

Fragmentation of colloidal nanoparticles by femtosecond laser-induced supercontinuum generation

S. Besner, A. V. Kabashin, and M. Meunier^{a)}

Laser Processing Laboratory, Department of Engineering Physics, École Polytechnique de Montréal, Case Postale 6079, Succursale Centre-ville, Montréal, Québec H3C 3A7, Canada

(Received 25 September 2006; accepted 19 October 2006; published online 8 December 2006)

A femtosecond laser-based method to control the size characteristics of gold colloidal nanoparticles is reported. The method uses the supercontinuum generation produced through a strong nonlinear-optical interaction of the femtosecond radiation with a liquid to fragment relatively large colloids and reduce their agglomeration. The fragmented species then recombine to form smaller, less dispersed, and much more stable nanoparticles in the solution. The size of the nanoparticles after the treatment is independent of the initial characteristics of colloids, but depends strongly on laser parameters and on the presence of chemically active species in the solution. © 2006 American Institute of Physics. [DOI: 10.1063/1.2402944]

Due to their unique size-dependent optical, physical, and chemical properties, metal nanoparticles have become increasingly popular in a variety of applications including biosensing and imaging,¹ nanoparticle-enhanced Raman scattering,² catalysis,³ and data storage.⁴ These applications generally require means to controllably vary the size characteristics of nanomaterials. For metal nanoparticles, such size modifications are mainly achieved through laser irradiation of a colloidal solution at a particular wavelength corresponding to the resonant excitation of surface plasmons^{5–10} or to an interband transition.^{11,12} Absorbing the energy of pumping radiation, the nanoparticles evaporate or fragment to form smaller colloids. However, despite its relative efficiency, this method enables to effectively treat only some discrete sizes and shapes of nanoparticles. Its practical usefulness becomes quite limited in the case of a broad nanoparticle size distribution or an arbitrary nanoparticle shape, when it is impossible to select a proper plasmon excitation wavelength for the whole ensemble of nanoparticles. Similar problems arise in the case of non-noble metal nanoparticles, when no plasmon-related absorption peak is present in the visible region.

In this letter, we report a laser-based method to control the size of colloidal nanoparticles, which is not related to a particular laser wavelength and therefore has no conditional requirements on the size, size dispersion, or type of nanoparticles in the solution. Our approach employs a self-transformation of an intense femtosecond laser radiation into a broadband white light supercontinuum which is used to fragment large colloids and thus reduce their size.

The experiments were carried out using a Ti:sapphire laser (Hurricane, Spectra Physics Lasers), providing 140 fs pulses centered at 800 nm with a repetition rate of 1 kHz. The laser light was focused in a quartz cuvette filled with 2 ml of colloidal solution. The solution was stirred during the laser treatment to homogenize the irradiation process. Since the phenomena of filamentation, self-focusing, and supercontinuum generation possess a threshold power of 4.4 MW (Ref. 13) and optical breakdown possesses an intensity threshold of 1.11×10^{13} W/cm²,¹⁴ supercontinuum generation can be triggered without any optical breakdown for

long focal length.¹⁵ Therefore, using relatively high laser energy (500 μ J) and long focal length ($f=7.5$ cm), we were able to achieve the regime of breakdown-free supercontinuum generation.

In our tests, we treated various types of nanoparticles. First, we used ultrapure nanoparticles prepared by recently introduced technique of femtosecond laser-based ablation in pure de-ionized water.^{16,17} Since no chemical precursor or capping ligand was used during the laser fabrication procedure, the nanoparticles had unique surface chemistry, which was free of impurities. As shown in Fig. 1, the laser-synthesized nanoparticles had a broad size distribution between 10 and 150 nm with a mean size and size dispersion of 55 and 34 nm, respectively. In addition, in some tests, we added 5 g/l of dextran ($M=6000$), a known biocompatible protective ligand¹⁸ to the laser-synthesized nanoparticle solution. Finally, we used monodisperse gold nanoparticles prepared by a chemical reduction method with mean sizes of 60 and 100 nm (SPI Corp.). The size distribution of the nanoparticles was examined by transmission electron microscopy (TEM). Solutions of nanoparticle (5 μ l) were dropped on a carbon-coated, formvar-covered copper grid and then dried in air. The UV-visible extinction spectra of the nanoparticle solution were acquired with a Hewlett-Packard 8452A diode array spectrophotometer.

We clearly observed, by a naked eye, the phenomenon of supercontinuum generation and its scattering by the nanoparticles in solution along the pathways of the laser beam. This

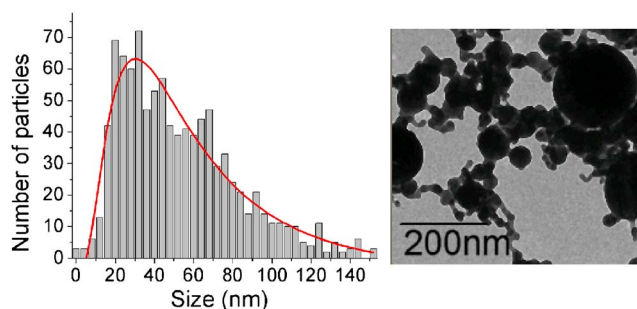


FIG. 1. (Color online) TEM micrograph images and corresponding size distributions of laser-synthesized gold nanoparticles.

^{a)}Electronic mail: michel.meunier@polymtl.ca

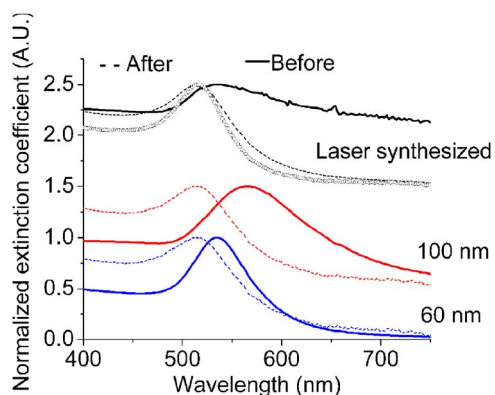


FIG. 2. (Color online) Optical extinction spectra of the gold nanoparticle solution before (solid line) and after (dashed line) 2 h of laser irradiation. The dotted curve shows the spectrum for 2 h irradiation of the laser-synthesized nanoparticles with the addition of 5 g/l of dextran.

light was composed of multiple filaments which is in good agreement with the observations of Liu *et al.*¹³ No bubble formation or strong local scattering was found, confirming the absence of any optical breakdown in the liquid. In the course of the treatment, the color of the solution progressively changed from pink-purple to clear red. As shown in Fig. 2, such color change was accompanied by a blueshift and narrowing of the plasmon-related peak in the extinction spectra. After 2 h of laser treatment, the final positions of the peaks were around 520 nm, which is generally associated with the excitation of localized plasmons of relatively small 3–30 nm gold nanoparticles.¹⁹

TEM measurements confirmed the size reduction effect, although the final size of the nanoparticles appeared to be quite different for different initial solutions. For laser-synthesized nanoparticles in pure de-ionized water, we observed only a moderate change of the size characteristics with the reduction of the mean size and size dispersion from 54 ± 36 to 20 ± 4 nm after 2 h of treatment [Fig. 3(a)]. Nevertheless, the treatment led to a drastic reduction of the nanoparticle agglomeration and a radical improvement of solution stability. While the untreated nanoparticles agglomerated within a few hours, samples treated by the described procedure did not show any sign of precipitation within several months after the preparation. Such stability of gold nanoparticles in the absence of any protective agent has never been reported in the literature and will be discussed elsewhere. In contrast, the size reduction effect was much more pronounced when dextran was added to the solution. As shown in Fig. 3(b), the presence of dextran led to a decrease of the size and size dispersion down to 6 ± 2 nm after 2 h of treatment. Similar effect was observed for the larger chemically prepared nanoparticles. Here, as shown in Figs. 3(c) and

3(d), the final size characteristics were 4.6 ± 1.5 and 5.3 ± 1.8 nm for the 100 and 60 nm initial colloids, respectively. Preliminary results on silicon and silver colloids also showed the same trend of size reduction under the irradiation of the white light based irradiation.

Our experiments showed that the final size distribution was almost independent of the initial size and shape of nanoparticles, but depended on the radiation parameters and on the presence of chemical additives. In fact, this suggests that the final size of the nanoparticles is determined by the chemical interaction of the fragmented species in the solution. TEM micrographs revealed the presence of nanoclusters as small as 1 nm. In the absence of chemical additives these nanoclusters coalesced and formed relatively large 20 ± 4 nm colloids [Fig. 3(a)]. In contrast, when dextran is added to the solution, the steric repulsion of the polymer chain limits the particle growth [Fig. 3(b)] as dextran is linked to the gold surface. This linkage should arise mainly from the hydrogen bond formation between the partially oxidized gold surface and the OH groups of the stabilizing agents.¹⁸ Similar effect took place in the case of chemically produced particles. Indeed, the fragmentation of the nanoparticles led to a release of trace amounts of sodium citrate, tannic acid, and potassium carbonate, which then enhanced the ionic repulsion of the gold particles in the solution and thus prevented nanoparticles from coalescence [Figs. 3(c) and 3(d)].

We reason that in the absence of the optical breakdown phenomenon, the fragmentation can be caused by at least three mechanisms: (1) direct absorption of the laser radiation, (2) absorption of energy of the white continuum, and (3) interband resonant multiphoton absorption. Here, the third mechanism can be disregarded since the efficiency of multiphoton absorption is negligible for laser intensities below 2×10^{12} W/cm²,²⁰ while the upper estimation of the intensity in our experiments gives $(1.4 \pm 0.3) \times 10^{12}$ W/cm², as measured by the knife-edge technique. The second mechanism is related to a nonlinear-optical interaction of femtosecond laser pulse with aqueous medium, leading to a severe broadening of the pulse from ~ 400 to ~ 1200 nm with a maximum intensity at around 800 nm. Here, depending on the initial pulse energy and on the focusing condition, $\sim 10\%$ of the initial energy centered at 800 nm was transferred in the spectral band of 400–650 nm. Such broadening can only occur for laser with a pulse width less than 1 ps since it results from the strong nonlinear interaction with the medium. The large blue wing is generally attributed to the free-electron generation, while the red wing is related to a combined effect of the instantaneous and delayed responses of the Kerr nonlinearity.¹⁵ As the blue wing of the white light pulse gains in intensity during the propagation, it approaches to the plasmon absorption peak of nanoparticles, resulting in

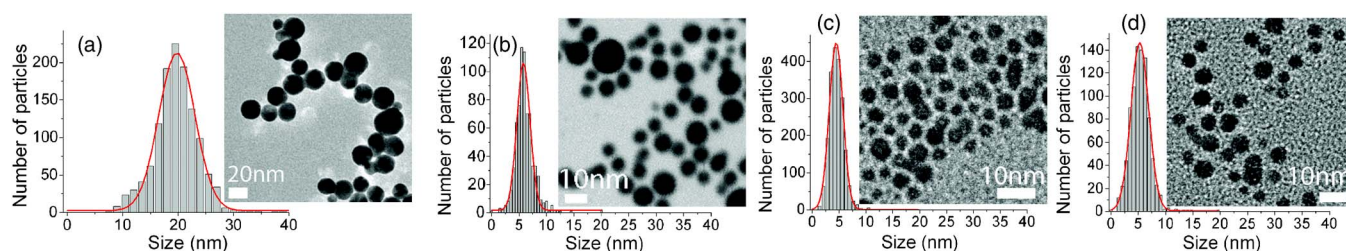


FIG. 3. (Color online) TEM micrograph images and corresponding size distributions after 2 h of laser irradiation of the laser-synthesized nanoparticles without (a) and with (b) the addition of dextran and of the chemically produced gold colloids of 100 nm (c) and 60 nm (d).

an increase of the total absorbed energy. Using experimental data on the white light emission and nanoparticle-based absorption spectra, we can compare efficiencies of white light continuum and direct 800 nm absorption. For 10–100 nm gold nanoparticles the absorption at 800 nm is known to be very weak, 20–50 times less intense than at resonance plasmon wavelength (520–550 nm). However, direct 800 nm absorption cannot be completely ruled out, taking into account a high intensity of radiation at the pumping wavelength. Our analysis shows that the ratio, $R=A_{\text{WL}}/A_{800}$, of the integral absorption of the white light (A_{WL}) on the integral absorption at 800 nm (A_{800}) is $R \sim 2.5$ for small (10–30 nm) and is $R \sim 1.5$ for large (60–100 nm) nanoparticles. Therefore, the white light based absorption was predominant in our conditions compared to a weak absorption at the pumping 800 nm wavelength.

It should be noted that this conclusion is consistent with the results of previous studies of gold nanoparticle absorption at 800 nm. In particular, Link *et al.*¹⁰ clearly observed the melting of nanorods and their conversion to nanoparticles under the irradiation of a small solution volume by 0.56 J/cm² femtosecond pulses, while even prolonged irradiation of nanoparticles did not change their size significantly. We believe that a low efficiency of nanoparticle fragmentation in these tests, using much higher laser intensities (in our tests, the fluence was estimated as 0.20 J/cm²), was explained by a much smaller solution volume, which minimized white light generation effects. Similar drop of the nanoparticle reduction efficiency took place in our tests, when the volume of the solution was decreased.

Finally, we reason that the fragmentation of nanoparticles can be caused by either the photothermal process, in which the particles vaporize at the boiling temperature,^{11,21} or through the Coulomb explosion induced by an electron ejection from thermionic^{12,22} or multiphoton ionization process.^{10,12,23} However, the absence of intermediate size nanoparticles even for short irradiation time suggests that the Coulomb explosion was the dominant fragmentation process.

In summary, we report a method to control the size of colloidal nanoparticles employing the femtosecond laser-based generation of white continuum. Any particles having a significant absorption cross section in the range of 400–1200 nm can be processed using this laser irradiation technique. The method does not require any specific initial nanoparticle size and does not involve any additional chemical precursors. When synthesized in pure de-ionized water,

the nanoparticles have unique surface chemistry, not reproducible with any other chemical nanofabrication routes, which makes them unique for surface enhanced raman spectroscopy and bioimaging *in vivo* applications.

The authors acknowledge the financial contribution from the Natural Sciences and Engineering Research Council of Canada and Canadian Institute for Photonics Innovations (CIPI).

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