

Full length article

Modifying the second order dispersion of femtosecond laser pulses to crack silver nanoparticles and control their dimensions

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HIGHLIGHTS

- Reduction is not depending on pulse intensity but on the second order dispersion.
- Silver nanoparticles dimension reduction depends on second order dispersion.
- Nanoparticle dimension became smaller for negative second order dispersion.

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ABSTRACT

The potential application of metallic nanoparticles had been attracting attention and interest from different areas of academia and industry. The nanoparticles properties and applications depend heavily on their dimension and shape, thus special interest is aimed to controlling the nanoparticles sizes. Ultrashort laser pulses are known to change metallic nanoparticles characteristics, but the interaction mechanism is still not completely understood. In this work we reduced the dimension of silver nanoparticles with ultrashort pulses and demonstrated that there is a dependence of the particles size on the second order dispersion introduced in the pulses, which became smaller as the dispersion becomes more negative. Based on the results, we propose that the Coulomb explosion that reduces the nanoparticles size is predominantly initiated by multiphotonic ionization for the intensities used (10^{14} W/cm²).

1. Introduction

Metallic nanoparticles (NPs) have fundamental importance in several applications, from industrial [1] to scientific [2] ones. On medicine [3] they had been applied for virus replication inhibition [4], antibacterial action [5,6] and cancer treatment [7].

Among the different methods to produce metallic NPs [8] there is a set of green techniques [9] that minimize the harm to the environment, such as the use of natural substances and photoreduction [10,11], which assist the NPs formation [12]. The green techniques present advantages when it is compared to traditional methods that uses chemical reduction [13] and produce pollutant residues. The metallic NPs dimensions play an important role on its interaction properties [14]. For these reasons, the control of their sizes and shapes during synthesis has a huge impact on their real-world applications.

A simple method to characterize the dimensions of metallic [15–18] NPs consists in measuring their absorption spectrum, which is a consequence of the collective oscillations of free electrons on the metallic NPs surface [19]. These collective oscillations are known as Surface Plasmon Resonances (SPR) [20], and strongly depend on the size and shape of the metallic NPs [21] once their allowed oscillation modes are limited by the nanoparticle size. The absorption spectrum of metallic NPs is red-shifted with the increasing of the NPs size. Navarro et al. [22] compared different types of gold, silver and gold–silver alloy NPs using optical spectroscopic methods, in order to understand the correlation between shape and size with their resonant light scattering (RLS).

When the dimension is much smaller than the excitation wavelength, Mie's theory must be applied to describe the interaction between the light and nanoparticles.

As described by Mie's theory, the plasmon band of metal

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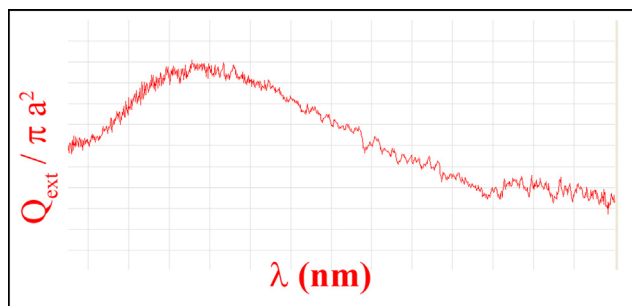


Fig. 1. Example of absorption spectrum of silver nanoparticles, being corresponded to Eq. (1).

nanoparticle involves dipole oscillations of the free electrons in the conduction band, which occupy states of energy immediately above the Fermi level [24–27]. It can be observed [23,28,29] that the calculated static dipole field contributes to the extinction (absorption plus scattering) and to the Rayleigh scattering of the electromagnetic field incident on the metallic sphere, with scattering efficiencies $Q_{\text{espalhamento}}$ and extinction $Q_{\text{extinção}}$ given, respectively, by:

$$Q_{\text{extinção}} = 4 \cdot \left(\frac{2 \cdot \pi \cdot a \cdot (\epsilon_0)^{\frac{1}{2}}}{\lambda} \right) \cdot \text{Im} \left(\frac{\epsilon_i - \epsilon_0}{\epsilon_i + 2 \cdot \epsilon_0} \right) \quad (1)$$

$$Q_{\text{espalhamento}} = \frac{8}{3} \cdot \left(\frac{2 \cdot \pi \cdot a \cdot (\epsilon_0)^{\frac{1}{2}}}{\lambda} \right)^4 \cdot \left| \frac{\epsilon_i - \epsilon_0}{\epsilon_i + 2 \cdot \epsilon_0} \right|^2 \quad (2)$$

As can be seen in Eqs. (1) and (2), scattering and extinction are also strongly dependent on the wavelength and radius of the metal sphere, which explains the change in the absorption spectra of the particles when they have a different size distribution. A typical experimental spectrum of absorption of a metal nanoparticle solution can be visualized in Fig. 1 and is governed by Eq. (1). In this spectrum, it is clear that there is an absorption peak that results from the average radius of the particles of the solution and whose width reflects the homogeneity of the nanoparticle rays. Therefore, when the size of the silver particles grows, the Absorption spectrum [30,31] is shifted to larger wavelengths.

It is possible to modify the metallic NPs dimensions and geometry by light irradiation, using either incoherent [8,32] or coherent [33–38] illumination. Ultrashort laser pulses in the femtosecond range had been used to synthesize and change the shape of metallic nanoparticles [36,39–42] by focusing the laser beam into solutions with nanoparticles or their precursors.

For solutions containing nanoparticles, the high intensity focused beam fragments the original particles, and a coalescence then occurs, resulting in new nanoparticles with different sizes. The mechanism causing the fragmentation of the metallic nanoparticles by femtosecond lasers is still not completely established [43,44]. Although the linear absorption of the supercontinuum generated in the visible range [42] plays an important role in the fragmentation of metallic NPs for non-focused beams, the high intensities reached in focused beams generate highly nonlinear processes that dominate the dynamics of the nanoparticles transformation. In this regime, the pulses high intensity initially ionizes the nanoparticles atoms either by multiphoton ionization (MPI) [45] or tunneling induced by the laser field [46], raising the free electrons density in the nanoparticle. These free electrons oscillate in the laser field, exponentially increasing their density by internal collisions in the nanoparticle until a critical density is exceeded and a Coulomb explosion occurs in the picosecond time frame [39,47]. These processes are assisted by ionization of the nanoparticle by the laser pulse, which can also occur by MPI or tunneling [48].

It had been demonstrated that femtosecond pulses with different temporal energy distributions produce NPs with different sizes

[33,35,36,44], indicating that the fragmentation dynamics depends on the pulse energy delivery rate. A fundamental characteristic of ultrashort pulses is their large spectral bandwidth [49], which can be amplitude and phase modulated to shape the pulse temporal profile and instantaneous frequency [50]. Pulse shaping techniques have attracted great interest from the scientific community, since many physical processes induced by light have been studied and controlled by the temporal conformation of femtosecond laser pulses [51,52], including changes on the geometry and size of silver NPs [35,36].

The temporal characteristics of ultrashort laser pulses can be controlled using a pulse shaper that introduces an arbitrary dispersion in their spectrum [53]. The most basic dispersion that can be added to a pulse and temporally modify it is the second order dispersion [54]. A pulse that has only linear or zero dispersion will be temporally broadened by the introduction of a second order dispersion, and its temporal duration will only depend on the absolute value of the dispersion regardless if it is positive or negative [49]. On the other hand, the instantaneous frequency of the pulse will depend on the signal of the second order dispersion: for positive dispersions the lower frequencies will be on the pulse leading edge, and the higher ones on its trailing edge (this frequency sweep is known as linear *chirp*, and is positive in this case). In this way, the pulses target will be initially hit by longer wavelength photons. For negative dispersion the situation is reversed, and the target is firstly hit by the shortest wavelength photons in the pulse [49] (negative *chirp*).

In a previous work [35] we demonstrated that the dimensions silver NPs irradiated by ultrashort laser pulses depend on their duration (in range from 48 fs to 250 fs) when introducing positive dispersion on their spectrum. A positive correlation was observed between the pulse duration and the NPs dimension, with the NPs becoming smaller as the pulses shorten. The aim of the present work was to investigate if this effect depends only on the pulse duration or also on the signal of the second order dispersion (*chirp*).

2. Materials and methods

The pulses chirp was varied from negative to positive values, and the irradiated solutions were characterized to study the dependence of femtosecond pulses irradiated silver NPs fragmentation on the pulses second order dispersion. We describe the initial solution of NPs production and laser irradiation involved in this work in the following sections.

2.1. Initial nanoparticle synthesis

To obtain the initial silver nanoparticles solution, 6.3 mL Tryptophan ($C_{11}H_{12}N_2O_2$) at 2.04 mmol/L and 9.6 mL Silver Nitrate ($AgNO_3$) at 2.01 mmol/L were mixed together in 34.1 mL milliQ water (final ratio $[Ag]/[Try] = 1$). This solution was irradiated for 5 min using a light from Xenon lamp (3.6 W/cm^2), in accordance with a previous described protocol [55]. This solution was diluted in water, at a ratio of 30% NPs solution to 70% water.

2.2. Experimental setup

A commercial Ti:Sapphire multipass amplifier (Odin Quantronix), seeded by a Main Oscillator (Mira-Seed, from Coherent) was used to generate 45 fs (FWHM) pulses in a 1 kHz repetition rate train, with 400 μJ of maximum energy and 40 nm of bandwidth, centered at 796 nm (Fig. 2).

An Acousto-Optic Programmable Dispersive Filter (AOPDF) [50] pulse shaper (Dazzler, from Fastlite) was placed between the main oscillator and the amplifier to introduce second order dispersions in the pulses in a controlled way. The pulses were temporally measured by a FROG [56] (Swamp Optics, model 8-20-USB) and a software that retrieved the temporal and spectral profiles of the pulses.

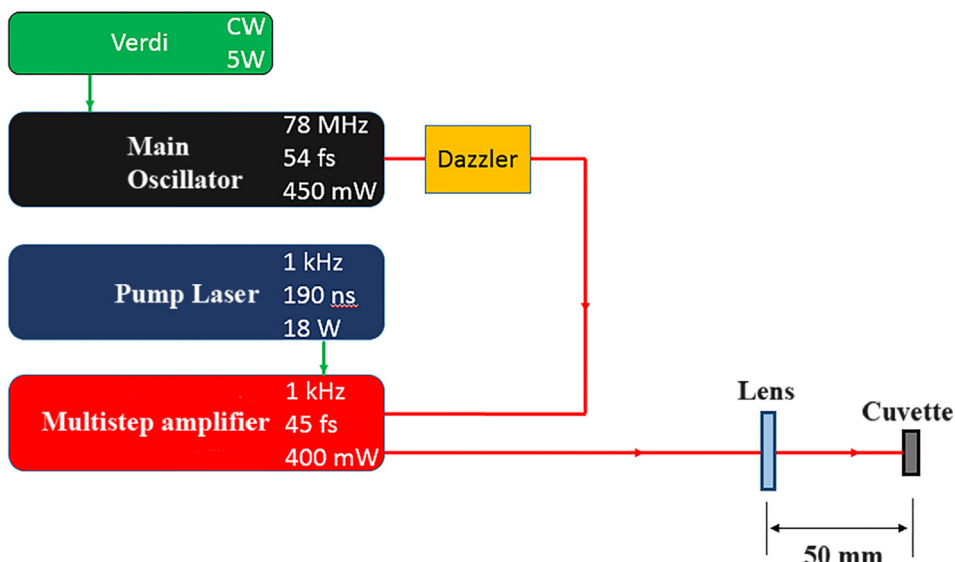


Fig. 2. Experimental Setup. A CPA system generates 400mW at 1 kHz and it is focused by lens with 50 mm focal length in a solution of silver nanoparticles contained in a quartz cuvette.

The laser pulses were focused by a 50 mm lens inside a 1 cm quartz cuvette (1 mm thick walls). This short focal distance lens was used to create a tight focus (50 μm beam waist) inside the solution without damaging the cuvette walls. The peak intensity reaches $1.1 \cdot 10^{14} \text{ W/cm}^2$ for the parameters described.

In order to evaluate the influence of second order dispersion on the silver NPs sizes modification, positive and negative dispersion pulses were focalized in the initial nanoparticles solution. Twenty-one samples of silver NPs solutions were irradiated by pulses with second order dispersion ranging from -3000 to 3000 fs^2 , with 300 fs^2 increments. In each experiment, 1.0 mL of the initial solution (30% nanoparticles) was poured into the cuvette and then irradiated for 10 min by the laser pulses (Fig. 3).

2.3. NPs dimension measurements

One of the technique to measure the average size of NPs in solution is the absorbance spectroscopy [57]. The wavelength of the maximum absorbance spectral peak is direct related to the NPs diameter [23,58]. In other words, a shorter absorption peak wavelength corresponds to a

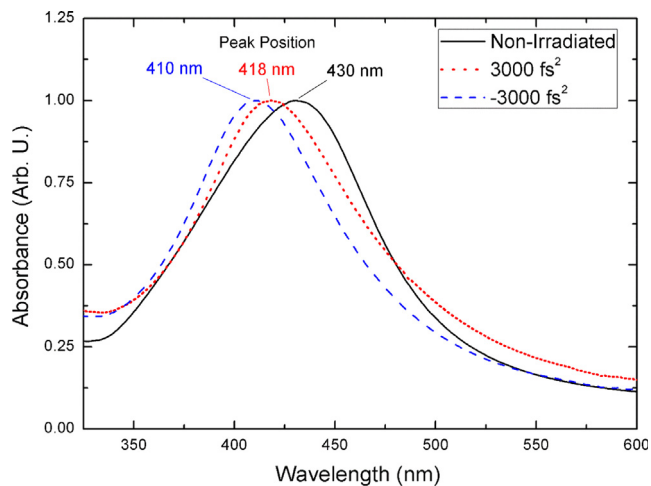


Fig. 3. Absorbance spectra of non-irradiated (dashed line) and irradiated with 3000 fs^2 (dotted line) and -3000 fs^2 (continuous line) second order dispersions nanoparticles solutions.

smaller NP.

The absorption spectra of the irradiated NPs solutions were measured by a Varian Cary 50 Bio UV/Visible spectrometer, using a quartz cuvette with 1 cm of optical path.

The spectroscopy data were analyzed using the Wolfram Mathematica© software.

3. Results and discussions

Fig. 3 presents the spectral absorbance of the non-irradiated (dashed line) nanoparticles solution along with the nanoparticles irradiated with 3000 fs^2 (dotted line) and -3000 fs^2 (continuous line) second order dispersion. These spectra show that the irradiation, either with positive or negative dispersion, shifts the peak to shorter wavelengths, evidencing that the nanoparticles sizes are reduced [59]. This effect is enhanced for the negative dispersion pulses (-3000 fs^2), indicating that both the pulse duration and its *chirp* play important roles in the fragmentation process.

Fig. 4 presents the peak wavelength of the irradiated NPs solutions spectral absorbance (left axis) and the pulse FWHM duration (right

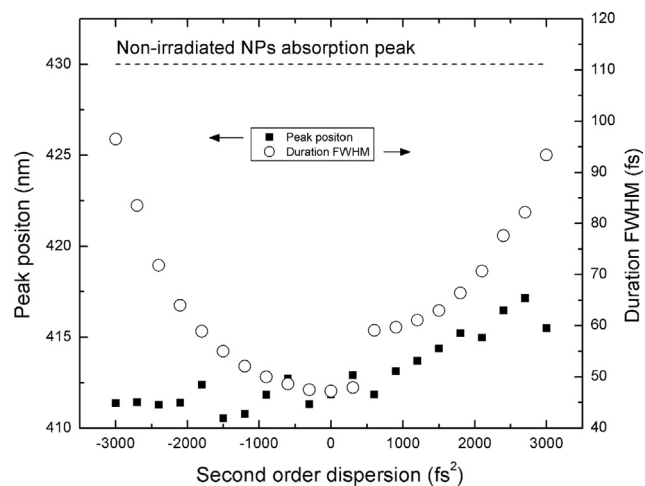


Fig. 4. Pulse duration and peak wavelength of the absorption spectra of the irradiated NPs solutions dependence on the 2nd order dispersion. The dashed line represents the non-irradiated NPs absorption peak.

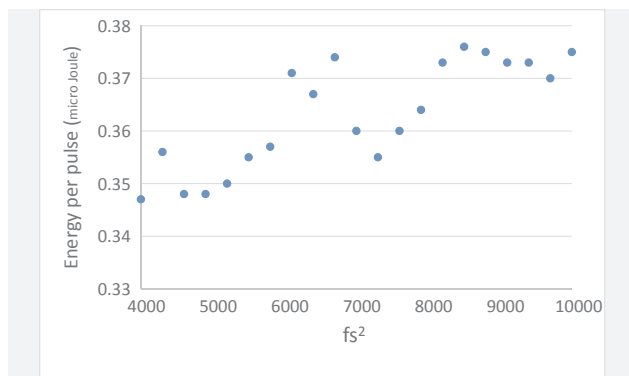


Fig. 5. Energy per pulse calculated as the division between power and repetition rate (1 kHz). The energy is given in μJ .

axis) dependence on the pulses dispersion ranging from -3000 fs^2 to 3000 fs^2 . It is possible to observe that, while the NPs sizes decrease as the pulses dispersion go from positive to negative values, reaching a constant value for dispersions below -1000 fs^2 , the pulses duration are almost symmetric around the zero dispersion, where a minimal duration is reached and then increases for both positive and negative dispersions. Apart from the jump in pulse duration around 600 fs^2 , which is due to residual third-order dispersion, negative and positive second order dispersion lead to an essentially symmetric laser pulse intensity around zero dispersion, a behavior that is clearly different from the absorption spectral peak shift. This shift asymmetry cannot be explained simply by an intensity dependent phenomenon, and we propose that the *chirp* introduced in the pulses by the second order dispersion, which is an odd function around zero, is responsible for this dependence.

There is no evidence that the second order dispersion affects the energy of a pulse, as can be seen in the Fig. 5. The behavior of the energy curve per pulse does not follow the behavior of the second order dispersion curve.

The Transmission Electronic Microscopy (TEM) micrographs for the irradiated NPs are shown on Fig. 6, along with their diameter distribution histograms under different irradiation condition, (A) non-irradiated, (B) 0 fs^2 (Fourier Transform Limited), (C) -3000 fs^2 and (D) 3000 fs^2 . The diameter distribution was measured, using the ImageJ software, on 12 micrographs for each irradiation condition. Fourier Transform Limited implies in the smallest possible pulse duration for a spectral profile [60].

The TEM micrographics and the NPs diameters distribution shown that different second order phase pulse components irradiation leads to differences in NPs average diameter. The average diameter of nanoparticles increases with the positive second order in phase introduced on the laser pulses, corroborating the finds of absorption spectroscopy method.

No formation of nitrides, sulfides or oxides were observed. These measurements were performed with the same silver nanoparticles solution and published in a previous work, using Fourier- transform infrared spectroscopy (FTIR) [61,62] technique.

The mechanism responsible for the fragmentation of metallic nanoparticles by femtosecond pulsed lasers [43] is still not completely established [43,44]. Nevertheless, it has been shown that the main mechanism of metallic NPs fragmentation is the Coulomb Explosion [39,48].

As described by Werner et al. [39], when high-intensity laser pulses irradiate metallic nanoparticles, the emission of thermionic electro occurs after established a Fermi distribution. Due to the nanoparticles dimension, it does not have enough electrons to equalize the charge unbalance caused by laser electric filed. So, the charges migrate to the nanoparticles surface and, when the repulsive force exceeds the bonding force, the Coulomb explosion occurs. In addition, during the

process, the relaxation of the hot electrons occurs, through the electron-phonon scattering, which causes the heating of the surface of the screen and its consequent remodeling.

As exposed earlier, the main process involved in the nanoparticles fragmentation is the Coulomb explosion, which is initiated either by multiphoton ionization (MPI) or tunneling ionization [48], as a consequence of the high intensity of the laser electric field.

The Keldysh parameter [48], γ , which relates the optical cycle period to the time it takes for an electron to tunnel across the potential distorted by the laser field, defines the transition from the MPI to the tunneling ionization, and is given by [46]:

$$\gamma = \sqrt{\frac{\epsilon cm_e \omega^2 I_p}{e^2 I}}, \quad (3)$$

where ϵ is the electric constant, c is the speed of light, m_e and e are the electron mass and charge, respectively, ω is the laser frequency, I_p is the ionizing potential and I is the laser intensity. For $\gamma \gg 1$ MPI is predominant, while tunneling ionization dominates for $\gamma \ll 1$ [63].

Starting from a single silver atom “nanoparticle”, which has a 7.58 eV ionizing potential, as atoms are added to the nanoparticle, its ionizing energy decreases to a minimum 4.26 eV, since the bulk silver work function ranges from 4.26 eV to 4.74 eV (depending on the crystalline structure). These values are used, along with the atom ionization Keldysh model [46] and the cluster ionization model [48] to calculate γ for the nanoparticles. Also, it is worth noting that these ionizing potentials correspond to 4.9 and 2.7 photons from the pulses spectrum center (796 nm, 1.56 eV), just below the resonances for the absorption of 5 and 3 photons.

Considering the intensity used in this work, for the 7.58 eV and 4.26 eV ionizing energies, the Keldysh parameter values calculated through Eq. (3) are 0.76 and 0.57, respectively. Although these values are below 1, they are sufficiently close to this limit to prevent the assignment of the predominant ionization mechanism to either tunneling or MPI, leading to the conclusion that both processes are occurring with similar probabilities.

The negative second order dispersion shifts the pulses leading edge to higher frequencies, and consequently the ionization process is initiated by the pulse bluer photons. As, just below the resonance for the multiphotonic absorption, more energetic photons increase the probability of the MPI process [64], we propose that a more efficient ionization is initiated, leading to a higher charge accumulation in the nanoparticle, resulting in a stronger Coulomb explosion that generates smaller fragments. These fragments finally coalesce into smaller nanoparticles, as observed by the blue-shift in the absorption spectra as the dispersion decreases. These results indicate that, within the intensities used here, the MPI plays a more important role in the nanoparticles modification than the tunneling, which is known to become a more efficient ionizing mechanism as the exciting field frequency decreases [46].

4. Conclusions

Femtosecond laser pulses with different second order dispersions were used to modify the dimension of silver nanoparticles, and we observed that their final size showed a dependence on the dispersion value and its signal: as the dispersion becomes more negative, the nanoparticles sizes decrease. This behavior is consequence of nonlinear processes, not dependent only on the pulses intensity. We propose that, for the intensities used ($\sim 10^{14} \text{ W/cm}^2$), the predominant mechanism for the nanoparticles ionization is the multiphoton absorption, that results in more violent Coulomb explosions due to enhanced energy absorption when the photon frequency increases.

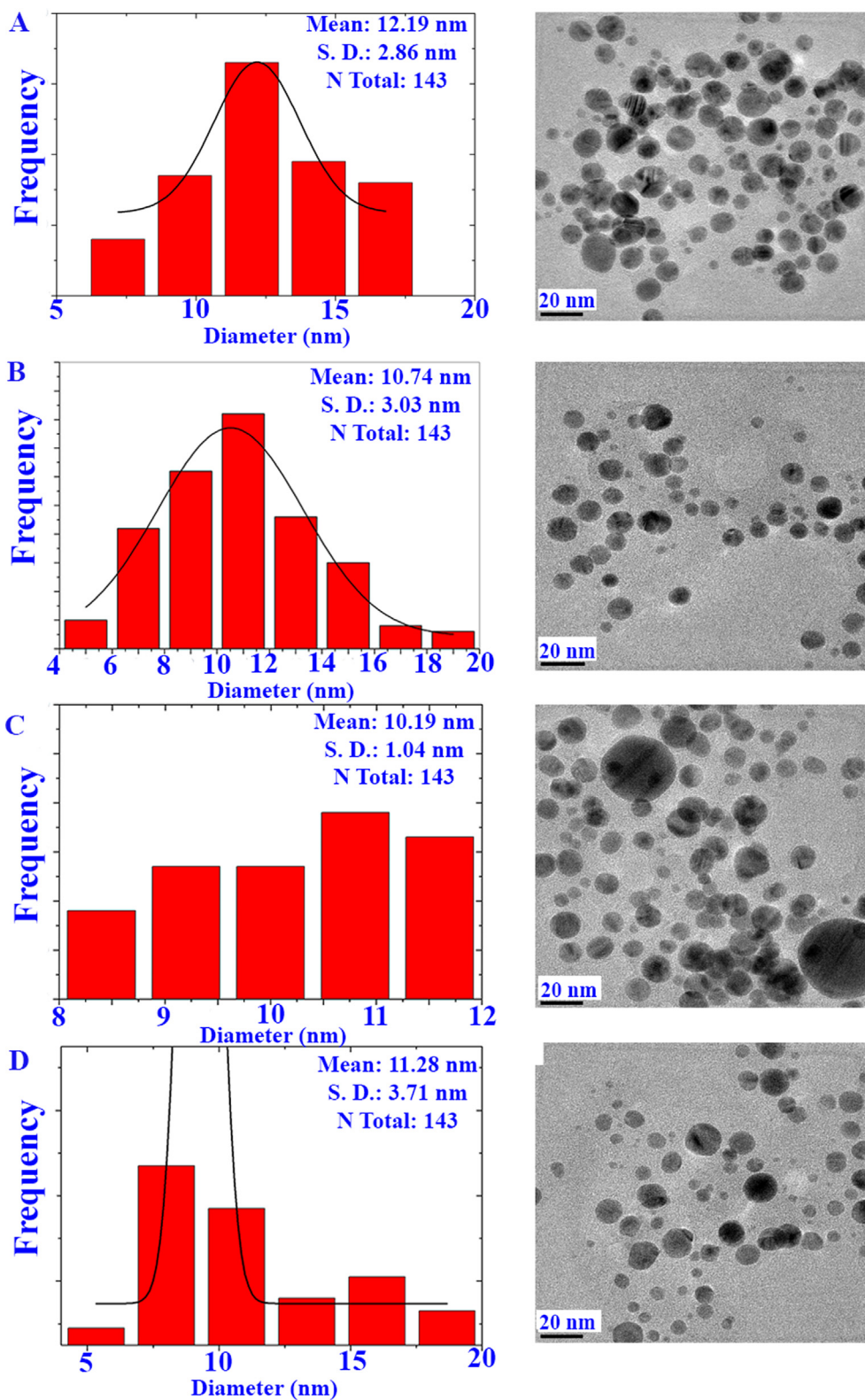


Fig. 6. TEM for the phase shift irradiated silver nanoparticles solutions. (A) non-irradiated; (B) Fourier Transform Limited; (C) -3000 fs^2 ; (D) 3000 fs^2 .

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