Optical Limiting of a Covalently Bonded Gold Nanoparticle/Polylysine Hybrid Material

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The optical limiting performance of a covalently bonded gold nanoparticle (∼2 nm)/polylysine hybrid material (AuNP−PLL) was investigated using 4.1 ns laser pulses at 532 nm. The hybrid material exhibits enhanced optical limiting in comparison to individual nanoparticles, presumably due to the interparticle electromagnetic interactions between particles in close proximity. Reverse saturable absorption and/or free carrier absorption were found to be the dominant contributor(s) to the optical limiting of the hybrid material.

Introduction

Nanoparticle materials have attracted great interest in recent years due to their unique electrical, physical, and optical properties at nanometer scale regime.[1] These properties may lead to potential applications in miniaturized electronic devices, catalysis, ultrafast optical communication, sensors, and data storage.[2] Among the different nanoparticle materials, a significant amount of work has been conducted on gold nanoparticles because of their ease-of-synthesis, chemical and thermal stability, and many interesting optical properties such as surface plasmon resonance, surface enhanced Raman scattering, and nonlinear optical effects. Recently, the nonlinear optical properties of gold nanoparticles in solution, solid state (gold-precipitated glasses), molecularly bridged assemblies and self-assembled nanoassemblies have been reported.[3] Gold nanoparticles were found to exhibit strong optical limiting for both nanosecond and picosecond laser pulses.[3a,b,d−k] Mostafavi and co-workers reported that the optical limiting of gold nanoparticles for nanosecond laser pulses exhibited size dependence, when the nanoparticle core diameter was smaller than 9 nm, no optical limiting was observed.[3a,b] The optical limiting mechanism for large gold nanoparticles was ascribed to nonlinear scattering.[3a,b] In contrast, Philip and co-workers discovered that gold nanoparticles with an average core size of 3.0±0.5 nm exhibited optical limiting for both 7 ns and 35 ps laser pulses.[3e,k] The optical limiting was attributed to free-carrier absorption.[3e,k]

It has been demonstrated that the properties of nanoparticle materials are not only related to the size and characteristics of individual nanoparticles but also are affected profoundly by the interparticle distance and interactions.[4] For example, the surface plasmon resonance absorption (SPR) band of individual gold nanoparticles with core diameter around 15 nm appears at ca. 510 nm. When these gold nanoparticles are linked together by DNA, the SPR band red-shifts, giving a blue or purple color to the nanoparticle solution.[5] Feldheim and co-workers demonstrated that molecularly bridged noncentrosymmetric nanoparticle trimers exhibited not only SPR absorption band shift but also larger second-order nonlinear optical response comparing to centrosymmetric monomers and dimers.[3c] A precise control of nanoparticle assemblies and interparticle organization is vital
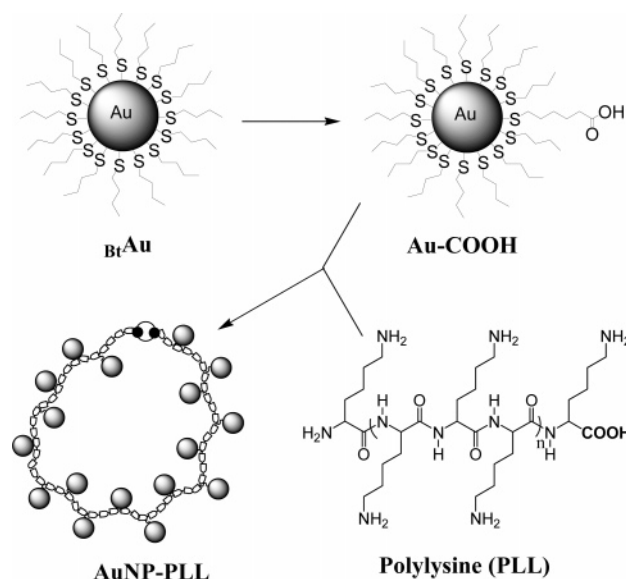
Figure 1. Structures of butanethiolate-protected gold nanoparticles (BtAu), single functionalized gold nanoparticles (Au−COOH), and gold nanoparticle/polylysine hybrid material (AuNP−PLL).

for the successful development of nanomaterials with expected properties.

Recently, several groups have demonstrated the synthesis and modification of gold nanoparticles with a single functional group attached to the surface.[6] The significance of such nanoparticles lies in that they can be essentially treated and used as molecules to react with other nanobuilding blocks or chemicals. As a result, nanomaterials may be assembled using traditional chemical reactions, with all the nanobuilding blocks covalently bonded together. Using a solid-phase synthesis technique, gold nanoparticles (∼2 nm) with a single carboxyl group attached on the surface (Au−COOH) were recently synthesized by Huo and co-workers from a butanethiolate-protected nanoparticle (BtAu).[6a] A nanoparticle/polylysine hybrid material (AuNP−PLL) was then prepared by a one-step in situ amide coupling reaction between the monofunctionalized gold nanoparticles and polylysine (Figure 1).[7] The nanoparticles were attached to the polymer backbone through the amino groups of lysine residues, just like beads dangling along a string. Interestingly, the polylysine chain was found to cyclize intramolecularly into ring structures, resulting in the formation of nanoparticle "necklaces".

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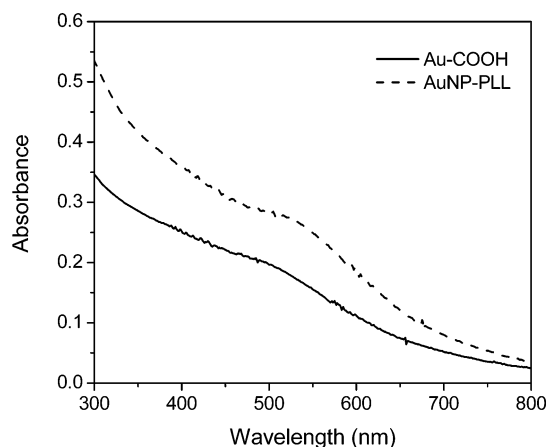
Figure 2. UV-vis spectra of the single functionalized gold nanoparticles (Au−COOH) and the nanoparticle/polylysine hybrid material (AuNP−PLL) in CH_2Cl_2/CH_3OH (1/1, with ∼1% trifluoroacetic acid).

Distinct from many existing self-assembled nanoparticle materials, this nanoparticle/polylysine hybrid material is soluble in organic solvents and can be dried, stored, and re-dispersed into different solvents or chemical systems while retaining its assembled structure. Because the nanoparticles are covalently bonded to a polymer backbone and the interparticle distance is well controlled and maintained throughout the material, this hybrid material provides a unique opportunity to study the effect of interparticle interactions on the optical limiting property of the material.

Experimental Section

The synthesis and characterization of monofunctionalized gold nanoparticles (Au−COOH) and gold nanoparticle/polylysine hybrid material (AuNP−PLL) has been reported previously by Huo and co-workers[6a,7] and was briefly summarized in the last paragraph of introduction. The gold nanoparticles and the hybrid material were dissolved in CH_2Cl_2/CH_3OH (1/1, with ∼1% trifluoroacetic acid) for all of the measurements. The electronic absorption spectra were measured using an Agilent 8453 UV−vis spectrophotometer in a 1-cm quartz cuvette. The transient difference absorption was investigated using an Edinburgh LP920 laser flash photolysis spectrometer. Samples were degassed with argon for 30 min and were excited by the third harmonic output (355 nm) of a Quantel Brilliant Nd:YAG laser; the laser pulse width (fwhm) was 4.1 ns, and the repetition rate was adjusted to 1 Hz.

The optical limiting measurements were carried out using 4.1 ns laser pulses at 532 nm. A Q-switched Quantel Brilliant Nd:YAG laser was used as the light source. The repetition rate of the laser was set to 10 Hz. Energies of the incident laser beam were attenuated by a combination of a half-wave plate and a polarizing cube beam splitter. The beam was then split by a wedged beam splitter. One of the reflected beams was used to monitor the incident energy. The diameter of the transmitted beam was reduced to half of the original size by a telescope and was focused by a 30-cm plano-convex lens (f/78.6) to the center of a 2-mm quartz cell. The radius of the beam waist was approximately 69 μm. The incident energy and the output energy were monitored by two Molectron J4−09 pyroelectric joule meters.

Results and Discussion

The electronic absorption spectra of the single nanoparticles and the hybrid material in solution are shown in Figure 2. The

broad shoulder above 500 nm is due to SPR absorption. Although it is generally known that the SPR absorption band becomes obvious only when the gold nanoparticle core diameter is around or larger than 3−5 nm, weak SPR absorption band can still be identified from both individual nanoparticles and the hybrid material. It is noted that the SPR band red-shifts approximately 20 nm for the hybrid material comparing to that of the single gold nanoparticles. The red shift of the SPR band indicates that there probably is a dipole−dipole interaction between particles in close proximity.[4c]

It is known that for optical limiting applications, the material is required to exhibit high linear transmittance at low incident energy, but low transmittance when the incident energy is above the limiting threshold. To verify the feasibility of the hybrid material for optical limiting, the nonlinear transmission of the hybrid material (AuNP−PLL) was investigated using 4.1 ns laser pulses at 532 nm. As shown in Figure 3A, the hybrid material exhibited significant optical limiting. The limiting threshold, defined as the incident fluence at which the transmittance drops to 90% of the linear transmission, is as low as ∼0.08 J/cm^2, and the transmission drops to 25% when the incident fluence is increased to ∼1.7 J/cm^2, corresponding to a transmission decrease of 67% compared to the linear transmission. In contrast, the limiting threshold for individual nanoparticles (Au−COOH) is approximately 0.63 J/cm^2, and the transmittance drops to 50% at incident fluence of 1.7 J/cm^2, corresponding to a 33% of transmission decrease. This result is similar to what has been reported by Philip and co-workers for ∼3 nm core size gold nanoparticles.[3k] It is clear that the hybrid material exhibits much stronger optical limiting than that of the single nanoparticles. Because polylysine is transparent at 532 nm, no optical limiting can be observed from the polylysine backbone. Therefore, it is reasonable to believe that the enhanced optical limiting behavior of the hybrid material arises from the electromagnetic interactions between gold nanoparticles in proximity, probably a dipole−dipole interaction.[4c] Such interactions could change the electron distribution on the particle surface and thus influence the polarizability of the nanoparticles, which in turn gives rise to enhanced optical limiting. The possible influence of the interactions between gold nanoparticles and polylysine can be tentatively ruled out based on the UV−vis absorption spectrum of the hybrid material, in which the UV band corresponding to the polylysine backbone does not change. This is indicative of negligible interactions between the nanoparticles and polylysine backbone because significant interactions will alter the surface electron density of the gold nanoparticle, resulting in damp and broadening of the surface plasmon absorption band, as well as a change of the absorption of the organic moieties bounded to the particle surface.[8] However, neither of these changes is seen in the UV−vis absorption spectrum of AuNP−PLL. Nevertheless, to completely understand the effect of interparticle interactions and particle−polylysine interactions on the observed optical limiting behavior, hybrid materials with varied interparticle distance need to be investigated. This requires the loading ratio of the nanoparticles to polylysine backbone to be varied; unfortunately, synthetically this still remains as a challenge. We are currently working on this problem.

As mentioned earlier, Philip and co-workers attributed the optical limiting of gold nanoparticles with particle size of 3±0.5 nm to free-carrier absorption.[3k] However, Goodson and co-workers ascribed the optical limiting from silver-dendrimer nanocomposites to thermally assisted scattering.[9] To determine whether the optical limiting of the hybrid material also emanates from nonlinear scattering, an aperture was placed in front of
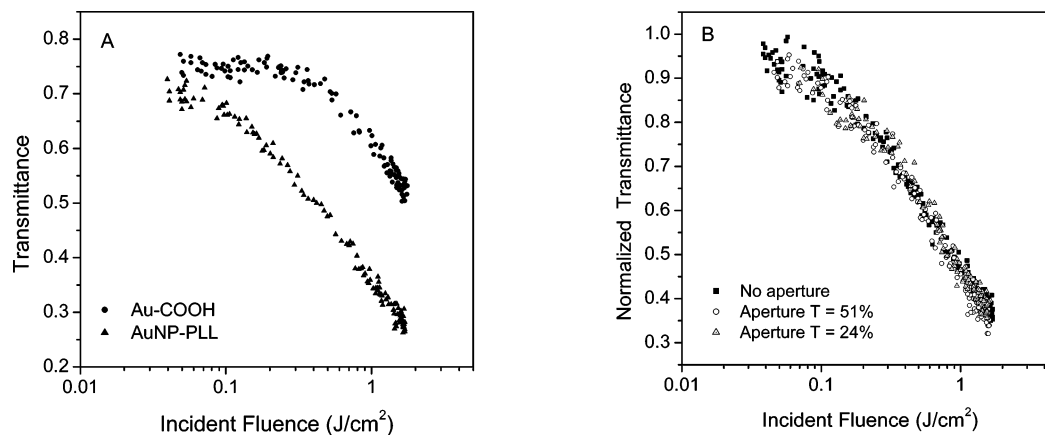
Figure 3. Optical limiting curves for (A) the individual gold nanoparticles (Au−COOH) and the nanoparticle/polylysine hybrid material (AuNP−PLL) in CH_2Cl_2/CH_3OH (1/1, with ~1% trifluoroacetic acid) and (B) the CH_2Cl_2/CH_3OH (1/1, with ~1% trifluoroacetic acid) solution of nanoparticle/polylysine hybrid material in the presence of different-size aperture. The measurements were conducted at 532 nm in a 2-mm cell. The pulse width of the laser is 4.1 ns. The linear transmission for all solutions is adjusted to 75%.
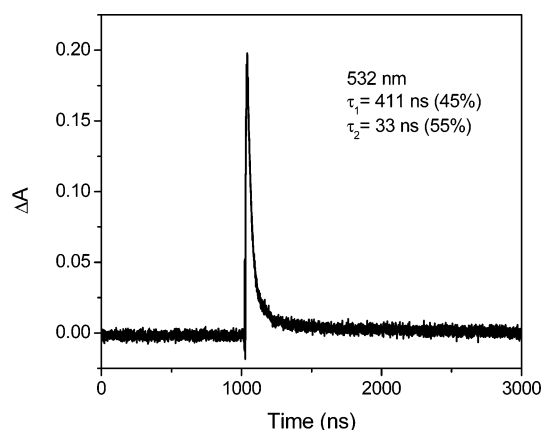
Figure 4. Transient absorption decay profile of the nanoparticle/polylysine hybrid material (AuNP−PLL) in CH_2Cl_2/CH_3OH (1/1, with ~1% trifluoroacetic acid) at 532 nm after 355 nm laser excitation (4.1 ns).

the detector that monitors the output energy of the light after passing through the sample. The size of the aperture was adjusted to allow for different amounts of light to pass through. It is expected that if the optical limiting is dominated by nonlinear scattering, the limiting performance will be influenced by the size of the aperture. A smaller aperture, i.e., a lower transmission ratio of the aperture, would give rise to a better optical limiting performance. However, the results shown in Figure 3B indicate that negligible scattering was observed from the solution of the hybrid material. This strongly suggests that nonlinear scattering is not the dominant contributor to the optical limiting of the hybrid material. Other nonlinear optical effects, such as nonlinear absorption could contribute to the optical limiting.

For materials with considerable linear absorption at the laser excitation wavelength, excited-state absorption rather than two-photon absorption, should be considered.[10] In the case of excited-state absorption cross-section higher than that of the ground-state absorption, reverse saturable absorption (RSA) will occur, which in turn will give rise to optical limiting. To determine whether this is the case for the nanoparticle/polymer hybrid material, the transient difference absorption of the hybrid material at 532 nm was monitored, which measures the difference between the excited-state absorption and the ground-state absorption. As shown in Figure 4, the transient difference absorption appears as a positive peak, suggesting that the excited-state absorption is stronger than that of the ground-state

absorption at this wavelength. Therefore, RSA should occur at 532 nm. Alternatively, the observed transient absorption could arise from free-carrier absorption (FCA) due to the fact that free carriers are generated when the electrons on the gold nanoparticles are excited.[3k] The FCA is phenomenologically similar to RSA, which can result in optical limiting of laser pulses. Since RSA and FCA usually develop on the time scale of the transient lifetime, and it is found that the decay of transient absorption of the hybrid material possesses a fast component of 33 ns and a slower process of 411 ns, both of which are sufficiently long for RSA or FCA of nanosecond laser pulses (4.1 ns) to occur. Thus, the major factor leading to the optical limiting of the hybrid material can be considered as the transient absorption discussed above, similar to what has been reported for individual gold nanoparticles with particle sizes of 3±0.5 nm.[3k] Transient absorption has also been observed for Au−COOH at 532 nm, with a fast ($\tau = 28$ ns) and a slow process ($\tau = 130$ ns). The extended lifetime of the transients for the hybrid material presumably arise from the interparticle couplings, and this could contribute to the enhanced optical limiting behavior. The possibility of these long-lived transients originating from the polylysine backbone can be excluded based on the fact that no transient absorption signal was observed from the pure polylysine solution. However, the mechanism for these much longer lifetimes is still not well understood and needs to be investigated further.

To gain further insight into the time scale of the optical limiting mechanism, the dependence of optical limiting on laser repetition rate has been investigated. Repetition rates of 1 and 10 Hz were employed in our study. As displayed in Figure 5, no pronounced difference was observed at different laser repetition rate. This further suggests that the mechanism that governs the optical limiting is relatively fast, which cannot be thermally assisted nonlinear scattering that usually occurs on a millisecond time scale.[10,11] Instead, transient absorption that occurs in a nanosecond time scale should be accountable for the independence of the optical limiting on the laser repetition rates.

A point worthy of mention is that a certain level of photofusion occurred during the optical limiting measurement. Repeated experimentation on the same spot of the solution resulted in a higher transmittance in comparison to the measurement conducted at a fresh solution, suggesting that the effective concentration of the nanoparticles within the laser irradiation area was reduced. This could result from the photofusion of
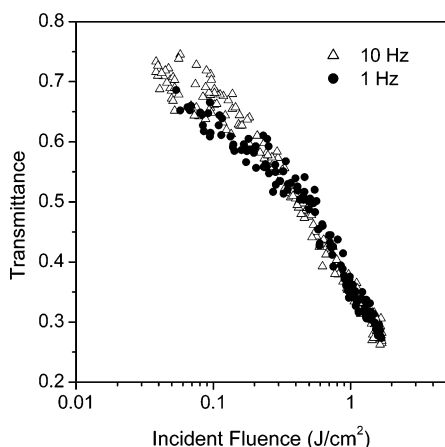
Figure 5. Optical limiting curves for the nanoparticle/polylysine hybrid material (AuNP−PLL) in CH_2Cl_2/CH_3OH (1/1, with ∼1% trifluoroacetic acid) at 532 nm at different laser repetition rates. The linear transmission of the solution is 75%, and the measurements are in a 2-mm cell.

the nanoparticles in close proximity. A nanoparticle size increase was observed from the TEM analysis of the hybrid material after repeated optical limiting measurements. For this reason, all of the results presented in this work were obtained using fresh solutions for each curve. Photofusion has been seen to be a common phenomenon for gold nanoparticles. For example, Kamat reported that larger segregated spherical particles formed after 532 nm laser pulse irradiation of thionicotinamide (TNA)-capped gold nanoparticle suspension.[12] El-Sayed and co-workers also observed the melting of gold nanorods into spherical particles induced by femtosecond laser pulses.[13]

Conclusion

The covalently bonded gold nanoparticle/polylysine hybrid material exhibits significant optical limiting for nanosecond laser pulses at 532 nm. Reverse saturable absorption and/or free-carrier absorption were demonstrated to be the dominant contributor(s) to the optical limiting behavior of the material. The enhanced optical limiting of the hybrid material is attributed to the electromagnetic interactions between nanoparticles in close proximity, which could influence the distribution of electrons on the particle surface and enhance the polarizability of the hybrid material. It is expected that by adjusting the density of nanoparticles loaded to the polymer, further quantitative information will be obtained on the influence of interparticle interactions on optical limiting. In our future research, gold nanoparticles larger than 10 nm will be used in order to combine the effects of nonlinear scattering from individual nanoparticles with the electromagnetic couplings in the hybrid material to further improve the optical limiting performances of the hybrid materials. In addition, polymers with different shape (such as star polymers) and molecular weight will be utilized to explore the optimal distance between the adjacent nanoparticles that can retain the interparticle interactions but prevent photofusion.

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