Strong Optical Limiting of Silver-Containing Nanocrystalline Particles in Stable Suspensions

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Metal and metal sulfide nanoparticles are prepared using a method that is based on the rapid expansion of supercritical fluid solution (RESS) into a liquid solution and characterized using transmission electron microscopy and X-ray diffraction methods. The nanoparticles form solution-like stable suspensions in the presence of a stabilization agent such as poly(*N*-vinyl-2-pyrrolidone) (PVP) polymer. The stable suspensions allow systematic nonlinear optical measurements. The nanocrystalline silver metal and silver sulfide particles in PVP polymer-stabilized ethanol suspensions of high linear transmittance exhibit excellent optical limiting properties, with the optical limiting responses toward nanosecond laser pulses at 532 nm being much stronger than those of benchmark materials [60]fullerene and chloroaluminum phthalocyanine in solution. A comparison of the results with those of stable suspensions of other nanoparticles including cadmium sulfide, lead sulfide, and nickel suggests that the optical limiting properties are unique to the nanoscopic silver-containing materials. Mechanistic issues concerning the optical limiting performance of the silver-containing nanocrystalline particles are discussed, and a nonlinear absorption mechanism is proposed.

Introduction

Nonlinear optical materials for the manipulation of optical beams in the passive method have received much recent attention.[1] There is great current interest in the development of organic and inorganic optical limiters for eye protection and optical switching applications.[1−4] Among potent optical limiters are materials that show strong nonlinear absorptions (or reverse saturable absorbers),[3] such as metallophthalocyanines,[5,6] fullerenes,[7−14] and mixed metal complexes and clusters.[15−17] Systems exhibiting strong transient light scattering due to photoinduced thermal processes, such as carbon black suspension, have also been investigated extensively for their strong optical limiting responses over a broad wavelength range.[18−20] Recently, there have been several studies of the optical limiting and nonlinear absorption properties of semiconductor nanoparticles.[21−24] For example, it was reported[21] that silver bromide particles trapped in nanosols exhibit interesting optical limiting characteristics.

We have recently developed a versatile method for the preparation of a series of polymer-protected metal and metal sulfide nanoparticles.[25,26] The method is based on the rapid expansion of supercritical fluid solution (RESS)[27,28] into a liquid solution.[25,26] The nanoparticles thus produced are relatively narrowly distributed in size and form highly stable suspensions in the presence of polymer as a stabilization agent. The stable suspensions of different metal and metal sulfide nanoparticles have allowed a systematic investigation of optical limiting properties of the nanoscopic materials under solution-like conditions. The results show that silver-containing nanocrystalline particles in polymer-stabilized suspensions of high linear transmittance strongly limit nanosecond laser pulses at 532 nm. The optical limiting responses of the suspensions are in fact significantly better than those of the benchmark materials fullerene and metallophthalocyanine in solution. Mechanistic issues on the optical limiting behavior of the nanoparticles are discussed.

Experimental Section

Materials. Silver nitrate ($AgNO_3$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), and sodium sulfide (Na_2S) were purchased from Aldrich. Lead nitrate ($Pb(NO_3)_2$) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) were purchased from Fisher Scientific. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was dried under vacuum at 100 °C for 16 h before use. [60]Fullerene (C_{60}, purity $>$99.5%) was obtained from BuckyUSA, and chloroaluminum phthalocyanine was purchased from Exciton. Both were used without further purification. Hydrazine and sodium borohydride ($NaBH_4$) were obtained from Aldrich and used as received. Anhydrous ammonia (purity $>$99.9999%) was purchased from Air Products and filtered before use. Dimethylformamide (DMF) and methanol were obtained from Mallinckrodt and used as received. Absolute ethanol was purchased from Fisher Scientific. It was distilled over molecular sieves and filtered before use. Water was deionized and purified by being passed through a Labconco WaterPros water purification system. Poly(*N*-vinyl-2-pyrrolidone) (PVP) of average molecular weight $M_w \approx 360\,000$ was obtained from Sigma and used without further purification.

Measurements. The apparatus for the preparation of nanoparticles through the rapid expansion of supercritical fluid solution (RESS) into a liquid solution process is illustrated in Figure 1. It consists of a syringe pump for pressure generation and pressure maintenance during RESS process and a gauge for monitoring the system pressure. The heating unit consists of a cylindrical solid copper block of high heat capacity in a tube furnace. The copper block is wrapped with stainless steel tubing coil and inserted tightly into a stainless steel tube to ensure close contacts between the tubing coil and the copper block for efficient heat transfer. The copper block/tubing coil

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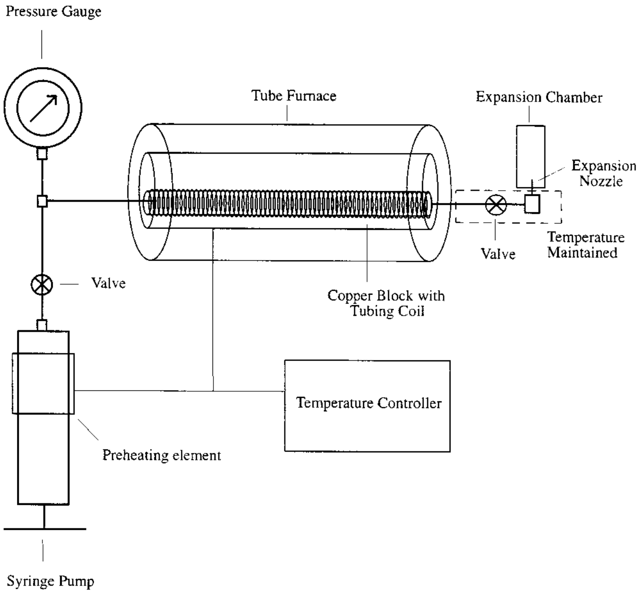

Figure 1. Experimental setup for the preparation of nanoparticles based on the rapid expansion of supercritical fluid solution (RESS) into a liquid solution.

assembly is preheated to a set temperature before each RESS experiment. For solutions of high critical temperature fluids, the syringe pump can be preheated to ensure that the solution reaches the designated temperature at the end of the tubing coil and becomes thermally equilibrated before rapid expansion. The expansion nozzle is a fused silica capillary hosted in a stainless steel tubing, which is inserted into the RESS chamber containing a room-temperature solution.

UV/vis absorption spectra were measured on a computer-controlled Shimadzu UV-2101PC spectrophotometer. Diffuse reflectance spectra were obtained using a Shimadzu UV-3100 spectrophotometer with ISR-3100 diffuse reflectance attachment. Powder X-ray diffraction measurements were carried out on a Scintag XDS-2000 powder diffraction system. Transmission electron microscopy (TEM) images were obtained using a Hitachi 600AB 100 kV transmission electron microscope.

The experimental setup for optical limiting measurements consists of a Continuum Surelite-I Q-switched Nd:YAG laser operated in the single-shot mode. The second harmonic from frequency doubling the infrared fundamental is isolated by use of the Surelite harmonic separation package. The laser beam is collimated, with the maximum energy at 532 nm of 160 mJ/pulse and a 5 ns pulse width (fwhm). The laser pulse energy is varied in the range of 10−160 mJ/pulse using a waveplate−polarizer combination. With the laser beam diameter of 6 mm, the corresponding input energy densities for optical limiting measurements are in the range of 0.035−0.57 J/cm^2. For higher energy densities of up to 2.2 J/cm^2, the laser beam diameter is reduced to 3 mm using a galilean style telescope, which consists of a plano-concave lens and a plano-convex lens. The detector is a Scientech Mentor MC2501 calorimeter controlled by a Scientech MD10 meter. A quartz cuvette of 2 mm optical path length was used in the optical limiting measurements.

Results and Discussion

Nanocrystalline silver sulfide (Ag_2S) particles were prepared in the rapid expansion of supercritical fluid solution (RESS) into liquid solution process using the setup shown in Figure 1. In the preparation, a solution of $AgNO_3$ in supercritical ammonia (0.5 mg/mL) at 200 °C was rapidly expanded through a nozzle into a room-temperature ethanol solution of Na_2S (25 mL, 0.7 mg/mL concentration). A silica capillary of 77 μm inner diameter hosted in a stainless steel tubing by applying epoxy resin was used as an expansion nozzle. The system pressure was maintained at 3000−3500 psia during the RESS process. The room-temperature solution in the RESS chamber (Figure 1) also contains 5 mg/mL of poly(*N*-vinyl-2-pyrrolidone) (PVP) polymer ($M_w \approx 360\,000$) as a stabilization agent. With the PVP polymer protection, the nanocrystalline Ag_2S particles form a very stable suspension in ethanol, which is in fact indistinguishable from a typical homogeneous solution. The absorption spectrum of the yellowish suspension is shown in Figure 2.

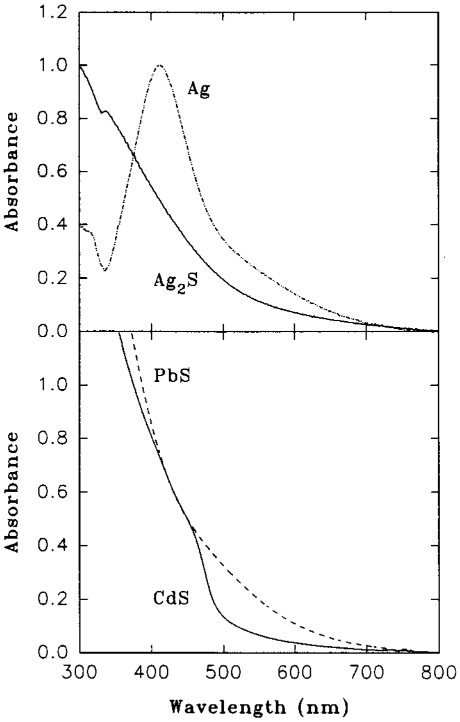

Figure 2. Absorption spectra of the nanocrystalline metal and metal sulfide particles in stable suspensions.

Transmission electron microscopy (TEM) and powder X-ray diffraction methods were used in the nanoparticle characterization. The as prepared nanocrystalline Ag_2S particles with the protective PVP polymer were deposited on a collodion film on a copper grid support for TEM measurements. A TEM image of the nanocrystalline Ag_2S particles is shown in Figure 3. A statistical analysis of the TEM image consisting of 200 particles yields an average Ag_2S particle size of 7.3 nm, with a size distribution standard deviation of 1.7 nm (Table 1). The powder X-ray diffraction pattern of the solid sample of PVP polymer-protected nanocrystalline Ag_2S particles agrees well with that of bulk Ag_2S (monoclinic) documented in the X-ray diffraction reference library. On the basis of the band broadening in the X-ray diffraction pattern,[29] the average size of the Ag_2S particles in the solid sample is ~20 nm, significantly larger than that for the as prepared Ag_2S particles.

A stable suspension of the PVP polymer-protected nanocrystalline Ag_2S particles in ethanol was measured for optical limiting responses toward the second harmonic of a Q-switched Nd:YAG laser at 532 nm. Dissolved oxygen and ammonia (from the nanoparticle preparation process) in the suspension were removed before optical limiting measurements by purging with argon gas. The suspension was very dilute and indistinguishable from a typical homogeneous solution, with a linear transmittance at 532 nm of 90%. Optical limiting measurements of the

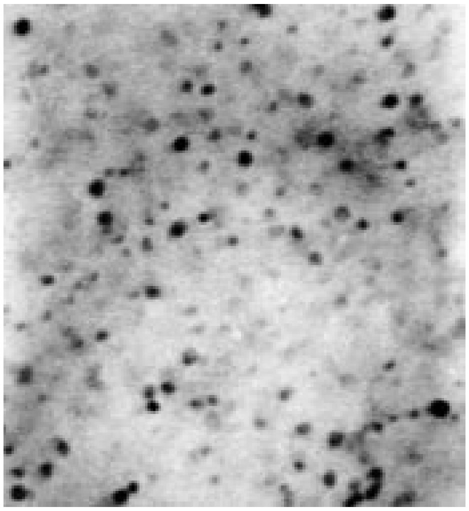

Figure 3. A TEM image of the nanocrystalline Ag_2S particles (1 mm = 5 nm).

TABLE 1: Physical and Structural Parameters of the Metal and Metal Sulfide Nanoparticles

particle	RESS solution	RT solution	stabilization agent	X-ray diffraction	TEM size (nm)	TEM σ (nm)[a]
Ag_2S	ammonia	ethanol	PVP	monoclinic	7.3	1.7
CdS	ammonia	water	gelatin	cubic	~5	
PbS	methanol	methanol	PVP	cubic	6.6	1.0
Ag metal	ammonia	ethanol	PVP	cubic	5.6	0.78
Ni metal	ethanol	DMF	PVP	cubic	5.8	0.54

[a] Size distribution standard deviation.

suspension were performed as a function of input light fluence I_{IN}. Fresh sample was used for each I_{IN} value to avoid possible effects of laser radiation on the nanoparticle suspension. As shown in Figure 4, the nanocrystalline Ag_2S particles in the PVP polymer-stabilized ethanol suspension exhibit strong optical limiting responses toward 5 ns (fwhm) laser pulses at 532 nm. The output light fluence I_{OUT} reaches a plateau at I_{IN} of only 0.23 J/cm^2. The saturated I_{OUT} value at the plateau is 0.11 J/cm^2. The strong optical limiting responses are not associated with the PVP polymer because no optical limiting was observed in the solution of PVP in ethanol. For comparison, strong optical limiters C_{60} and chloroaluminum phthalocyanine as benchmark materials were investigated under the same experimental conditions. As shown in Figure 4, the optical limiting responses of the nanocrystalline Ag_2S particles are considerably stronger than those of C_{60} in toluene solution and chloroaluminum phthalocyanine in DMF solution of the same linear transmittance of 90%.

Also, for comparison, other metal sulfide nanocrystalline particles including cadmium sulfide (CdS) and lead sulfide (PbS) were prepared using the same RESS into liquid solution method.[25,26] The nanoparticles also form stable suspensions under the protection of a stabilization agent. The physical and structural parameters of the CdS and PbS nanoparticles from TEM and powder X-ray diffraction characterizations are summarized in Table 1. The absorption spectra of the metal sulfide nanoparticles are shown in Figure 2. The nanocrystalline CdS and PbS particles in stabilized methanol and water suspensions, respectively, were measured for optical limiting responses toward 5 ns laser pulses at 532 nm. The results are clearly different from that of the nanocrystalline Ag_2S particles, as compared in Figure 4. The optical limiting responses of both CdS and PbS nanoparticles are much weaker than those of the Ag_2S nanoparticles, though the difference is somewhat smaller for the PbS nanoparticles. The comparison of optical limiting results shown in Figure 4 seems to suggest that the excellent optical limiting properties of the nanocrystalline Ag_2S particles are specific with respect to the silver (Ag) element. Similarly, strong optical limiting responses were observed in a stable suspension of Ag metal nanoparticles.

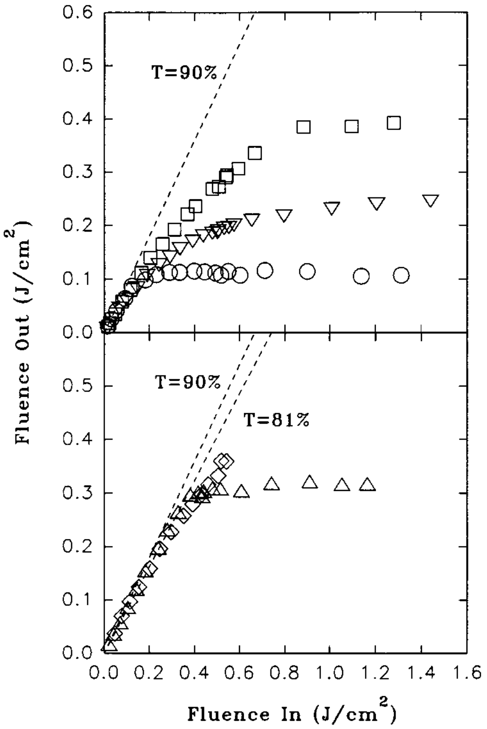

Figure 4. Optical limiting responses of the nanocrystalline Ag_2S particles in a PVP polymer-stabilized ethanol suspension (○) of 90% linear transmittance at 532 are compared with those of C_{60} in toluene (□) and chloroaluminum phthalocyanine in DMF (▽) of the same linear transmittance and those of the CdS nanoparticle suspension (◇) of 81% linear transmittance and the PbS nanoparticle suspension (△) of 90% linear transmittance.

Nanocrystalline Ag particles were prepared in the RESS into liquid solution process, coupled with chemical reduction. In the preparation, a solution of $AgNO_3$ in supercritical ammonia (0.5 mg/mL) at 160 °C and 4000 psia was rapidly expanded into a room-temperature hydrazine solution in ethanol (5 μL/mL) to form nanocrystalline Ag metal particles. Under the PVP polymer protection, the Ag nanoparticles form a very stable suspension in ethanol, which appears indistinguishable from a typical homogeneous solution. The absorption spectrum of the yellow-colored suspension is also shown in Figure 2. The spectrum consists of an intense absorption band peaking at ~410 nm, characteristic of plasmon absorption.[30,31] The as prepared nanocrystalline Ag metal particles with the protective PVP polymer were deposited on a collodion film on a copper grid support for TEM measurements. A TEM image of the nanocrystalline Ag metal particles is shown in Figure 5. A statistical analysis of the TEM image consisting of 180 particles yields an average Ag particle size of 5.6 nm, with a size distribution standard deviation of 0.78 nm (Table 1). The PVP polymer-protected nanocrystalline Ag metal particles in the solid state were also characterized by powder X-ray diffraction method. The diffraction pattern matches well with that of the bulk Ag metal (face centered cubic) documented in the X-ray diffraction reference library. In the solid sample, the average size of the Ag particles was estimated to be ~14 nm on the basis of the

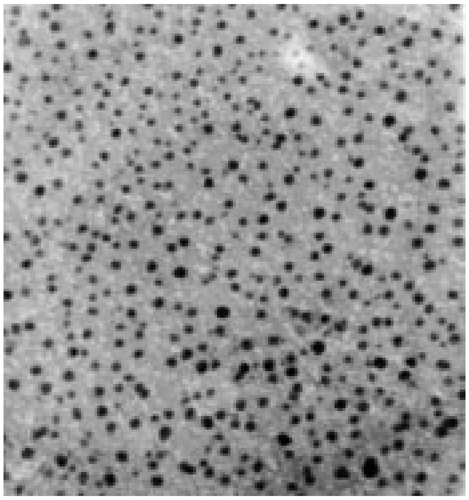

Figure 5. TEM image of the nanocrystalline Ag metal particles (1 mm = 4 nm).

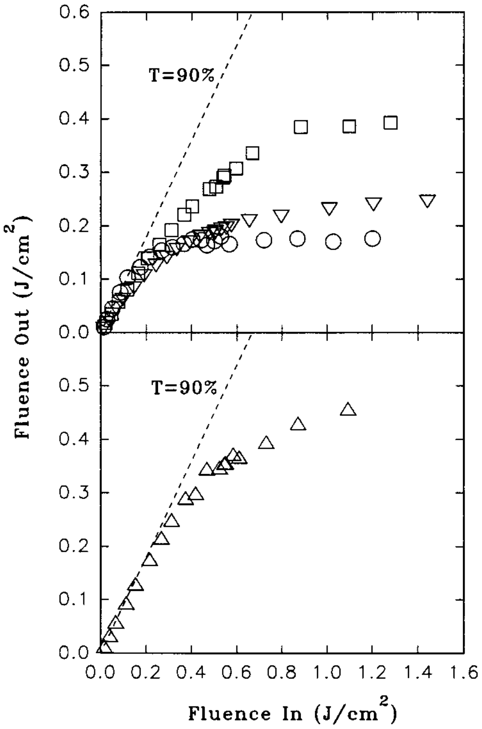

Figure 6. Optical limiting responses of the nanocrystalline Ag metal particles in PVP polymer-stabilized ethanol suspension (○) of 90% linear transmittance at 532 are compared with those of C_{60} in toluene (□), chloroaluminum phthalocyanine in DMF (▽), and the Ni metal nanoparticles in DMF suspension (△) of the same linear transmittance.

band broadening in the X-ray diffraction pattern,[29] which is also significantly larger than that for the as prepared Ag particles.

The nanocrystalline Ag metal particles in PVP polymer-stabilized ethanol suspension were studied for optical limiting properties. As shown in Figure 6, the suspension of 90% linear transmittance exhibits strong optical limiting responses toward 5 ns laser pulses at 532 nm. Before optical limiting measurements, the suspension was purged with argon gas to remove dissolved oxygen and ammonia (from the nanoparticle preparation process). The output light fluence I_{OUT} reaches a plateau at input fluence I_{IN} of 0.37 J/cm^2, and the saturated I_{OUT} value at the plateau is 0.18 J/cm^2. Again, the optical limiting responses of the PVP polymer-protected nanocrystalline Ag metal particles are stronger than those of C_{60} in toluene solution and chloroaluminum phthalocyanine in DMF solution of the same linear transmittance (Figure 6).

For comparison, nickel (Ni) metal nanoparticles were prepared using the RESS into liquid solution/chemical reduction method for optical limiting measurements.[26] A solution of $NiCl_2$ in supercritical ethanol was used in the rapid expansion, and sodium borohydride ($NaBH_4$) was used as a chemical reducing agent. The Ni metal nanoparticles thus prepared form a stable suspension in DMF under the PVP polymer protection. The physical and structural parameters of the Ni nanoparticles from TEM and powder X-ray diffraction characterizations are also summarized in Table 1. Optical limiting properties of the Ni metal nanoparticles in PVP polymer-stabilized DMF suspension were studied. As shown in Figure 6, the Ni metal nanoparticles exhibit only marginal optical limiting responses toward 5 ns laser pulses at 532 nm, significantly different from the nanocrystalline Ag metal particles.

The optical limiting properties of the nanocrystalline Ag metal particles and Ag_2S particles are unique to these silver-containing nanoscopic materials. However, no meaningful optical limiting responses were observed in a homogeneous solution of silver ions. The aqueous solution of $AgNO_3$ hardly absorbs at 532 nm even at a high solution concentration, exhibiting no nonlinear optical behavior.

Since the silver-containing nanocrystalline particles are in suspensions, optical limiting contributions from transient scatterings that are associated with photothermal processes should be considered. For a suspension of light-absorbing carbon black particles, strong optical limiting responses have been observed.[18−20] The optical limiting of carbon black suspension has been explained in the literature in terms of the optical breakdown of absorbing carbon black particles and the associated liquid solvent.[19,20] In such a mechanism, the attenuation of nanosecond laser pulses is attributed to the formation of scattering shock waves as a result of the optical breakdown. However, for the optical limiting results of the nanoparticles in stable suspensions reported here, it seems difficult to explain the specificity in the strong optical limiting with silver-containing nanocrystalline particles within the mechanistic framework for carbon black suspensions. A more likely scenario is that the observed optical limiting responses in suspensions of the other nanoparticles, especially the Ni metal nanoparticles, are contributed by similar mechanistic processes to those in carbon black suspensions. The optical limiting properties of the silver-containing nanocrystalline particles in stable suspensions are probably dominated by a different mechanism.

It is well-documented that silver nanoparticles have interesting photoelectrochemical properties.[31,32] Recently, Kamat and coworkers reported[23] that silver colloids of particle diameter 40−60 nm exhibit a strong and broad transient absorption in the visible and near-infrared wavelength region when subjected to laser pulse excitation. The absorption growth monitored at 600 nm follows a single-exponential kinetic equation, with a lifetime of 1.5 ± 0.1 ns.[23] The broad transient absorption has been assigned to a transient state that is generated in a photoinduced intraparticle charge separation process, namely $(Ag^+e^-)_x$. Similar photoinduced redox processes were proposed to be responsible for the optical limiting characteristics of silver bromide nanosols comprising ∼6 nm particles of silver bromide.[21] In addition, strong nonlinear absorption at 532 nm was observed in Ag_2S/CdS nanocomposites of ∼10 nm in diameter.[22] The nonlinear absorption was attributed to the free-carrier absorption that is associated with the coating of CdS particles with Ag_2S.[22]

Similarly, the strong optical limiting responses of the nanocrystalline Ag metal and Ag_2S particles toward nanosecond laser pulses (Figures 4 and 6) may be dominated by a nonlinear absorption mechanism. The photoinduced electron ejection produces electron holes in the nanoparticle structure, resulting in strong free-carrier absorption on the nanosecond time scale. That the optical limiting responses of the Ag metal nanoparticles are somewhat weaker than those of the Ag_2S nanoparticles (Figures 4 and 6) is probably due to the fact that the Ag_2S nanoparticles in stable suspension have a lower ground-state absorption cross section at 532 nm. In this regard, since the absorption of metal sulfide nanoparticles generally blue shifts with decreasing average particle size, better optical limiting performance may be achieved with nanocrystalline Ag_2S particles of even smaller sizes.

In principle, CdS and PbS nanoparticles are similar to Ag_2S nanoparticles as semiconductors so that the same photoinduced intraparticle charge separation and free carrier absorption may be expected. But, as reflected in the relatively weak optical limiting responses, the nonlinear absorptions of the nanocrystalline CdS and PbS particles in stable suspensions must be weak at 532 nm. The suspension of CdS nanoparticles has particularly poor optical limiting performance (Figure 5). As reported in the literature,[22] there is enhanced nonlinear absorption when CdS nanoparticles are coated with Ag_2S to form nanocomposites. The enhancement could be due simply to the much stronger nonlinear absorption of Ag_2S particles in the nanocomposites. However, whether the presence of CdS or other particles in nanocomposites with Ag_2S increases the efficiency of photoinduced charge separation and/or the free carrier absorption cross section of nanocrystalline Ag_2S particles remains an interesting question for further investigations.

The results reported here suggest that nanoscopic materials may represent a new class of potent optical limiters. The optical limiting performance of the silver-containing nanocrystalline particles in stable suspensions is obviously among the best of all known optical limiting materials. As compared in Figures 4 and 6, the optical limiting responses of the silver-containing nanoparticles toward nanosecond laser pulses at 532 nm are significantly better than those of C_{60} and chloroaluminum phthalocyanine in solution, which are considered as benchmarks for high-performance optical limiters. The silver-containing nanoparticles have relatively flat and weak absorption in much of the visible region, and their transient absorption is also broad.[23] Therefore, the nanoscopic silver-based materials may be used as broad band optical limiters. Between the Ag metal nanoparticles and Ag_2S nanoparticles, the former is chemically somewhat less stable than the latter, i.e., more susceptible to oxidation under ambient conditions. Thus, the nanocrystalline Ag_2S particles, which also have better optical limiting performance, are more advantageous in practical laser attenuation applications.

The polymer-protected nanocrystalline Ag metal and Ag_2S particles prepared using the RESS-based method are of relatively narrow size distributions and improved surface properties,[25] which are important to the efficient intraparticle free carrier generation. The nanoparticle suspensions thus obtained are very stable and indistinguishable from typical homogeneous solutions, which allows further processing and fabrication for nonlinear optical devices.

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Supporting Information Available: Statistical analyses of particle sizes and size distributions from TEM results and powder X-ray diffraction patterns of the Ag_2S and Ag metal nanoparticles (5 pages). Ordering information is given on any current masthead page.

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