

Dielectric Medium Effects on Collective Surface Plasmon Coupling Interactions in Oligothiophene-Linked Gold Nanoparticles

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The near-field coupling interactions between surface plasmon modes of neighboring metal nanoparticles (NPs) are investigated in thin films of oligothiophene-linked Au NPs. The oligothiophene linker facilitates near-field coupling between adjacent NPs, and disruption of the conjugation in the oligothiophene by chemical oxidation leads to a decrease in surface plasmon resonance (SPR) coupling between neighboring particles. The SPR coupling between NPs was found to be highly dependent on the dielectric constant of the medium that the films are exposed to, where a higher dielectric medium leads to weaker coupling. The dependence of the SPR coupling on the dielectric constant of the medium is explained using electrodynamic theory.

Introduction

Surface-plasmon-based photonics (plasmonics) has been an area of increasing focus due to the possibility of integrating optical components into the currently used electronic circuits.^{1,2} Limitations imposed by the diffraction of light relegate optical devices to a minimum size of a few hundred nanometers,¹ while electronic circuits may be presently fabricated with dimensions below 100 nm. Plasmonics presents a possible solution to this challenge where optical signals are converted to electromagnetic waves propagated on the surface of a nanostructured metal. Metal nanoparticles (NPs) interact strongly with visible light, resulting in the collective oscillation of free electrons in the conduction band known as surface plasmon resonance (SPR).³ The dipole field resulting from SPR of a metal NP can induce plasmon oscillations in other neighboring metal NPs via near-field electrodynamic interactions.⁴ An electromagnetic waveguide with a linear array of closely spaced metal NPs where the lateral width is much less than the wavelength of light may be envisioned.⁵ This has recently been demonstrated experimentally.⁶

The ability of plasmon-based waveguides to transmit information between neighboring NPs is dependent on the strength of the near-field coupling between NPs.¹ For example, the strength of this interaction is influenced by the interparticle distance where SPR coupling between Au NPs has been shown to decrease as the distance between the particles increases.⁴ Thus, further probing this coupling interaction may lead to a better understanding of this interaction and ultimately assist in the design of improved plasmonic wires. SPR coupling between Au NPs may be investigated using UV–vis absorption spectroscopy, as SPR coupling results in a broad band at 600–800 nm,⁷ red-shifted from the SPR band of isolated Au NPs.⁸ In this Letter, we probe the SPR coupling interaction between neighboring NPs linked by conjugated oligothiophenes. The

effect of the dielectric environment on the near-field coupling interactions between adjacent NPs is also examined.

Experimental Methods

General. [(*n*-Bu)₄N]PF₆ was used as a supporting electrolyte and was purified by triple crystallization from ethanol and dried at 90 °C under vacuum for 3 days. Methylene chloride used for cyclic voltammetry was purified by passing through an activated alumina tower. Electronic absorption spectra were obtained on a Varian Cary 5000 UV–vis–near-IR spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Leybold MAX200 equipped with an Al K α source with a pass energy of 192 eV; the sampling area was 2 \times 4 mm².

Synthesis of NPs and Electrodeposition. Oligothiophene-capped Au NPs were prepared according to the literature procedure.⁹ Electrochemical deposition was carried out using a Pine AFCBP1 bipotentiostat in dry methylene chloride using a sealed glass three-electrode electrochemical cell. A silver wire (reference electrode), platinum wire (counter electrode), and ITO/glass (working electrode) were used. The ITO/glass working electrode surface was cleaned with acetone and dried with N₂ before use. The deposition solution consisted of 10 mg of 2-diphenylphosphinoterthiophene-capped Au NPs dissolved in 10 mL of methylene chloride containing 0.1 M [(*n*-Bu)₄N]PF₆. Films were grown by repeated scanning from 0 to +1.8 V at 100 mV s⁻¹. After electrodeposition, samples were washed copiously with CH₂Cl₂ to remove traces of unlinked NPs and electrolyte.

Spectroelectrochemistry Measurements. A Varian Cary 5000 UV–vis–near-IR spectrometer was used with a Pine AFCBP1 bipotentiostat for potential control. A 1-cm-path-length quartz cell was used with a Pt wire counter electrode and a Ag wire quasi-reference electrode (QRE). Electrodeposited samples of oligothiophene-capped Au NPs on ITO/glass were used as the working electrode and placed perpendicular to the beam path. An area of the working electrode coated with deposited material was defined with a mask and placed in the beam path.

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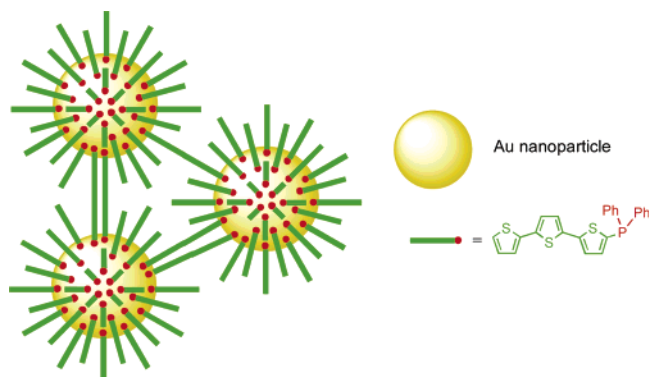


Figure 1. Schematic of electropolymerized oligothiophene-capped gold nanoparticles.

The cell was filled with 0.1 M $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ in dry CH_2Cl_2 and the top of the cell fitted with a Teflon cap with three contacts for the electrodes. A reference spectrum was taken of solvent and electrolyte with a blank ITO working electrode in the beam path. The selected potential was applied to the working electrode for 1–2 min to allow the film to reach steady state, and the optical spectrum was measured. The applied potential was increased at 200 mV increments from 0 to 1400 mV versus Ag QRE and subsequently decreased with the same potential intervals to check for reversibility.

UV– O_3 Oxidation. An as-deposited film was fitted with a circular optical mask (diameter 1 cm) to ensure that UV–vis–near-IR spectra of an identical area were measured. The spectrum of the film was taken before exposure to O_3 , and then, the film was exposed to UV-generated O_3 (the concentration of O_3 is between 50 and 600 ppb)¹⁰ at 1.5 h increments for 6 h. The absorption spectrum was measured after each 1.5 h increment.

Results and Discussion

Recently, it has been demonstrated that using conjugated organic groups to connect adjacent NPs may provide a conductive link,^{11,12} resulting in the perturbation of the coupled surface plasmon.¹² The π electrons of the conjugated linker interact with the NP dipoles, resulting in perturbation of the surface plasmon.¹² Our group has recently reported the preparation of thin films where Au NPs are linked by conjugated oligothiophene (OT) groups.⁹ Absorption spectra of these NP films revealed, in addition to the $\pi \rightarrow \pi^*$ band (**A**, Figure 2), a broad band in the near-IR (>800 nm) (**B**). No coupling of SPR modes from dipole–dipole interactions of proximal NPs is expected when the cross-linker dimension is close to that of the NP diameter.¹³ Since the average particle diameter ($d_{\text{mean}} = 1.7 \pm 0.4$ nm) is smaller than the interparticle spacing (~ 2.5 nm), the observed absorption in the near-IR cannot be attributed to dipole–dipole interactions arising from proximity effects. Larger particles ($d_{\text{mean}} = 2.6 \pm 0.3$ nm) were also electrodeposited; however, the absorption spectra showed no significant difference from those of the smaller NPs. This suggests the possibility that the polarizability of the OT linker facilitates dipole interactions between adjacent NPs, resulting in a collective SPR band.

The NP films were prepared by oxidative electrochemical coupling and were removed from solution in a reduced (0 V) state.⁹ Since oxidized OTs typically show absorption in the near-IR (NIR),¹⁴ the possibility that the low energy absorption band is due to residual oligothiophene radical cations was investigated. Spectroelectrochemistry (Supporting Information Figure S1) shows the formation of polarons and subsequently bipo-

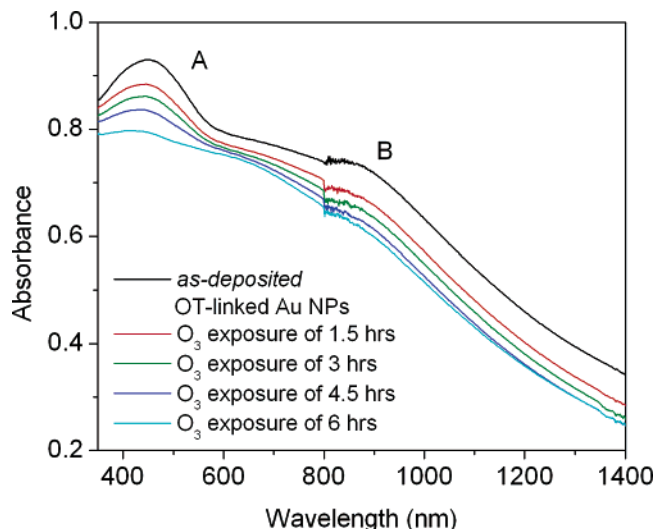


Figure 2. UV–vis–NIR absorption spectra of as-deposited OT-linked Au NP films and with exposure to UV-generated ozone.

larons in the film with increasing applied voltage. No absorption due to polarons was observed below an applied potential of 400 mV. On the basis of this experiment, it is concluded that band **B** cannot be attributed to radical cations.

To explore the possibility that the polarizability of the conjugated linker facilitates dipole interactions between adjacent NPs, the conjugated bridge was disrupted *in situ* while maintaining the same interparticle spacing. UV-generated ozone was used to oxidize the OT groups linking the Au NPs. Polythiophene (PT) has been oxidized in this fashion, resulting in the formation of sulfone and carboxyl groups and a decrease in conjugation.¹⁰ These harsh conditions result in irreversible chemical modifications of the polymer backbone, rather than the reversible introduction of charge carriers by mild electrochemical doping. Figure 2 shows the UV–vis–NIR absorption spectra of the film as a function of oxidation time. Two significant changes are observed: first, the $\pi \rightarrow \pi^*$ band at 460 nm (**A**) blue-shifts and decreases in intensity, and second, band **B** decreases in intensity. The observed changes to the $\pi \rightarrow \pi^*$ band are attributed to the disruption of conjugation in the OT linker where there is cleavage of the oligomer backbone as a result of oxidation. XPS analysis of oxidized NP films confirms this (Supporting Information Figure S2). Before oxidation, only one peak is observed in the C 1s and S 2p regions at binding energies (BEs) of 285.0 and 164.4 eV, respectively. When the film is oxidized for 1.5 h with O_3 , a small peak appears in the C 1s region at a higher BE (288.7 eV) attributed to formation of carboxyl groups,¹⁰ indicating C=C bond cleavage in thiophene.¹⁵ A much larger peak (168.7 eV) also appears in the S 2p region after O_3 exposure corresponding to the formation of sulfones. The degree of oxidation can be monitored from the XPS ratios of thienyl sulfur relative to sulfone (Supporting Information Table S1). The amount of sulfone increases up to 4.5 h of oxidation. After 6 h, the amount of sulfone present starts to decrease, likely because full oxidation of sulfur to SO_2 is occurring concomitantly, liberating the gas and thus rendering it undetectable by XPS.¹⁵ The loss of sulfur in the thienyl groups is consistent with disruption of conjugation in the OT linker due to bond cleavage.

More interesting is the decrease in intensity of band **B** with increasing exposure to O_3 . XPS data for Au before and after exposure to O_3 showed no change, indicating that no Au oxidation occurred. The decrease in the intensity of the coupled SPR band **B** occurs concurrently with the disruption of

conjugation in the linker. This differs from observations of NP films that are annealed at temperatures between 150 and 500 °C for 3 h at each temperature. With an increase in annealing temperature, there is also a decrease in the wavelength of the $\pi \rightarrow \pi^*$ band, while band **B** blue-shifts to 579 nm and sharpens (Supporting Information Figure S3). The decrease in the $\pi \rightarrow \pi^*$ band in the annealed films is due to thermal decomposition of the OT linker. The changes in **B** for the annealed films result from increases in the size of the Au NPs (Supporting Information Figure S4),¹⁶ and the blue-shift indicates the SPR band is due to isolated uncoupled NPs.¹⁷ The ozone-treated films do not show a strong band at 579 nm, indicating that the Au NPs do not aggregate under these conditions. Thus, the decrease in the coupled SPR band **B** occurring simultaneously with the disruption of conjugation in the linker suggests that, prior to oxidation, adjacent NPs are interacting via a mechanism involving the conjugated bridge. A similar dependence of the coupled SPR band on the type of bridge (partially conjugated or nonconjugated) linking Au NPs has been reported.¹² In this case, all three partially conjugated linkers showed red-shifted SPR bands due to stronger coupling relative to their nonconjugated counterparts. One material in particular, where the Au NPs are linked by 1,4-phenylene-bis(dithiocarbamate), showed strong SPR coupling interactions with a broad absorption in the near-IR (>800 nm). This strong electrodynamic coupling between Au NPs that are spaced by approximately 1 nm was explained by overlap of the molecular orbitals of the conjugated bridge with the Au NP wave functions. It is possible that a similar mechanism is occurring here, facilitating near-field coupling.

The nature of the dielectric medium between NPs should also influence coupled SPR interactions. The solvent dependence of the SPR absorption for unlinked individual Au^{18,19} and Ag²⁰ NPs has been previously studied; however, only two previous reports of the solvent effects on coupled plasmon absorptions of Au NPs exist.^{21,22} In unlinked Au NPs,^{18,19} the absorbance increases and red-shifts as the dielectric constant of the solvent is increased consistent with the predictions of Mie theory for the behavior of isolated non-interacting particles.^{23,24} A similar result is observed for Ag NPs immersed in various dielectric environments.²⁰ For solvent effects on coupled plasmon absorptions of closely spaced Au NPs,²¹ Yamada reports no change in absorbance intensity and only minor shifts to the absorption maximum as the dielectric medium was varied. The shifts reported were slightly larger than those predicted by Mie theory; this was attributed to the interparticle interactions affecting the plasmon oscillations. Zamborini et al.²² showed that for weakly coupled linked Au NPs the surface plasmon band decreases in intensity and slightly blue-shifts as the linked NP film is immersed in acetone and CH₂Cl₂ (relative to air). This response was explained as a partitioning of the organic solvent into the film (swelling), which increases the interparticle distance. Recent work by Zou et al.²⁵ has shown that, for Ag NPs that are spaced by the wavelength of light, the red-shift in the plasmon absorption when exposed to a higher dielectric medium is amplified compared to the individual NPs due to mixing of the photonic resonances with the plasmon resonances. Here, we specifically probe for the effect of the dielectric medium on Au NPs experiencing strong interparticle coupling interactions and find the intensity of the near-IR band in the OT-linked Au NP films varies significantly upon immersion of the film in different solvents and as a dry film in air (Figure 3 and Supporting Information Figure S5a).

Nonlinear fits of the absorption spectra show that, as the oligothiophene-linked film is immersed in solvent, the lower

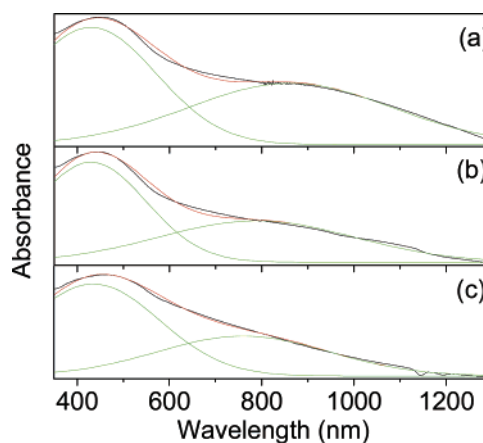


Figure 3. Nonlinear curve fits of UV-vis-NIR absorption spectra of as-deposited OT-linked Au NPs in (a) air, (b) water, and (c) toluene.

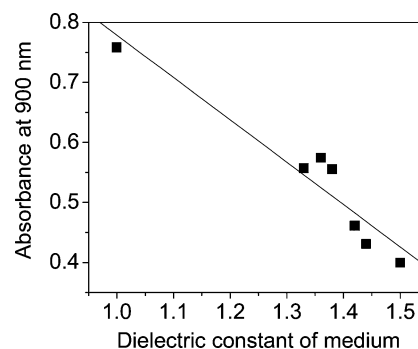


Figure 4. Absorbance of OT-linked Au NP film at 900 nm as a function of the static dielectric constant of the medium.

energy band decreases in intensity and blue-shifts (Figure 3). This effect is completely reversible; comparison of the absorption spectrum of a film after immersion in solvent and dried is identical to the spectrum of the dry film prior to immersion. Plotting the absorption at 900 nm reveals a dependence of the coupled surface plasmon absorption on the static dielectric constant of the solvent (Figure 4) where a higher dielectric medium leads to weaker coupling. Earlier work on the dielectric medium dependence of the surface plasmon band for individual^{18–20} and weakly coupled^{21,25} metal NPs all showed red-shifts with increasing dielectric constant of the medium, and these dependences have all been explained using Mie theory. The dielectric medium dependence observed here is opposite to the trend predicted by Mie theory such that the plasmon band blue-shifts as the dielectric constant of the medium is increased. Mie theory can only predict the effect of the dielectric constant of the medium on the optical resonance wavelength (SPR λ_{max}) of isolated spherical particles.²⁶ Since band **B** is attributed to coupling interactions, Mie theory is not able to adequately explain the observed changes, and classical electrodynamics is used to explain the results. Classically, placing a dielectric material between two electrical point charges reduces the force between them, equivalent to increasing the distance between the charges.²⁷ It has been shown that increasing the distance between NPs reduces the dipole–dipole interaction between them and results in a blue-shift of the collective SPR band.⁴ Thus, the introduction of a higher dielectric constant medium between SPR coupled NPs reduces the dipole coupling between adjacent particles, producing an equivalent result to moving the NPs further apart.

The observed blue-shift (>100 nm) and decrease in absorbance ($\Delta A = 0.4$) in the coupled surface plasmon band for the oligothiophene-linked Au NPs is much larger compared to the

slight changes (~ 10 nm and $\Delta A \approx 0.15$) due to film swelling reported by Zamborini.²² In these films, alkyl linkers are used and the observed effects attributed to the flexibility of these chains. Although oligothiophene-linked Au NP films do show some film swelling when exposed to solvent vapors,²⁸ the rigidity of the oligothiophene linkers suggests that this swelling does not result in significant changes in interparticle distances. Furthermore, film swelling is highly dependent on the nature of the capping group attached to the NP where the capping group dictates the solubility of the NPs in a specific solvent;²⁹ here, the same solvent dependence of the coupled SPR band is observed when the Au NPs are linked with an oligothiophene linker containing ethylenedioxythiophene groups (Supporting Information Figure S5b). Although the contribution of film swelling to the observed shifts is impossible to determine from these results, it appears from these comparisons that the contribution is minimal.

Conclusions

The role of a conjugated oligothiophene linker on the plasmon coupling interaction between Au NPs has been probed, and it was found that the coupled plasmon resonance shifts to a lower wavelength as the conjugation in the linker is disrupted. This indicates that the oligothiophene linker acts as a bridge facilitating near-field coupling between adjacent NPs. This SPR coupling between NPs was found to be dependent on the dielectric constant of the medium where a higher dielectric medium leads to weaker coupling. This phenomenon was explained using classical electrodynamic theory. These results may be useful for the design and fabrication of next generation plasmonic devices.

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Supporting Information Available: XPS spectra, tables of XPS data, UV–vis–NIR absorption spectra, TEM images of annealed films, and spectroelectrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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