Charge-Induced Shifts in Chiral Surface Plasmon Modes in Gold Nanorod Assemblies

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A detailed investigation of the effect of electron injection on the chiral plasmon modes of helical nanorod assemblies is presented. An increased surface plasmon frequency of the electron gas due to the addition of electrons leads to a blue-shift in the corresponding chiral surface plasmon modes. The mechanism behind the shift in plasmonic chirality due to nanorod charging is investigated using theoretical simulations. Charging of the nanorods alters the surface electron density, thereby modifying the plasma frequency and causing a change in the dielectric function. The nature of the plasmon shift and the intensity of chiral surface plasmons are found to be largely dependent on the extent of electron addition. At extended periods of time, the blue shifted band slowly shifts back toward the red, due to transfer of electrons back to the medium, leading to discharging of the nanorods.

1. Introduction

Localized surface plasmon resonances (LSPR) in noble metal nanoparticles have gathered enormous interest due to the wide variety of applications of this phenomenon in the fields of optoelectronic and photonic devices, biosensing and, active waveguides, among others.[1–5] A related phenomenon that has gathered vast research interest in recent years is the generation of chiral surface plasmon modes, through the creation of (typically metallic) chiral nanostructures.[6–9] Chirality can be induced in plasmonic nanomaterials, either by using a chiral ligand as capping agent or by assembling nanoparticle building blocks on a chiral template.[10–13] The intrinsic chiral nature of biomolecules such as DNA, amino acids, and proteins has enabled the use of these materials as ligands/templates to induce chirality in plasmonic nanoparticles.[14–16] The complementarity of specific functional groups in these biomolecules has been extensively used for the design and synthesis of a wide range of chiral nanoarchitectures that display circular dichroism (CD) signals at the LSPR wavelengths. This research has in turn generated a wide range of applications for chiral plasmons in the fields of chiral biodetection, enantioselective sensing, and catalysis.[17–20]

An often neglected parameter that can significantly influence the plasmon resonance frequency is the free electron density of the plasmonic nanoparticles.[21,22] In plasmonic nanoparticles such as gold and silver, the spatial confinement of conduction electrons can lead to intense absorption and scattering, at resonance frequencies which largely depend on the electron density. Chemical charging or discharging is therefore an effective tool to tune surface plasmon resonance frequencies in plasmonic nanoparticles, through alteration of the electron density. As a general observation, an increase in free electron density results in a blue-shift of the LSPR band, while removal of charges leads to a shift toward longer wavelengths.[23–27] LSPR shifts due to changes in the electron density of silver and gold nanoparticles have been previously described.[23,24] In these reports, nanoparticles either in colloidal solution or immobilized on solid surfaces were charged through the addition of a strong reducing
agent or by applying an electrochemical potential.\cite{24,26} Mulvaney and co-workers have experimentally demonstrated that Au nanorods exhibit a drastic extinction blue-shift when their free electron density is increased, through oxidation of added borohydride ions.\cite{24} The same group demonstrated a similar effect for a single gold nanorod immobilized on an indium tin oxide (ITO) surface and immersed in an ionic gel capacitor.\cite{25,26} Charging and discharging of nanostructures with different sizes and shapes has been the subject of various experimental and theoretical investigations by various groups.\cite{28,29} Although, the effect of charging on the extinction spectral features of plasmonic nanoparticles is well understood, it remains to be shown if electron charging may have a similar effect on the chiral surface plasmon modes of plasmonic nanoassemblies. With this question in mind, we have investigated the effect of chemical charging on the chiral LSPR modes generated when gold nanorods are assembled on a helical structure, templated by amyloid protein fibrils.\cite{17} Our results indeed confirm that chiral LSPR modes exhibit a significant wavelength shift in circular dichroism, upon charge injection into the nanorods within the helical assemblies. The observed effects were validated by numerical simulations using a realistic model.

2. Results and Discussion

For the generation of chiral plasmonic nanostructures, small gold nanorods (length $= 23$ nm, width $= 7$ nm) were used as the plasmonic building blocks and $\alpha$-synuclein nanofibrils were employed as the chiral template. Such small gold nanorods were synthesized following a seedless growth method, while $\alpha$-synuclein fibrils were generated by incubating the protein at high concentration on a shaker (details provided in the Experimental Section).\cite{30–32} Addition of the nanofibrils into the Au nanorod colloidal dispersion resulted in gradual binding of nanorods on the fibril surface, as recently reported.\cite{17} The helical arrangement of Au nanorods on the chiral template results in a coupled longitudinal plasmon band at the near-IR region of the extinction spectrum and a chiral plasmonic signal in the corresponding CD spectrum (Figure 1a,b). These spectral changes were accompanied by broadening of the LSPR band due to the presence of nanorod assemblies of different sizes and a significant polydispersity in interparticle distances. Details of the helical assembly of Au nanorods using protein fibrils as templates, as well as the origin of plasmonic CD, have been reported in detail, on the basis of cryo-transmission electron microscopy (TEM) tomography and theoretical modeling, respectively.\cite{17} We further investigated the effects of charge injection through the stepwise addition of a solution of sodium borohydride, a strong reducing agent, into the dispersion of Au nanorod-protein fibril nanocomposite structures. An LSPR blue-shift of $\approx 25$ nm was observed immediately after addition of sodium borohydride, which then gradually shifted further into the blue, over a period of 15 min (Figure 1c). A total blue-shift of 55 nm was recorded for the longitudinal plasmon band of Au nanorods, upon addition of 0.01 M sodium borohydride. Interestingly, the CD profile, corresponding to the chiral plasmon mode, also exhibited a gradual blue-shift accompanied by a slight increase in intensity. Changes in the CD spectra were monitored over time and found to saturate after 15 min (Figure 1d). The positive CD spectral peak of the nanocomposite at 808 nm shifted down to 770 nm, upon addition of sodium borohydride. The recorded spectral shift was consistent in both the positive and negative peaks of the CD profile.

Based on earlier experimental and theoretical reports on nanoparticle charging we postulated that both shifts in extinction and CD peaks arise from the increased electron density in the Au nanorods, within the nanocomposite structure.\cite{23–27} To understand the role of electron charging on chiral surface plasmon modes, a full-wave frequency-domain electromagnetic solver based on the boundary element method was employed to run the numerical simulations.\cite{31–33} Using the parameters obtained from TEM images of the nanocomposites, we modeled double-helical assemblies of Au nanorods comprising a sequence of 120 rods. Charging of the nanorods alters its electron density, thereby modifying the plasma frequency and causing in turn a change in the dielectric function. The changes in electron density ($\Delta N$) and the corresponding modified dielectric function during nanorod charging were taken into account for simulating the helical assemblies (details provided in the Experimental Section). The LSPR shift from an initial wavelength ($\lambda_0$) to the final wavelength ($\lambda$) during charging is given by\cite{24}

$$\Delta\lambda = \lambda - \lambda_0 = -\frac{\Delta N}{2N} \frac{\lambda_p}{N} \sqrt{\varepsilon + \left(\frac{1}{L^2} - 1\right)} \varepsilon_m,$$

where $N$ is the conduction electron density, $\lambda_p$ is the bulk gold plasma wavelength (130 nm), $L$ the depolarization factor, which is dependent upon the shape of the particle, $\varepsilon$ is the high-frequency dielectric constant of gold, and $\varepsilon_m$ is the dielectric constant of the medium. Extinction and CD spectra of Au nanorod assemblies were thus simulated considering varying degrees of Au nanorod charging ($\Delta N = 0.00, 0.05, 0.10, 0.15,$ and 0.20).
Extinction cross-sections of the helical Au nanorod assemblies were calculated under the excitation of left- and right-handed circularly polarized, axially impinging plane waves (Figure 2a). Both curves were then combined to calculate CD spectra. The position and intensity of the chiral plasmon band were found to be highly dependent on the extent of nanorod charging (Figure 2b). Modeling of the “neutral” (no charging) helical nanorod assembly resulted in a bisignate CD signal with a positive CD peak at 875 nm. As expected, a gradual blue-shift of the chiral plasmon band was observed as the level of charging was increased. Positive peaks at 831 and 794 nm were obtained for calculated ΔN values of 0.10 and 0.20, respectively. The blue-shift in the chiral plasmon band was accompanied by a small increase in the intensity. The simulated chiral LSPR shifts for the charged nanocomposites are in good agreement with the experimental spectra (vide supra). Slight variations in peak positions and the larger FWHM observed in the experimental spectra can be attributed to the polydispersity of the samples, which is not accounted for in the simulations.

We further investigated the effect of varying interparticle distance on the chemical charging and plasmon coupling efficiencies of helical nanorod assemblies. Since our methodology does not allow for a precise control over the interparticle distance, we carried out numerical simulations in which the distance between nanorods in the helical assembly was varied. In addition to the interparticle spacing of 4 nm described in Figure 2, simulations were run with interparticle spacings of 2, 6, and 8 nm. For a short interparticle distance of 2 nm, the positive peak in the CD spectrum was observed at 908 nm, but it was found to shift to 868 and 828 nm for ΔN values of 0.1 and 0.2, respectively. Under similar conditions, CD peak positions were observed at 843, 803, and 763 nm for nanorods positioned at an interparticle distance of 8 nm (Figure S1, Supporting Information). These results indicate that by increasing the distance between nanorods the plasmon coupling efficiency is reduced. However, the extent of the blue-shift in the chiral plasmon mode due to charge injection remained constant; blue shifts of 40 and 80 nm for ΔN values of 0.1 and 0.2, respectively, were obtained in all cases. We conclude that, varying the interparticle distance on charged Au nanorods has a small effect on the net blue-shift or the coupling efficiency for chiral plasmon modes.

We finally analyzed the stability of Au nanorod-protein fibril nanocomposites in the presence of sodium borohydride, by monitoring the spectral changes over longer time periods. The blue shifted chiral plasmon band remained stable without any further shift for about 2 h. However, the LSPR band gradually shifted back toward the low energy spectral region, after 2 h (Figure 3a,b). We observed a slow red-shift for about 30 min; however, the original spectrum was not fully recovered even after leaving the solution undisturbed for several hours. It is well known that a major portion of borohydride ions get consumed by oxidation over time. As a result, the injected electrons on the nanorods are slowly transferred back, either to water or to oxygen in solution. This results in a slow red-shift of the LSPR band, which we observed both in the extinction and the CD spectra. To further confirm that the shift in CD signal is due to electron charging/discharging, and not due to the deformation of nanofibrils, nanorods or the nanorod-nanofibril assembly, the hybrid nanostructures were examined by TEM, before and after the addition of sodium borohydride. It was confirmed by TEM that synuclein nanofibrils remained stable after addition of sodium borohydride (Figure S2, Supporting Information). TEM images demonstrated that neither the shape nor the size of Au nanorods attached to synuclein nanofibrils were modified by sodium borohydride (Figure 4a,b).
The images monitored after 4 h of borohydride addition also showed stable structures (Figure 4c). Further confirmation of the stability of the hybrid structures was obtained by monitoring TEM images of nanostructures that had been incubated in the reducing solution for a longer period of time (Figure S3, Supporting Information). The nanocomposites remained stable for 3 d, thereby confirming that the observed blue-shift upon addition of the reducing agent and the subsequent red-shift after 2 h were not due to any instability of the nanostructure, but to the electron charging/discharging effects operating in the nanorods. The key point to note is that the concentrations of sodium borohydride in these studies are too low to cause any structural deformation of the nanocomposites.

3. Conclusions

In summary, we have demonstrated the possibility of tuning chiral surface plasmon modes in helical nanorod assemblies, driven by charge injection. Addition of electrons into assembled nanorods using a chemical reducing agent leads to an increase in the surface plasmon frequency, thereby resulting in a blue-shift of the chiral CD surface plasmon band. Theoretical simulations showed that the charging of nanorods alters the surface electron density, thereby modifying the plasma frequency, causing a change in the dielectric function. The blue-shift in the chiral plasmon band increased with further electron injection, but when left for longer time, the band shifted back toward the red, showing a discharging effect with time. The charging/discharging methods described herein can function as a new approach for the effective tuning of the chiral surface plasmon modes in nanocomposites, which is extremely important in the field of chiral biosensing and metamaterials.

We propose, e.g., that redox activity in the vicinity of nanoparticles capped by biomolecules, can be detected through the charge-induced shift of chiral plasmons, which should thus find applications in chiral biosensing.

4. Experimental Section

**Synthesis of Au Nanorods:** Au nanorods were synthesized following a seedless growth method.[30] HAuCl₄ (100 µL, 0.05 M) was added to 10.0 mL of cetyltrimethylammonium bromide (CTAB; 0.1 M) and shaken. Following this, AgNO₃ (250 µL, 4.0 × 10⁻³ M) was added, and the solution was gently shaken. HCl (12.0 µL, 37 wt%) was introduced to obtain a pH close to 1.0, followed by addition of 70 µL of ascorbic acid (78.8 × 10⁻³ M) under gentle stirring until the solution became clear. In the final step, ice-cold NaBH₄ (10 µL, 0.01 M) was injected into the growth solution and allowed to react for 6 h. The growth solution was centrifuged twice at 14 500 rpm to remove excess CTAB and other reagents, and re-dispersed in water.

**Fibrillation of α-Synuclein:** α-Synuclein was expressed in *Escherichia coli* BL21 cells carrying a pT7-7 plasmid encoding the SNCA gene with the A53T variant; and the extraction and purification was carried out following a previously reported protocol.[31] Fibrillation was carried out by incubating a high concentration of protein on a shaker for 3 d. 500 µL of α-synuclein protein at 100 × 10⁻⁶ M were fibrillated in a thermo-shaker TR100-G (Optyc Ivymen System) for 3 d at 37°C and 600 rpm.

**Theoretical Simulations:** A full-wave frequency-domain electromagnetic solver based on boundary element methods was used to run the numerical simulations. In virtue of the equivalence theorem and Huygens surfaces, surface currents (both electric and magnetic) radiating in unbounded homogeneous regions replace the interfaces (surface boundaries). This approach rendered a set of self-consistent integro-differential boundary equations with those surface currents as unknowns. The equations were then discretized and tested in a variational sense with the method of moments and Galerkin’s testing procedure.[32] Further spectral acceleration techniques (fast multipole methods) were resorted to in order to compress the system and make it tractable in the case of large-scale problems.[32,33]

With regard to modeling, the metals complex electric permittivity during electron injection was taken into account. The procedure described earlier was adopted herein, by which the dielectric function was split into an interband component and a free-electron component.[24] Thus, by subtracting the contribution of the Drude model[36] from the total dielectric function (calculated by Johnson and Christy),[37] the interband transitions could be isolated. The new dielectric function could then be easily obtained by adding to this interband component the modified Drude component with the new conduction electron density after electron charging.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**
The authors declare no conflict of interest.

**Keywords**
amyloid fibers, Au nanorods, charging effects, electromagnetic modeling, plasmonic chirality

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[1] P. Mulvaney, Langmuir **1996**, *12*, 788.
[2] L. M. Liz-Marzán, Mater. Today **2004**, *7*, 26.
[3] N. J. Halas, S. Lal, W.-S. Chang, S. Link, P. Nordlander, Chem. Rev. **2011**, *111*, 3913.
[4] A. Kristensen, J. K. W. Yang, S. I. Bozhevolnyi, S. Link, P. Nordlander, N. J. Halas, N. A. Mortensen, Nat. Rev. Mater. **2017**, *2*, 16088.
[5] X. Wu, C. Hao, J. Kumar, H. Kuang, N. A. Kotov, L. M. Liz-Marzan, C. Xu, Chem. Soc. Rev. **2018**, *47*, 4677.
[6] W. Ma, L. Xu, A. F. de Moura, X. Wu, H. Kuang, C. Xu, N. A. Kotov, Chem. Rev. **2017**, *117*, 8041.
[7] V. K. Valev, J. J. Baumberg, C. Sibilia, T. Verbiest, Adv. Mater. **2013**, *25*, 2517.
[8] K. W. Smith, S. Link, W.-S. Chang, J. Photochem. Photobiol., C **2017**, *17*, 32, 40.
[9] J. Kumar, K. G. Thomas, L. M. Liz-Marzán, Chem. Commun. **2016**, *52*, 12555.
[10] H.-E. Lee, H.-Y. Ahn, J. Mun, Y. Y. Lee, M. Kim, N. H. Cho, K. Chang, W. S. Kim, J. Rh, K. T. Nam, Nature **2018**, *556*, 360.
[11] J. Cheng, G. L. Saux, J. Gao, T. Buffet, E. Y. Battie, P. Barois, V. Ponsinet, M.-H. Delville, O. Ersen, R. Oda, ACS Nano **2017**, *11*, 3806.
[12] A. Guerrero-Martinez, B. Auguie, J. L. Alonso-Gomez, Z. Dzolic, S. Gomez-Grana, M. Z. inic, M. M. Cid, L. M. Liz- Marzán, Angew. Chem., Int. Ed. **2011**, *50*, 5499.
[13] A. Kuzyk, R. Schreiber, Z. Fan, G. Pardatscher, E.-M. Roller, A. Hugel, F. C. Simmel, A. O. Govorov, T. Liedl, Nature **2012**, *483*, 311.
[14] J. George, K. G. Thomas, J. Am. Chem. Soc. **2010**, *132*, 2502.
[15] C. Zhou, X. Duan, N. Liu, Acc. Chem. Res. **2017**, *50*, 2906.
[16] X. Lan, Q. Wang, Adv. Mater. **2016**, *28*, 10499.
[17] J. Kumar, H. Eraña, E. López-Martínez, N. Claes, V. F. Martín, D. M. Solís, B. Sals, A. C. Cortajarena, J. Castilla, L. M. Liz-Marzán, Proc. Natl. Acad. Sci. USA **2018**, *115*, 3225.
[18] W. Ma, H. Kuang, L. Xu, L. Ding, C. Xu, L. Wang, N. A. Kotov, Nat. Commun. **2013**, *4*, 2689.
[19] F. Zhu, X. Li, Y. Li, M. Yan, S. Liu, Anal. Chem. **2015**, *87*, 357.
[20] L. Xu, Y. Gao, H. Kuang, L. M. Liz-Marzán, C. Xu, Angew. Chem., Int. Ed. **2018**, *57*, 10544.
[21] M. D. Scanlon, P. Peljo, M. A. Méndez, E. Smirnov, H. H. Giraulta, Chem. Sci. **2015**, *6*, 2705.
[22] T. Hirakawa, P. V. Kamat, Langmuir **2004**, *20*, 5645.
[23] T. Ung, M. Giersig, D. Dunstan, P. Mulvaney, Langmuir **1997**, *13*, 1773.
[24] P. Mulvaney, J. Perez-Juste, M. Giersig, L. M. Liz-Marzán, C. Pecharyroman, Plasmonics **2006**, *1*, 61.
[25] C. Novo, A. M. Funston, A. K. Gooding, P. Mulvaney, J. Am. Chem. Soc. **2009**, *131*, 14664.
[26] S. S. E. Collins, X. Wei, T. G. McKenzie, A. M. Funston, P. Mulvaney, Nano Lett. **2016**, *16*, 6863.
[27] R. Chapman, P. Mulvaney, Chem. Phys. Lett. **2001**, *349*, 358.
[28] B. K. Juluri, Y. B. Zheng, D. Ahmed, L. Jensen, T. J. Huang, J. Phys. Chem. C **2008**, *112*, 7309.
[29] M. Chirea, S. S. E. Collins, X. Wei, P. Mulvaney, J. Phys. Chem. Lett. **2014**, *5*, 4331.
[30] M. R. K. Ali, B. Snyder, M. A. El-Sayed, Langmuir **2012**, *28*, 9807.
[31] W. Hoyer, T. Antony, D. Cherny, G. Heim, T. M. Jovin, V. Subramaniam, J. Mol. Biol. **2002**, *322*, 383.
[32] B. Sot, A. Rubio-Murhoz, A. Leal-Quintero, J. Martinez-Sabando, M. Marcilla, C. Roodveldt, J. M. Valpuesta, Sci. Rep. **2017**, *7*, 48059.
[33] D. M. Solís, F. Obelleiro, J. M. Taboada, IEEE Trans. Antennas Propag. **2017**, *65*, 5356.
[34] D. M. Solís, M. G. Araújo, L. Landesa, S. García, J. M. Taboada, F. Obelleiro, IEEE Photonics J. **2015**, *7*, 4800709.
[35] D. M. Solís, J. M. Taboada, F. Obelleiro, IEEE Photonics J. **2016**, *8*, 4803014.
[36] C. Oubre, P. Nordlander, J. Phys. Chem. B **2004**, *108*, 17740.
[37] P. B. Johnson, R. W. Christy, Phys. Rev. B **1972**, *6*, 4370.