Optical Limiting Behavior of Nanosized Polyicosahedral Gold−Silver Clusters Based on Third-Order Nonlinear Optical Effects

Hong Zhang,*[†,‖] David E. Zelmon,[†] Luogen Deng,[‡]
Hua-Kuang Liu,[‡] and Boon K. Teo*[§]

Materials Directorate
Air Force Research Laboratory (AFRL/MLPO)
Wright-Patterson Air Force Base
Fairborn, Ohio 45433
Lumin, Inc., 1936 Huntington Drive
South Pasadena, California 91030
Department of Chemistry, 845 West Taylor Street
University of Illinois at Chicago
Chicago, Illinois 60607

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The advent of high power lasers, in both civilian and military applications, makes the search for efficient optical limiters for a wide range of personnel (e.g., eye) and equipment (e.g., sensor) protection the highest priority.[1] An ideal optical limiter exhibits a high, *linear* transmission below a certain "limiting" threshold, but its intensity is greatly attenuated (opaque with constant, low, and *nonlinear* transmittance) above the threshold[1] (cf. Chart 1, Supporting Information). Among many promising optical limiting materials, organometallic, metallophthalocyanines, metalloporphrins, and metal clusters containing a small number of metal atoms have attracted considerable attention.[1−4] Compared to organic optical limiting materials, these compounds have the advantage of multiple electronic transitions such as metal−ligand charge transfers. However, these systems often suffer from low damage threshold and inefficient optical limiting.

We report herein a highly efficient optical limiter based on a nanosized metal cluster, the 38-metal-atom cluster $(Ph_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (**1**)[5,6] of a single size, shape, and structure. Previous studies have indicated that metal nanoparticles not only exhibit greatly enhanced optical nonlinearities over those of bulk metal, but are also capable of enhancing the optical nonlinearities of organic molecules attached or close to the particle surface.[7] The present study represents the first observation of a new class of highly efficient optical limiting materials based on a novel series of vertex-sharing polyicosahedral Au−Ag supraclusters synthesized and characterized in our laboratory.[6]

Optical limiting measurements were performed using frequency-doubled Nd:YAG laser as the light source to generate 12-ns pulses (30 Hz) at 532 nm. The experimental setup is depicted in Chart 2, Supporting Information. The standard Air Force test bed was used. The collimated laser beam was focused on the sample by a lens with 20 cm focal length. The sample was positioned on the focal plane. The quasi-parallel (slightly converging) incident beam had a spot size of about 0.5 mm. Two detectors were used, one to detect the output energy and one to monitor the input energy. The output beam detector was positioned at 36 cm from the sample. The results for both solid and solution samples were calibrated with a calibration curve which was recorded before the sample was inserted. The solution sample was housed in a sample cell made of two pieces of transparent glasses separated by a Teflon ring gasket measuring 380 μm in thickness. The solid sample, in the form of a free-standing PMMA film of 0.5 mm in thickness, was clamped to the sample holder. The measurements were performed with and without an aperture (5 mm in diameter) placed at 6 cm in front of the detector. The purpose of the aperture was to block out peripheral scattered light entering the detector. Since the results are quite similar, only the latter are reported herein.

Figure 1, a and b are plots of the transmitted versus incident energies, depicting the optical limiting responses of solid (dispersed in organic polymer PMMA) and ethanol solution samples of **1**. It is apparent from Figure 1a that for solid samples, the optical limiting threshold occurs at around 32 μJ and that the limiting output energy is about 1.5 μJ for an input energy of up to 110 μJ. Permanent, irreversible damage was observed at the test spot only for input energies above 110 μJ and was caused by the breakdown of the PMMA host material rather than that of **1** itself. In solution, the optical limiting response occurred at a threshold of 14 μJ with a limiting output of 8 μJ for input energies of up to 85 μJ (Figure 1b). This trend was reversible, indicating that there was no damage to the test spot. Below the limiting threshold, the linear transmittance of the solid and solution samples were 15% (Figure 1a) and 40% (Figure 1b), respectively. Above the threshold, the maximum output energies for the solid and solution sample were about 2 and 8 μJ, respectively, indicating that the limiting response of the solid sample was four times more efficient than that of the solution.

The origin of the optical limiting behavior observed for both solid and solution samples of **1** is currently under investigation. We believe that the optical limiting behavior observed for **1** is intimately related to the third-order nonlinear optical effect, $\chi^{(3)}$, or, specifically, the Kerr effect.[8,9] In other words, since the valence

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[†] Air Force Research Laboratory (AFRL/MLPO), Wright-Patterson AFB.

[‡] Lumin, Inc.

[‖] Current address: Science and Technology Center, Northrop Grumman Corporation, Baltimore, MD 21090.

[§] Department of Chemistry, University of Illinois at Chicago.

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(5) **1** was synthesized as previously described[6] and characterized by elemental analysis and by UV−vis spectroscopy. The solid sample was prepared by dispersing **1** in a polymer host such as poly(methyl methacrylate) (PMMA) with approximately 2% loading by wt and cast into a thin disc of 0.5 mm in thickness and 2 cm in diameter. The solution sample was prepared by dissolving **1** in absolute ethanol, followed by filtering through a 0.2 μm syringe filter. The solution sample concentration was adjusted to yield an optical density of 0.85.

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(7) (a) For example, "bare" ellipsoidal silver particles measuring 100 × 100 × 300 nm^3 exhibit 900 times enhancement in $\chi^{(3)}$ over that of the bulk metal (Chemla, D. S.; Herritage, J. P.; Liao, P. F.; Isaccs, E. D. *Phys. Rev. B* **1983**, *27*, *4553* and references therein). (b) This optical phenomenon results from the surface plasma (or local field enhancement) effect in metal nanoparticles. Although not directly related to the present study, it is interesting to note that the surface plasmon peak at 380 nm of colloidal Ag particles (average diameter 76 Å) was found to be masked by gold-coating layers of 3.2−50 Å and red-shifted to the corresponding plasmon at 520 nm expected for pure Au particles at ≥30 Å coating (see Mulvaney, P.; Ciersig, M.; Henglein, A. *J. Phys. Chem.* **1993**, *97*, 7061). Hence, the optical limiting effect observed here may be further enhanced in the case of pure Ag clusters, provided that surface plasmon is the dominant mechanism.

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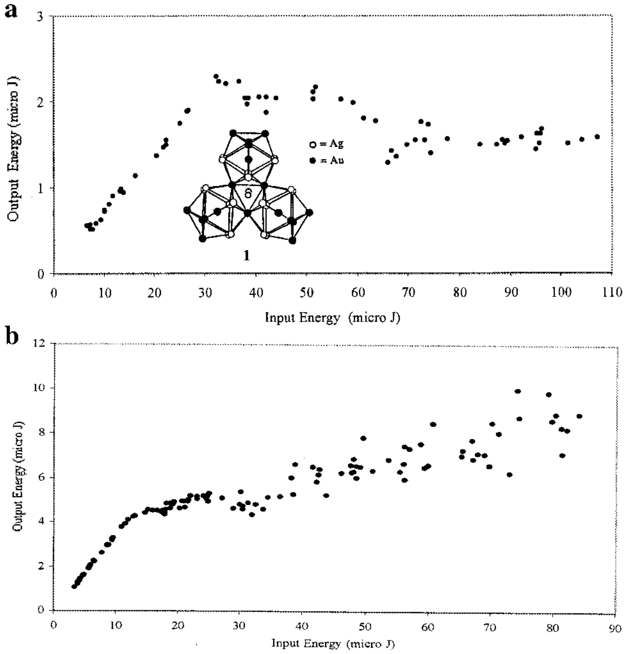

Figure 1. Optical limiting behavior of (a) solid sample (dispersed in PMMA) and (b) ethanol solution of the nanocluster, $(Ph_3P)_{12}Au_{18}Ag_{20}Cl_{14}$(**1**), plotted as transmitted versus incident energies for 12-ns, 532 nm laser pulses. For the sake of clarity, the ligands in **1** are not shown in the inset.

electrons in a large metal cluster such as **1** are highly delocalized and free-electron-like, they behave like metal when subject to the large electric field of the intense laser beam. It is known that there is, in general, a 3−6 orders-of-magnitude enhancement of the third-order susceptibility, $\chi^{(3)}$, of “bare” metal particles over that of the bulk metal.[7,11] These enhancements in $\chi^{(3)}$ were attributed to electromagnetic effects, in a way analogous to the surface-enhanced Raman scattering (SERS)[12] and other nonlinear optical effects associated with a roughened metal surface.[13] Since the refractive index, $n(\omega) = n_0 + \Delta n(\omega)$, has a field-induced term $\Delta n(\omega) = \chi^{(3)}(\omega)|E(\omega)^2|/2n_0$ that depends linearly on $\chi^{(3)}$ and quadratically on the electric field, $E(\omega)$, of the incident beam,[8a] the orders-of-magnitude enhancement in $\chi^{(3)}$ for isolated metal particles of dimensions smaller than the optical wavelength causes a change in the refractive index (grating) within the laser path, refracting away the incident light.[14]

In conclusion, in either solid film or in solution, structurally well-defined large bimetallic Au−Ag clusters such as **1** can achieve nearly 2 orders of magnitude of attenuation of high-intensity laser power. More importantly, it opens the door to a new class of highly promising optical limiting materials based on nanosized metal clusters. Work is in progress to design and fabricate new optical limiters based on nanosized metal clusters and to understand their optical limiting mechanism(s).[14]

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Supporting Information Available: Chart 1 shows an idealized optical limiter and Chart 2 depicts the experimental setup (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) It should be emphasized, however, that we cannot rule out mechanisms[1] such as reverse saturable absorption (RSA), two-photon absorption (TPA), free-carrier absorption (FCA), induced scattering due to local heating (thermal effects), etc. We also cannot rule out scattering mechanisms involving the characteristic plasmon resonance(s) of the Au−Ag nanoclusters, especially when the wavelength of the incident laser light approaches, or coincides with, that of the plasmon resonance of the metal cluster (which occurs at 495 mn for **1**).[10] In fact, at or near resonance, plasmon scattering may be operative. Experiments such as Z-scans using fs and ps laser pulses are being planned to gauge the relative importance of these mechanisms.

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(11) The third-order nonlinear optical properties (such as the Kerr effect) measured at the surface-mediated resonance of the metal nanoparticles was found to be enhanced by several orders of magnitude over those measured off-resonance.[7,15]

(12) See, for example: Van Duyne, R. P. In *Laser Excitation of Raman Scattering from Adsorbed Molecules on Electrode Surfaces, Chemical and Biochemical Applications of Lasers*; Moore, C. B., Ed.; Academic: New York, 1978; Vol. 4.

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(14) Generally speaking, there are three major contributions to the $\chi^{(3)}$ of metallic particles.[15] The first originates from the interband electric-dipole transitions between the states of the d valence bands and the states of the s−p conduction band. It has a very fast response time in the femtosecond regime ($\sim 10^{-13}$ s). The second is the hot electron excitation near the surface plasmon resonance, which has a response time of ps. The third is the thermal contribution which has a very slow response time of ns. For the Au:TiO_2 composites,[15] for example, it has been demonstrated that, on the fs time scale, the thermal contribution can be ignored, and the $\chi^{(3)}$ can be attributed mainly to the interband electric-dipole transitions with partial contribution from the hot electron excitation. Since Nd:YAG laser of 532 nm and 12 ns (30 Hz) was used in the present study, it is likely that all three mechanisms are operative here. Work is in progress to measure the $\chi^{(3)}$ of **1** and related clusters (via four-wave mixing or heterodyned optical Kerr effect[16]) and to gauge the relative importance of these three contributions using fs and ps laser pulses.

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