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Interparticle Electromagnetic Coupling in Assembled Gold-Necklace Nanoparticles

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Progress in nanoscale optoelectronic devices based on noble metal nanoparticles has been an active area of current nanoscience research.[1−6] This is in large part due to the application of metal nanoparticles in photonics or plasmonics[1−3] and nonlinear optics.[4−8] There has also been recent interest in the self-assembly of metal nanoparticles into 1D metal chains[2] as well as 2D and 3D super lattices.[9] When these particles are patterned in arrays, they may exhibit efficient interparticle electromagnetic coupling. Significant efforts have been made to utilize their special photophysical properties as they are found to regulate optical properties. Increased surface-enhanced scattering, two-photon absorption (TPA), and four wave mixing properties are observed for closely spaced nanoparticles (aggregates) in thin film materials or in embedded matrices.[7] Due to the random nature of aggregates, direct correlations of the structure-nonlinear optical properties are not easily obtained. Thus, it is necessary to prepare aggregate materials with the use of assembly methods to make discrete arrays of particles and to illustrate the enhancement properties more clearly. Huo and coworkers[9] have synthesized gold−polylysine hybrid materials to form a necklace arrangement of Au nanoparticles. Sun et al.[10] have found that the optical limiting properties of these Au-necklace particles are enhanced in comparison to the monocarboxylated Au nanoparticles. The enhancement of nonlinear optical properties has been ascribed to the electromagnetic interactions between the nanoparticles in close proximity.[10]

Here, we examine the nature of the electromagnetic coupling and its influence on nonlinear properties of these Au-necklace particles (Au-neck) with the aid of time-resolved spectroscopy.[11,12] Comparisons are made with monocarboxylated Au nanoparticles (Au-Np) (structures are shown in Scheme 1). The syntheses of the Au-neck and monocarboxylated gold-NP are provided elsewhere.[9] From the TEM measurements (Supporting Information), it can be observed that these particles consist of nanoparticles of 2−3 nm size and are connected very close to each other in the form of a necklace.

Figure 1A shows the optical absorption spectra of Au-Np and Au-neck dispersed in dichloromethane/methanol (2/1 v/v) and 1% trifluoroacetic acid. It can be observed that the Au-Nps show a surface plasmon resonance peak, which is common to Au nanoparticles of this size. Interestingly, the Au-neck particles show a slightly red shifted and broader plasmon absorption with respect to spherical Au nanoparticles, suggesting electronic interaction with close lying Au nanoparticles. A similar absorption spectrum has been observed for Au−DNA nanocomposites and has also been ascribed to static electromagnetic coupling between neighboring Au nanoparticles.[13]

Two color pump−probe measurements[14] have been carried out on these organized Au-neck particles, and the corresponding electron dynamics has been compared with the dynamics found in Au-Np. Shown in Figure 1B are the transient absorption spectra of both Au-Np and Au-neck at a time delay of 500 fs after excitation at 390 nm. Similar to what has been observed for Au nanoparticles,[15] Au-Nps have shown a negative absorption in the region of 480−600 nm with a maximum at 530 nm and a positive absorption with a maximum at 470 nm. Analogous transient absorption features are observed for the Au-neck, except both the bleach maximum and absorption maximum are shifted to longer wavelengths (550 and 500 nm, respectively). This shift to longer wavelengths is consistent with the optical absorption maximum and most likely arises from the electromagnetic interaction from the static electronic coupling between the neighboring particles in the Au-neck. It has been observed that, as the time delay is increased from 100 to 800 fs (Supporting Information) for the case of Au-neck, both positive absorption and bleach have increased in amplitude, while a decay of surface plasmon bleach is observed in case of Au-Np. The growth of surface plasmon bleach has been observed in previous ultrafast measurements of Au nanoparticles[15c] and is explained by electron−electron scattering, which occurs on a time scale of 100−500 fs. After the electron−electron scattering, the hot electrons relax with a decay profile which has two components related to electron−phonon and phonon−phonon relaxation processes.[15]

Scheme 1

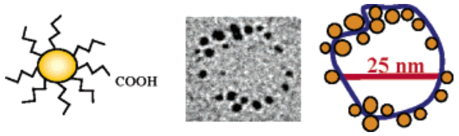

Figure 2 shows the kinetic traces of the surface plasmon bleach at the peak wavelength of 550 nm for the Au-neck and 530 nm for the Au-Np in the same solvent at the same pump-power. The kinetics in Figure 2A shows the electron−electron scattering, which is considerably slower for the Au-neck than the Au-Np. This could arise from efficient dipolar coupling between the plasmons of two neighboring particles. In addition to this, the recovery of bleach (Figure 2B) is also found to be substantially slower for the Au-neck over the Au-Np. Pump-power dependent measurements on Au-neck and Au-Np have shown that the electron−electron scattering is weakly dependent on pump-power for Au-neck while electron−phonon relaxation dynamics is very much dependent on pump-power (see Supporting Information).

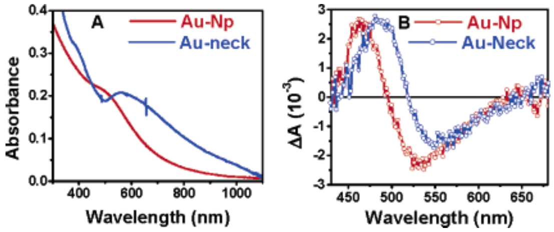

Figure 1. (A) Optical absorption spectra of Au-Np and Au-neck nanoparticles. (B) Transient absorption spectra at a time delay of 500 fs for Au-Np and Au-neck.

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10.1021/ja067123p CCC: $37.00

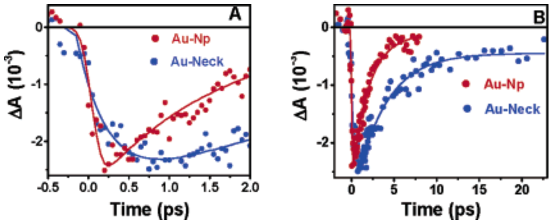

Figure 2. Kinetics decay profiles for Au-Np and at the peak of their bleach wavelengths (A) in short time window and (B) long time window after excitation at 390 nm.

The zero pump-power electron−phonon relaxation time has been obtained by extrapolating the decay time constants obtained at different pump-powers. A time constant of 2.01 ± 0.3 ps has been observed for Au-neck, which is significantly longer than what has been obtained for spherical Au nanoparticles of different sizes (∼0.75 ps).[15] The corresponding electron−phonon coupling coefficients obtained from the two-temperature model are 9.4×10^{15} and 2.4×10^{16} W m^{-3} K^{-1} for Au-neck and Au-Np, respectively.

These present results of slower electron−electron scattering (∼580 ± 100 fs) and slower electron−phonon relaxation for the Au-neck in comparison to Au-Np (∼200 ± 80 fs) are quite unexpected. Normally, electron−electron scattering for Au nanoparticles with pump−probe spectroscopy is on the order of ∼250 fs for this particle size[16a] and increases with decreasing pump-power.[16b] As mentioned above, we observed a weak pump-power dependence on the electron−electron scattering time. As the particle sizes of the isolated nanoparticles in Au-neck and Au-Np are similar, the observed slower internal thermalization in Au-neck may be due to the specific arrangement of gold nanoparticles in a necklace fashion.

Indeed, the slower electron−phonon relaxation for the Au-Np was not expected. Size-dependent electron−phonon relaxation measurements (low pump-power) carried out on the nanoparticles in the size range of 3−50 nm have shown that the dynamics is closer to the bulk electron−phonon relaxation time observed in metal films (∼750 fs).[15,16] However, measurements have shown that electron−phonon relaxation processes are dependent on the environment. El-Sayed and co-workers[17] have observed slower electron−phonon relaxation in case of metal nanoparticles dispersed in $MgSO_4$ powder, and this has been attributed to the low thermal conductivity of the surrounding environment.[17] In the present case, we have compared the Au-Np and Au-neck systems consisting of the same size nanoparticles and in the same solvent environment. Thus, the effect of particle size and surrounding environment is ruled out here. It can also be argued that the metal necklace particles can be considered as simple metal nanoparticle aggregates.[18] However, faster electron−phonon relaxation has been observed for metal nanoparticles with aggregation.[18]

In light of above discussions of electron dynamics, the observed results can be explained on the basis of qualitative and phenomenological model of dipole−dipole electrostatic interaction between the neighboring particles arranged in circular geometry. Upon photoexcitation of Au-neck, the electron temperature increases and internal thermalization takes place not only between the electrons in the same nanoparticle but also with electrons in the neighboring particle due to strong electromagnetic coupling between neighboring particles. In this way, electron−electron scattering takes place in the necklace; thus it takes longer than it would normally for isolated gold nanoparticles. Since this involves an interparticle phenomenon, very weak pump-power dependence is observed. The electron−phonon relaxation in the case of the present small Au nanoparticles is dominated by electron-surface scattering. As the electrons are entirely coupled in the spherical geometrical surface, the electron−phonon coupling is decreased due to weaker electron-surface scattering; hence one can observe slower electron−phonon relaxation. This is analogous to that of exciton dynamics in molecular *J*-aggregates, where the exciton−phonon relaxation is slower in aggregates. However, experiments and modeling are underway to obtain the quantitative explanation for the observed results.

This observed phenomenon of interparticle electromagnetic coupling over the entire necklace of particles can have vital implications in linear, nonlinear optical, and surface-enhanced resonance Raman spectroscopies. Surface-induced phenomenon becomes dominant in the present case of small nanoparticles (both Au-Np and Au-neck). This is a manifestation of quantum confinement in the nonlinear response and is different from that of nonlinear enhancement due to dielectric confinement. In the case of necklace particles, as they behave as coupled particles, the “available” surface is considerably larger than the isolated nanoparticles, and hence surface-induced confinement enhances the nonlinear optical properties.

In summary, the present investigations of the ultrafast electron dynamics in the Au-neck system have shown the presence of strong electromagnetic coupling between the neighboring particles. A decrease in electron−phonon coupling due to inefficient electron-surface scattering in the necklace geometry is the suggested mechanism behind the enhanced optical limiting effects observed for the Au-necklace particles.

Acknowledgment. We thank the National Science Foundation (T.G.) for financial support.

Supporting Information Available: TEM pictures and complete transient absorption results. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA067123P