coupling with an inverse distance dependence dominates; they can affect the spectral line shape.⁶³ For the interparticle distances that are comparable to the NP size or smaller, near field interactions are important. Brongersma *et al.*^{27,29} report an inverse distance-cubed (center-to-center distance between two adjacent NPs) dependence for the plasmon peak energy of 50 nm diameter NPs at distances of 75 nm to 125 nm, which is consistent with the predictions of the point dipole model. In a simulation study using the T-matrix method, Harris *et al.*⁵² have reported an inverse distance dependence for the wavelength shift of nanosphere chains at very small gap separations, and this behavior is compared to the van der Waals interaction between spheres at very short interparticle distances.⁶⁴ A number of works^{43,47,48} report an exponential decay in the peak shift ratio

with increasing inter-particle gap scaled by the NP size for the longitudinally coupled plasmon between two NPs. This relationship was reported to yield a universal decay constant irrespective of NP shape, size, material or the type of resonance giving rise to the 'plasmon ruler equation'⁴³:

$$\frac{\lambda - \lambda_0}{\lambda_0} = \alpha \cdot \exp\left(-\frac{d/L}{\tau}\right) \quad \text{Eqn 2}$$

in which λ is the resonance wavelength of the NP dimer, λ_0 is the resonance wavelength of an isolated NP, d is the inter-particle spacing between the NPs in the dimer, and τ is the characteristic decay constant. In order to explore the effect of the inter-NP separation on the DSPR, the resonance energy was compared with these existing models.

Figure 6(a) shows a plot of the natural logarithm of the DSPR peak wavelength shift ratio ($\frac{\lambda - \lambda_0}{\lambda_0}$) versus d/L , the ratio of the interparticle distance (d) to the length (L) of the square NP. For each chain length the data display a linear behavior, and it is possible to extract the decay constant and maximum fractional wavelength shift from the slope and the intercept of the best fit line; see Figure 6(a). Figure 6(b) shows how the fractional wavelength shift and its characteristic decay constant depend on the NP chain length. The data in Figure 6(b) indicate that the decay constant for two square NP chain is around 0.58 ± 0.2 , which is much larger than what has been found for coupled Au disks (~ 0.2).⁴³ From Figure 6(b) it is evident that the decay constant increases for a three NP chain as compared to a two NP chain, and then decreases with further increase in the chain length until it plateaus at about 0.8 ± 0.1 . This high value may reflect a shape dependence of the decay constant as suggested by Tabor *et al.*⁶⁵, a dependence on the material response (Ag vs Au), or a combination of the two. This observation suggests the existence of very strong near neighbor coupling in square shaped NP chains.

Different functional forms were used to evaluate the effect of the interparticle distance on the coupling constant A , which was obtained from fits of the data by Equation 1; see Figure 7(a). Figures 7(b) through 7(d) show different functional relationships for the decay of A with the interparticle separation. Because some previous works have predicted that a power law function should exhibit a good fit for strongly coupled plasmonic systems,^{66–69} a log-log plot of the coupling constant versus the inter-NP distance was performed; see Figure 7(b). As the inter-NP distance increases the numerical value of the coupling constant decreases, and its fall-off can be described by a power law of the form $A \propto d^{-0.42}$. In order to further investigate these results FDTD calculations were performed to obtain the transmission spectra of NP chains of different gap separations. The transmission spectra were fitted by a Breit-Wigner-Fano lineshape⁷⁰ in order to deconvolute the DSPR peak and extract its wavelength position; then Equation 1 was used to obtain the coupling constant A . A log-log plot of these coupling constant A values and the inter-particle distance d exhibit a relationship of, $A \propto d^{-0.3}$ that is similar to the experimental data. (see Figure S5 in supporting information).

Figure 7(c) shows a plot of the log of the coupling constant versus the log of the center-to-center distance, and a fit (red curve) by an equation of the form $A \propto (L+d)^{-x}$, where now $(L+d)$ is the center-to-center separation between two NPs. If a simple point dipole model was appropriate, then one expects to find a slope of -3 , which is represented by the dashed line and clearly gives a poor fit. From the slope of the best fit line a value of -1.5 is extracted for the exponent; *i.e.*, the coupling constant has a $(L+d)^{-1.5}$ distance dependence. The fact that the distance dependence deviates from the point dipole prediction is not surprising, as the gaps studied here are small compared to the size of the NP. These observations demonstrate

that the extended nature of the charge distribution is important to consider for these large non-spherical NPs.

Figure 7(d) shows a plot of the $\ln(-A)$ versus distance, and a fit to an exponential decay dependence. The single exponential decay fit gives a slope of -0.0058 nm^{-1} , indicating a characteristic decay length of $\sim 172 \text{ nm}$; or if it is scaled by the NP length of 170 nm it is ~ 1.0 . FDTD simulations (see Figure S5(b)) are in good agreement with this result. All these analyses suggest that the coupling between square NPs in these one dimensional chains is much stronger than that reported for dimers and chains of other shaped NPs.

4.0 EFFECT OF SAM ON NP CHAIN OPTICAL RESPONSE

Given that the localized surface plasmon resonance (LSPR) of NPs is strongly dependent on molecular adsorbates⁷¹, the sensitivity of the DSPR's peak wavelength to an adsorbed molecular film was tested by forming alkanethiol self-assembled monolayers (SAMs) of different lengths on different square NP chains.

Figure 8(a) shows the normalized transmittance spectrum for an array with $d = 830 \text{ nm}$ LSPR mode that is untreated and compares it to that for Ag NPs that are coated with a dodecanethiol SAM. Analysis of the two spectra shows that the SAM shifts the peak wavelength by $\sim 11 \text{ nm}$ to the red. Figure 8(b) shows the transmission spectra of a six nanoparticle chain with $\sim 30 \text{ nm}$ interparticle distance (corrected for the NP density) after modifying the metal NP surface with different chain length alkanethiol SAMs. The transmission spectra display very large red shifts in the DSPR wavelength that depends on the length of the alkyl chains of the SAM and are much larger than that found for the isolated NPs in Figure 8(a). For example, when the NP chains were chemically modified by a 1-dodecanethiol SAM, the six NP chain ($d = 30 \text{ nm}$) showed a shift of 115 nm , as compared to the $\sim 11 \text{ nm}$ shift in Figure 8(a). The ellipsometric thickness calculated using the SAM prepared on plain Ag films prepared in the same manner shows that the coverage lies in the expected range (Figure S6).

Figure 9 shows a plot of the SAM induced λ_{DSPR} shift versus the NP chain length ($d = 30 \text{ nm}$), where the shifts were extracted from transmission spectra of the arrays before and after SAM modification. It is evident that when the number of NPs in the chain increases the resonance wavelength shift increases for a given alkanethiol SAM thickness.

The resonance wavelengths of the SAM coated chain arrays were analyzed by using Eqn 1. The coupling constant A was found for the NP chain arrays without a SAM (A_{Air}) and with a SAM (A_{SAM}), and they are tabulated in Table 1 for different alkanethiol chain lengths. It can be noted that even though the samples are fabricated using the same procedure, the coupling constant A_{Air} varies between the different devices. It is assumed that these differences arise from variations in the fabrication, i.e. – changes in NP size and inter-NP distance. The parameter values in Table 1 show that the coupling constant, A , increases after SAM formation by about 10%.

Enhancement in the electromagnetic coupling between metal NP dimers with an increase in dielectric constant of the medium near the NP surface has been reported in few previous studies,^{72,73} and it has been attributed to a reduction in the coulombic restoring force acting on the electrons. That is, as the medium dielectric constant increases, the induced polarization in the NP increases resulting in an increased dipole moment for the NP. The larger dipole should lead to a larger interaction energy between the NPs, even though the increased dielectric constant would act to shield some of this interaction. This mechanism for the enhanced coupling in the presence of a SAM can account for the enhanced sensitivity of the DSPR to molecular adsorbates.

5.0 CONCLUSION

In this work, the optical response of one dimensional chains of square shaped NPs fabricated using electron beam lithography have been investigated and compared with an analytical model. It was shown experimentally that under longitudinal polarization and at short interparticle distances the chains exhibited a delocalized surface plasmon mode (DSPR). For a given interparticle distance, it was observed that the wavelength position of the DSPR initially red shifts with increasing number of NPs in the chain and reaches an asymptotic value. The application of the plasmon ruler equation to the square NP dimer gave rise to a longer characteristic decay constant than is reported for spherical or disk shaped NPs. This difference may reflect the influence of NP shape on the plasmon coupling.

An analytical expression based on a tight binding model was used to obtain a coupling constant for the interparticle coupling strength from the observed spectral shifts. The coupling constant displayed an $\sim d^{-0.42}$ distance dependence over the range of interparticle distances studied here. This distance dependence is much stronger than that predicted by a point dipole model or van der Waals interaction models for different shaped NPs.

The sensitivity of the DSPR wavelength for molecular absorbates was found to be larger than that previously reported for LSPR modes of individual NPs and NP dimers; thus the large redshifts in the peak wavelength position of NP chains is a promising sensing strategy.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Sketch of optical set-up used during the optical characterization of the samples. The yellow lines indicate the light pathway.

Figure 2.

a) The transmission spectra of a square nanoparticle tetramer chain are plotted for different inter-particle separations. b) SEM images are shown for five of the square NP tetramer chains in panel A. The scale bar is 400 nm.

Figure 3.

Panel a) shows the SEM images for square nanoparticle chains (the scale bar is 1000 nm). Panel b) and c) shows the evolution of transmission spectra of those chains under b) longitudinal and c) transverse polarization, collected in air. d) The wavelength maximums of the DSPR are plotted against the NP chain length (see text for details). The error bars in these peak wavelength positions are smaller than size of the symbol e) The DSPR peak area normalized per NP is plotted versus the NP chain length. The red dashed line is given as a guide to eye.

Figure 4.

a) Electric field intensity enhancement ($|E|^2/|E_0|^2$) profiles are shown for a four NP chain with three different nanoparticle separations (d). The direction of the light polarization is parallel to the major axis of the clusters. The scale bar ranges from an amplitude of 0–700. b) The electric field intensity at the x-y center of the cluster is plotted against the inter-particle distance. The red dashed line is given as a guide to eye.

Figure 5.

The resonance energy maximum of the D SPR is plotted versus the number of NPs in the chain under longitudinal (■) and transverse (□) polarization; the red line shows a fit to the data by Equation 1. This analysis is for a 36 nm fixed inter-particle distance.

Figure 6.

(a) The scaled DSPR wavelength shift ratio is plotted versus the scaled gap ratio for different chain lengths of square NP chains. The slope of the best linear fit for each chain length provides the decay constant and these values are plotted in panel (b).

Figure 7.

(a) The resonance energy maximum of the DSPR is plotted versus the number of NPs in the chain under longitudinal polarization for different inter-particle distances, similar to panel 6(a), to obtain a coupling constant A . A plot of the log of the coupling constants versus the log of the center-to-center distances between nanoparticles is shown in (b), and the natural logarithm of the coupling constant ($-A$) versus the center-to-center distance between NPs in the chain is shown in (c). Panel (d) shows a plot and analyses for an exponential function. In panel b, c, and d the solid red line is the best fit to a line, and in panel c the red dashed line indicates the point dipole model.

Figure 8.

Transmission spectra are shown for (a) NPs with large inter-particle separation ($d = 830$ nm) before (black) and after 1-dodecanethiol modifications and (b) for a six NP chain array ($d = 30$ nm) before (black) and after SAM modification (other colors).

Figure 9.

The plot of the DSPR peak shift upon SAM adsorption vs. the number of NPs in the chains ($d = 30$ nm).

Table 1

Coupling constant, A of square nanoparticle array samples with ~ 30 nm inter-particle distance indicating its value before and after SAM preparation. Increment in the coupling constant can be seen after SAM preparation.

Alkanethiol SAM	Coupling constant before SAM preparation (A_{Air})	Coupling constant after SAM preparation (A_{SAM})
Octanethiol	-0.309 ± 0.005	-0.331 ± 0.008
Decanethiol	-0.29 ± 0.02	-0.32 ± 0.01
Dodecanethiol	-0.261 ± 0.005	-0.307 ± 0.003
Octadecanethiol	-0.257 ± 0.007	-0.271 ± 0.002