

Effect of laser energy and pulses on size and concentration of gold nanoparticles in DDDW by LALP method

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Abstract

The size and the concentration of the gold nanoparticles (GNPs) synthesized in double distilled deionized water (DDDW) have been found to be affected by the laser energy and the number of pulses.

The absorption spectra of the nanoparticles DDDW, and the surface plasmon resonance (SPR) peaks were measured, and found to be located between (509 and 524)nm using the UV- Vis spectrophotometer. SPR calculations, images of transmission electron microscope, and dynamic light scattering (DLS) method were used to determine the size of GNPs, which found to be ranged between (3.5 and 27) nm. The concentrations of GNPs in colloidal solutions found to be ranged between (37 and 142) ppm, and measured by atomic absorption spectroscopy (AAS).

Key words

Pulsed laser ablation, gold nanoparticles, synthesis of GNPs, surface plasmon resonance.

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تأثير طاقة و نبضات الليزر على حجم و تركيز جسيمات الذهب النانوية في الماء

مزودج التقطير بطريقة الاستئصال بالليزر في الطور السائل

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الخلاصة

ان حجم و تركيز جسيمات الذهب النانوية المحضرة في الماء مزودج التقطير وجد انها تتاثر بكل من طاقة و عدد نبضات الليزر.

قيس طيف الامتصاص و قمم الرنين البلازموني السطحي للجسيمات الذهبية النانوية باستخدام مطياف الاشعة فوق البنفسجية و الاشعة المرئية و وجد انها تقع بين (509 و 524) nm. و قد استخدمت حسابات معتمدة على قمم الامتصاص البلازموني و صور المجهر الالكتروني النافذ و طريقة استطارة الضوء الحركية (DLS) لتحديد حجم جسيمات الذهب النانوية، و التي تراوحت بين (3.5 و 27) nm. و حددت قيم تراكيز الجسيمات الذهبية النانوية بين (37 و 142)، و التي حددت باستخدام مطياف الامتصاص الذري (AAS).

Introduction

Nanotechnology begins as a scientific mode in 1957 by a suggestion by R. Feynman, when he anticipated concepts that are nowadays commonly used in nanotechnology such as bottom up and top down approaches to the fabrication of miniaturized objects [1]. The term

“Nanotechnology” has been in use as early as 1974 when its basic concept was presented by Taniguchi in international conference of product engineers in Japan [2]. In September 1981 was the first scientific article on molecular nanotechnology [3]. The term nanoparticle (NPs) usually refers

to condensed phase particles with size in the range of 1 – 100 nm [1].

Because of the NPs unique properties of small size, large surface area to volume ratio [4], they have optical, electrical, magnetic, chemical, and mechanical properties which are completely different from bulk materials [5]. There is a growing interest in the fabrication of nanomaterials and their applications in various fields of life and technology such as electronics, health care, energy generation, and storage [6].

The GNPs have a long storied history in the usage, alike , in art or medicine from B.C years to present days [7]. The use of gold particles of extremely small size was only first published in 1971 [8].

General properties of gold

Gold belongs to Group II (IB) of the periodic table of the elements and often being referred to as the “coinage metals. The physical appearance of gold is yellow. Gold isn't soluble in mineral acids, but it is soluble in aqua regia (Con. HCl and Con. HNO₃ in 3:1 ratios). Au³⁺ is hard acids. Gold is unique in a number of respects. It is the most electronegative metal, comparable to selenium, and only slightly more electropositive than sulfur and iodine. Its electron affinity is greater than that of oxygen. The Au⁺/Au⁰ has a reduction potential value of +1.62 V. Gold is one of the few metallic elements that can be used in nanoscale devices and systems due to its resistance to oxidation [9]. Although gold is a noble metal and a commonly used material because of its resistance to oxidation and interesting electrical, magnetic, optical, and physical properties, it forms many and diverse compounds. The oxidation state of gold in its compound ranges from –1 to +5, but Au(I) and Au(III) dominate. Only salts and radioisotopes

of gold are of pharmacological value, as elemental (metallic) gold is inert to all chemicals it encounters inside the body. Pure gold is non-toxic and non-irritating when ingested and is sometimes used as a food decoration in the form of gold leaf [10].

There are many of methodologies for classification of the techniques and methods of nanomaterials' synthesis credential on, assembly and dismemberment, matter phase, nature of phase (physical, chemical, and biological), consorting with the environment or not, or on the dimensions or shapes of the result materials

Among the physical methods, pulsed laser ablation has been demonstrated to be a powerful and versatile technique for preparing high-purity nanoparticles or nanofilms. In general, the targets used for the preparation of nanoparticles or films by laser ablation are bulk sizes, and the lasers are either excimer, pulsed yttrium aluminum garnet (YAG), or femtosecond lasers [11]. Laser ablation/irradiation in liquid (LAL)[12], so-called pulsed laser ablation (PLA) is a simple and “green” technique that normally operates in water or organic liquids under ambient conditions [13]. The introduction in laser fragmentation in liquid has become a well-established technique to produce nanoparticles in 1987 [12].

Laser ablation of solids in liquids is an efficient way for the generation of a large variety of metallic nanospheres (NSs) and nanoparticles (NPs). Under sufficiently high laser fluence the surface of the target melts, and the melt is subsequently dispersed into the surrounding liquid under the recoil pressure of its vapor [14]. The synthesis procedure of the metal nanoparticles affects the final colloidal state and its evolution in terms of aggregation, reaction and

core shell formation [15]. So far, NSs have been realized on Ag, Au, and Ta in this way. Formation of NSs on both Ag and Au leads to visible coloration of both the exposed areas of the target or the liquid, and the color is determined by the position of the plasmon resonance of the free electrons in the nano-relief [14]. Fig. 1 explains the LAL setup for nanoparticle growth.

In noble metals, the decrease in size below the electron mean free path (the distance the electron travels between scattering collisions with the lattice centers) gives rise to intense absorption in the visible-near-UV. As a consequence, the free electrons shall have a coherent oscillation from one surface of particle to other, causing what is called the surface plasmon absorption. Such strong absorption induces strong coupling of the nanoparticles to the electromagnetic radiation of light [16].

Colloidal solutions of gold nanoparticles have a deep red colour which becomes progressively more yellow as the particle size increases [2]. Color changing in nanoparticles display by the absorption and/or emission wavelengths [2, 7].

Materials and methods

Gold NPs were synthesized by pulsed laser ablation of gold target in double distilled water DDDW. The gold target (purity of 99.99%) was fixed at bottom of glass vessel containing of 4 ml of DDDW, the level of water up to the target surface is 8 mm, the high of laser source is 15 cm, The ablation was achieved using focused output of pulsed Nd: YAG laser (type HUAFEI) operating with a repetition rate of 6 Hz and pulse width of 10 ns. Ablation is carried out with laser operating at 1064 nm wavelengths with (300, 400, 500, and 600) mJ by (100, 150, 250 and 300)

pulses. The absorbance spectra of the nanoparticles solution and the surface plasmon resonance (SPR) peaks have been measured by UV-Vis spectrophotometer type (SP8001), the concentrations of NPs in the solutions were measured with atomic absorption spectrometer (AAS) type (GBC 933 pulse).

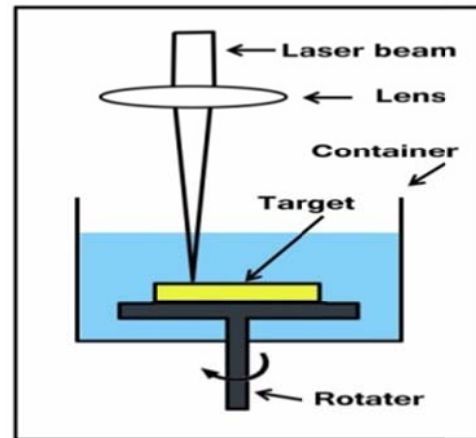


Fig. 1: LAL setup for nanoparticle synthesis.

The diameter of particles (d) have been measured by using the TEM imaging, DLS method, and the Khlebtsov's relation (1) [17].

$$d = \begin{cases} 3 + 7.5 \times 10^{-4} X^4, & X > 23 \\ \frac{[\sqrt{X - 17} - 1]}{0.006}, & X \leq 23 \end{cases} \quad (1)$$

where $X = \lambda - 500$

Results and discussion

The SPR resonates the collective oscillations of the conductive electrons. The eigen frequency of such a collection oscillator doesn't coincide with the wave frequency, and determined by many factors, including the concentration, the effective mass of the conduction electrons, the shape, structure, size, and the influence of the environment, as shown in the relation [18]:

$$\lambda_{max} = \lambda_o = \lambda_p [\epsilon_{ib} + 2\epsilon_m]^{1/2} \quad (2)$$

where λ_o is the resonance plasma wavelength, $\lambda_p = 2\pi c/\omega_p$ is the wavelength of volume oscillations of an electron plasma with the frequency of the volume plasma oscillations ω_p , ϵ_{ib} is the contribution of interband electronic transitions, and ϵ_m is the

permittivity of a homogeneous dielectric medium.

The SPR spectra of the prepared GNPs in DDDW were measured at room temperature and found to be located at (509-524) nm as shown in Fig. 2.

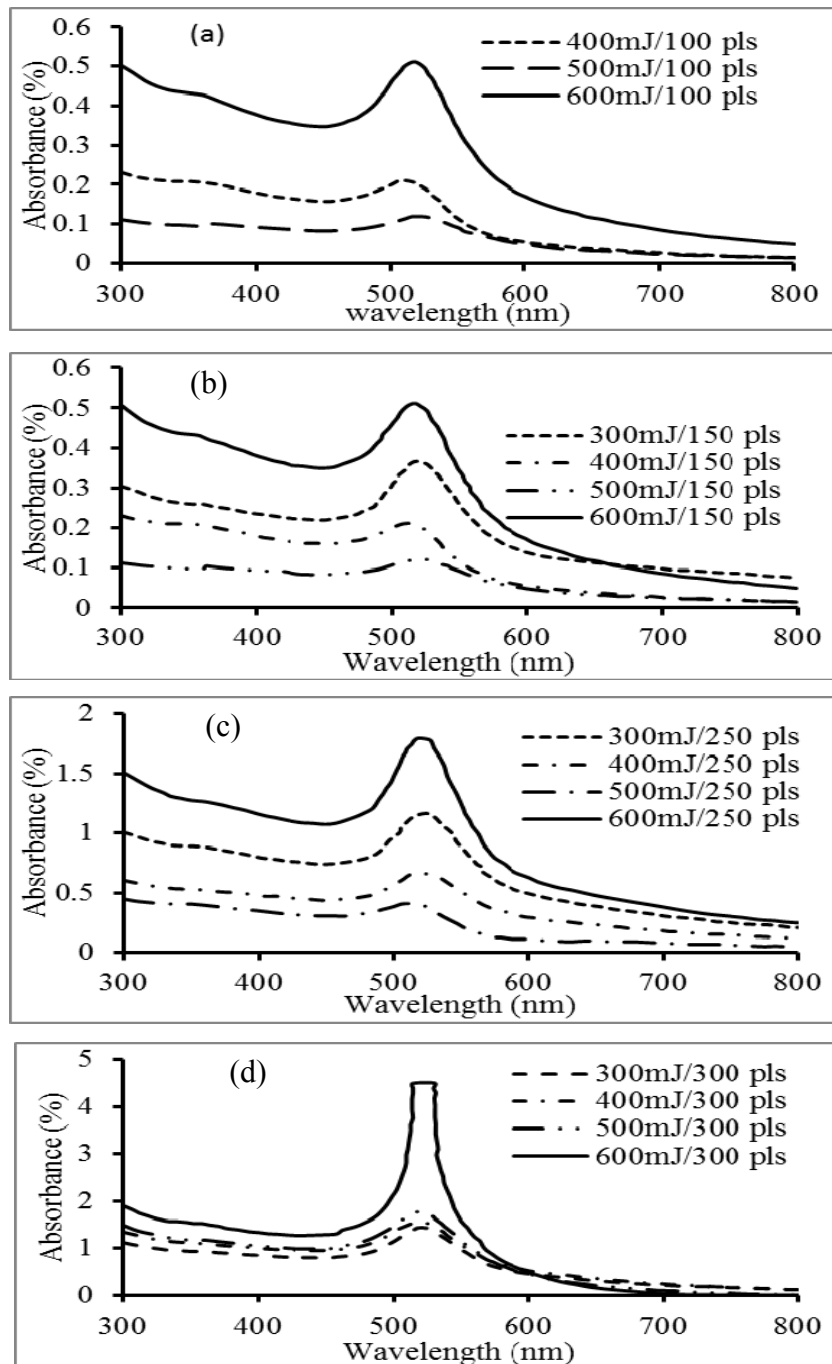


Fig. 2: SPE spectra of GNPs in DDDW for various energies, (a) 100 pulses, (b) 150 pulses, (c) 250 pulses, and (d) 300 pulses.

Fig. 3 shows, the TEM images, and the size distribution size of the prepared GNPs with (300, 400, 500 and 600) mJ, and 300 pulses of laser. The comparative measurements between the sizes of the three ways listed above were shown in Fig. 4, the

size measurements have been shown that the values of size were measured by transmission electron microscope images with SPR calculations even closer than those measured in way that DLS.

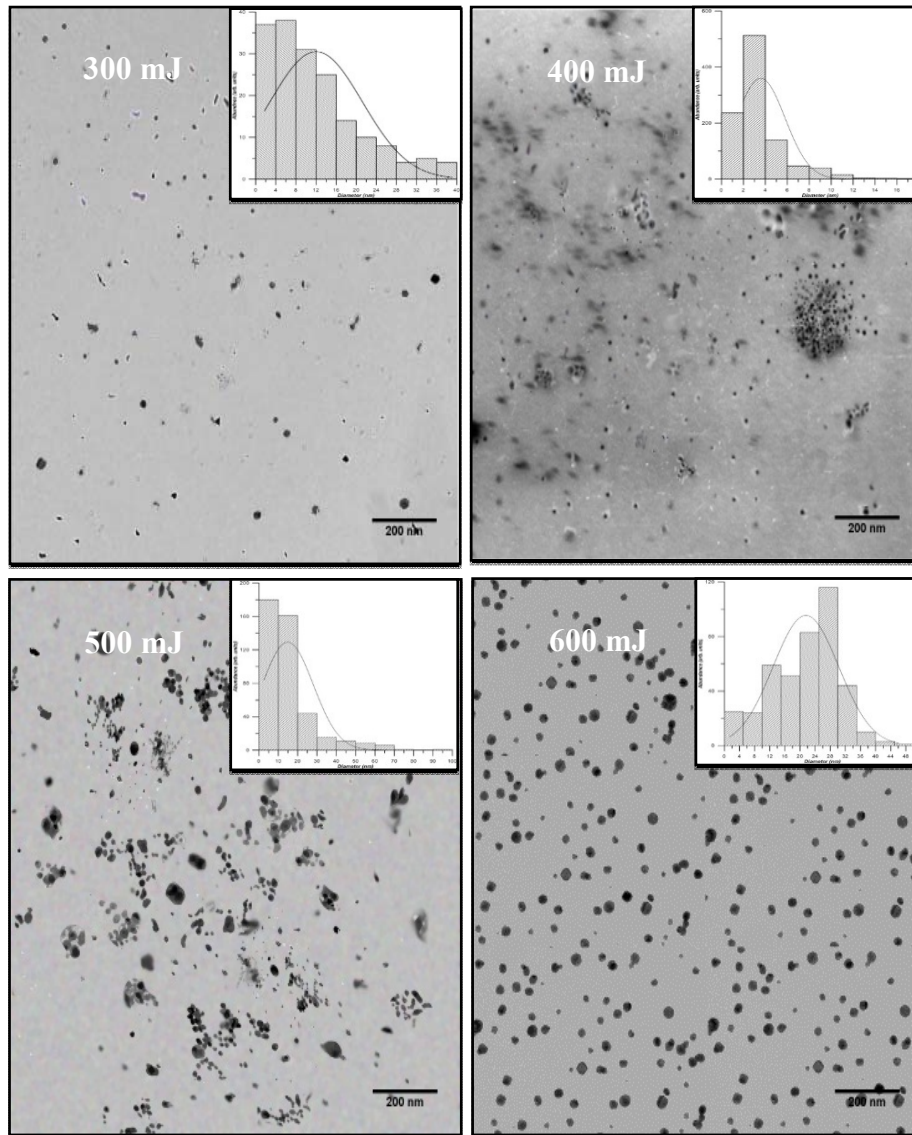


Fig. 3: TEM images of prepared GNPs with 300 pulses at (300, 400, 500 and 600) mJ in DDDW.

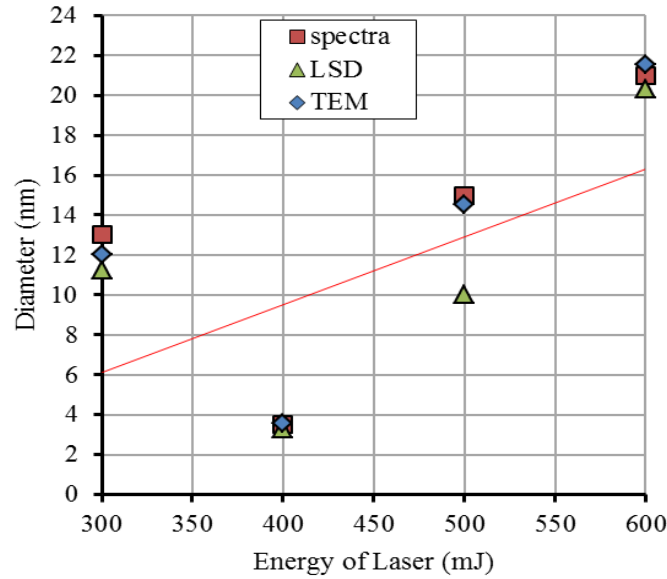


Fig. 4: Diameters of the prepared GNPs in (300, 400, 500 and 600) mJ with 300 pulses were measured by UV-Vis. Spectra, LDS method and TEM images in DDDW.

Second, some particles or clusters stick around the path of laser beam, forming new targets imbed it, that will attenuate the laser beam by scattering absorption, in additional, the possibility of fragments of these GNPs to smaller particles. Moreover, the concentration of GNPs affected the intensity of the specific absorption wavelength as shown in the Fig. 5, as

Giusti et al. and Immam et al explained [19, 20]. This work coincides with the second interpretation with prepared GNPs by 600mJ with 500 pulses were shot by 600 mJ with 100 pulses laser for four times, and the SPR peak has been measured in each time sequence. The SPR peak shifted to blue region by (0.15, 0.17, 0.2 and 0.23) % as shown in Fig. 6.

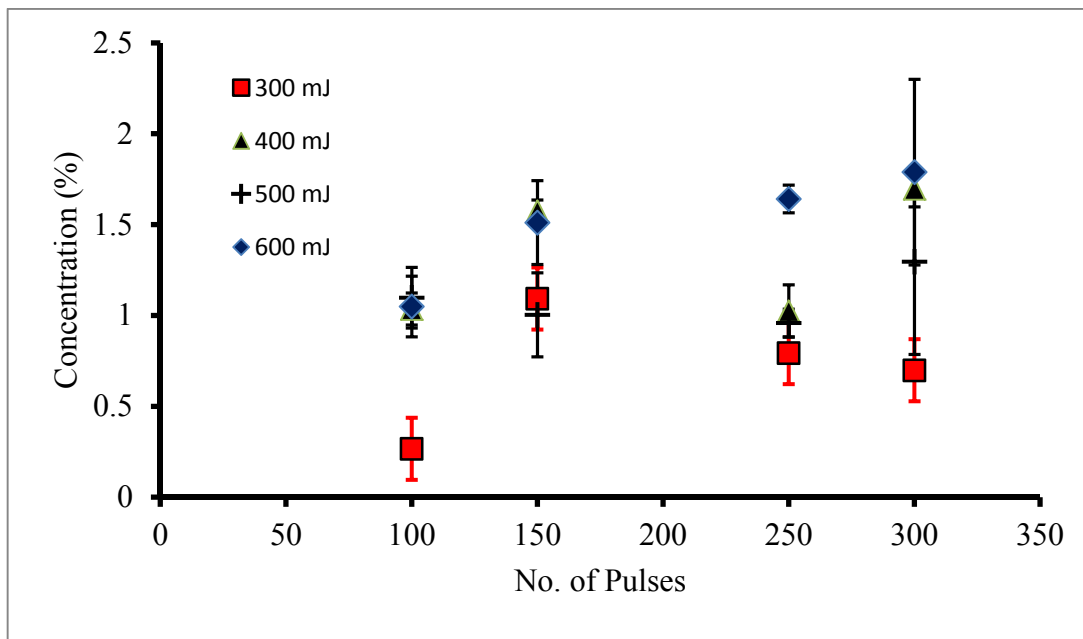


Fig. 5: A rate of GNPs concentration in DDDW.

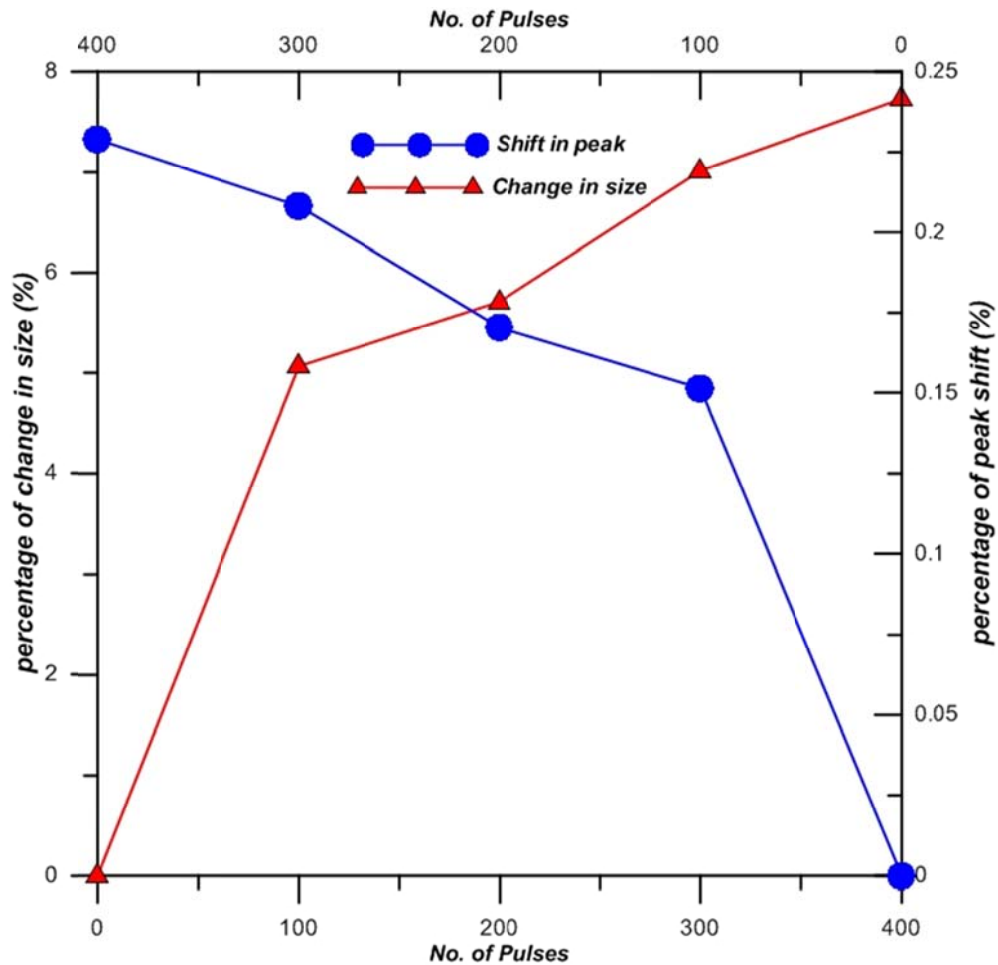


Fig. 6: The percentage of absorption peak shift, and the percentage of decreasing in the average diameter of GNPs, when they have been shoot via 600 mJ laser with 100 pulses for four times.

Conclusions

The LALP method is a lower cost and green method to GNPs synthesis in multifarious solutions. Size and concentration controlled by laser fluence, and the number / rate shots of laser. A linear relation between the size of GNPs and the laser energy, although the size and concentration of GNPs depend on several factors as laser energy, and number/rate of pulses, but these factors didn't enough to control on the size and concentration because of the formation of the particles' cloud upon the surface of the target, which prevents the laser beam to have a sufficient energy to ablate a new particle from the surface of a target because of the scattering and absorption processes, which have been

implemented by the suspended particles.

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