Synthesis of nanohybrid materials by femtosecond laser ablation in liquid medium

A Said, L Sajti, S Giorgio and W Marine
Centre de Recherche en Matière condensée et Nanosciences UPR CNRS 7251, Université de la Méditerranée, Case 901, 163 Avenue de Luminy, 13288 Marseille Cedex 9, France

E-mail: aurore@crmcn.univ-mrs.fr, sajti@crmcn.univ-mrs.fr, giorgio@crmcn.univ-mrs.fr, marine@crmcn.univ-mrs.fr

Abstract. ZnO nanoparticles were synthesized by means of femtosecond laser ablation of a ZnO target in different pure liquids such as deionized water and ethanol, and in solutions of do- and octa-decanethiol. Samples produced in water at low laser fluence contained nanoparticles whose radius is less than the Bohr radius as revealed by photoluminescence measurements that illustrate explicitly the effect of quantum confinement directly linked to the presence of nanoparticles. In fact, particles of about 1 nm in diameter were identified by AFM and TEM observations, which also show the increase in ablated particle size when increasing the fluence. Processing in ethanol and at low fluence led to the formation of ZnO particles of a few nanometers in diameter. When ablating in thiol solutions, slow cluster-growth promotes the formation of faceted particles.

1. Introduction

The domain of optical bio-sensing has recently experienced a colossal growth because of the convergence of life sciences and nanosciences, which would yield hybrid nanodevices having novel tailor-made multifunctionalities. Composed of an inorganic matrix hosting organic functional molecules, these nanohybrids could be applied as nanoprobes in high resolution imaging at the single cell level, in medical diagnostics and therapeutics.

Because of their size-dependent properties, metal and semiconductor nanoparticles prepared in liquid medium are now thoroughly studied for their potential use in material synthesis and optical detection. Thus, the control of particle size is the key factor in the synthesis of colloids, which were initially prepared by nanosecond laser ablation. For instance, Mafuné et al. reported efficient production, in an aqueous solution of surfactant, of size-controlled silver [1] and gold [2] nanoparticles with laser ablation by properly optimizing the surfactant concentration and the laser irradiation power. They enlarged their studies by further irradiation of solution that contained platinum nanoparticles, which are fragmented under irradiation into smaller nanoparticles [3]. Shafeev et al. have synthesized Ti, Si, Ag and Au under ablation of corresponding metal targets in different liquid media (water, ethanol and dichloroethane) [4-5]. They illustrated as well the dependence of the size of these nanoparticles on both the laser fluence and the nature of the liquid. The same group had successfully realized the formation of nanoparticles of ZnSe and CdS by ablation of their bulk semiconductors in several liquids [6]. In addition, the size of silver nanoparticles synthesized in water was found to
decrease upon decreasing the irradiation wavelength, as confirmed by Tsuji et al. [7]. Furthermore, Liang et al. demonstrated the possibility of producing oxide nanocrystals [8] and nanostructured magnesium hydroxide [9], as well as the preparation of zinc hydroxide [10], by laser ablation in pure water or in surfactant solutions. Moreover, the zinc oxide nanoparticles, representing our field of interest, of average diameters ranging from 12 to 40 nm, were reported, for the first time, to be effectively prepared in several surfactant solutions by Usui et al. [11]. But unfortunately, nanosecond laser ablation had led to the formation of ZnO nanoparticles with strong size dispersion.

The zinc oxide semiconductor of 3.37eV band gap [12] is an adequate candidate to be applied in developed emission materials owing to its distinctive optical and electrical properties. These properties can be further enhanced by crystallization at the nanometer scale in consequence of the effect of quantum confinement due to particle size reduction [13]. Nevertheless, pulsed femtosecond laser emerge as a pioneer process to ablate several kinds of metals in solution. Indeed, it was shown that the size of silver colloids prepared by femtosecond pulses were less dispersed than that of colloids prepared by nanosecond pulses [14]. Formation of gold nanoparticles with 2 nm mean size in aqueous biocompatible cyclodextrins solution was achieved by Kabashin et al. [15], who also confirmed the presence of two distinct particle populations, one of a mean size of 5 to 20 nm and the other is of higher dispersion with larger particles [16,17]. Even though the physical aspects of the femtosecond laser ablation in liquids are still ambiguous, it is quite evident that nanoparticles can be generated from this technique.

In this communication, we produced nanocrystalline particles of ZnO by pulsed femtosecond laser ablation in different pure liquids (deionized water, ethanol) and in solutions of do- and octa-decanethiol whose molecules can open the possibility of grafting numerous functional molecules. The influence of the liquid medium and the laser parameters was inspected in order to stage-manage the nanoparticles size as well as their morphology.

2. Experimental
A commercial Ti:Sapphire oscillator with a regenerative amplifier operating at a wavelength of 800 nm was used. This system (TSA, Spectra Physics) delivers 90 femtoseconds FWHM pulses at a repetition rate of 10 Hz. The radiation was guided through apertures followed by a lens of 10 cm focal length to impinge vertically on the surface of a 1cm-diameter sintered ZnO target settled on the bottom of a glass container filled with 15 ml of fluid, which corresponds to a thickness of about 3.5 cm of liquid layer above the target. The target was manufactured by compressing the ZnO powder (99,999 % purity Aldrich Chemical Inc.) and sintering at 600 °C for 2 days. Through the ablation procedure, the target was continuously moved across the beam to assure uniform target consumption. All ablation runs were carried out at room temperature and at atmospheric pressure. In fact, the ablated species were produced in diverse solutions under several laser conditions which are manifested by using different fluences along with diverse number of pulses.

A MultiMode SPM (NanoScopeIII) was used to execute the Atomic Force Microscopy (AFM) analyses in order to find the average grain size and to image the surface topography at atomic scale of the samples. These samples were prepared by drying, on mica substrates and at room temperature, droplets of ablated cluster solution. In addition, the size and morphology of the so-ablated nanoclusters were studied by the High Resolution Transmission Electron Microscopy HRTEM (JEOL, 300 kV). Owing 1.6 Å as resolution, this HRTEM operates on samples obtained after dehydration at room temperature of a specimen solution drop on an amorphous carbon film coating a copper mesh. Furthermore, the optical properties of the ZnO colloidal suspensions were assessed by photoluminescence measurements done by the excitation of a 325 nm He-Cd laser and a mercury lamp operating at 254 nm. Spectra were collected by a Peltier cooled photomultiplier (Hamamatsu) tied to a grating monochromator.
3. Results and discussion

3.1. Ablation in deionised water

Figure 1 shows the image taken by AFM of the ZnO clusters synthesized in deionised water at a fluence of 3 J/cm² where ZnO particles of about 1 nanometer were detected.

Figure 1. AFM image of ZnO nanoparticles prepared in deionized water at 3 J/cm² and 2000 shots.

On the other hand, increasing the laser fluence led to the growing in the size of the ZnO nanoparticles as depicted in figure 2. The mean particle size increased from 1 nm to 11 nm when the laser fluence was varied from 3 J/cm² to 11 J/cm².

Indeed the presence of small ZnO particles at low fluence was validated by the photoluminescence measurements that show the effect of the quantum confinement demonstrated by the increasing of the band gap energy [18]. Figure 3 illustrates the existence of additional photoluminescence peaks, which are located by fitting the original plot, in the photoluminescence spectrum of ZnO produced at laser fluence of 3 J/cm². Essentially, these peaks correspond to several particle sizes, which depend on the actual value of the band gap energy ($E_g^*$). The relationship between the band gap energy and the size of the particles considered as spherical particles can be given by the following equation [19]:

$$E_g^* = E_g + \frac{\hbar^2}{8\mu R^2} - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_e R}$$  \hspace{1cm} (3.1)

where, $E_g$ is the bulk band gap of the semiconductor material, $\mu$ the effective mass of the exciton given by $1/\mu = 1/m_e^* + 1/m_h^*$ ($m_e^*$ is the electron effective mass and $m_h^*$ is the hole effective mass), $R$ the radius of the particle, $\varepsilon_0$ is the vacuum permittivity and $\varepsilon_e$ the relative permittivity. The corrections to be done on the bulk band gap energy are given by two terms. The first one is the confinement term that is proportional to $R^{-2}$ and the second one stands for the Coulomb interaction term that is usually negligible [20].
The peak that appears, in figure 3, at the wavelength 307 nm indicates the increasing of the band gap energy and it is basically coming from ZnO particles having 1.83 nm as radius, according to calculation done through the band gap equation (3.1). This particle radius is effectively less than the Bohr radius being 2.34 nm [21]. This exciting information appears to be consistent with the results reached through AFM as already mentioned. Furthermore, the second peak positioned at 325 nm corresponds to particle radius of 2.24 nm, which is roughly equal to the radius of the previous particle plus the ZnO characteristic monolayer dimension of 0.3 nm. The same reasoning can be applied to the 2.83 nm particle-radius whose peak appears at 340 nm. And as expected, the bulk ZnO free and bounded exciton peaks appear at a wavelength of 364 and 379 nm, respectively, while the broad peak that appears at the violet 425 nm corresponds to ZnO emission in solution with OH⁻ excess ions [22].

Then again, the effect of the laser fluence on the ZnO nanoparticle size exposed by AFM analyses was confirmed by photoluminescence plots. These data revealed a considerable particle size growth when the laser fluence was increased from 3 J/cm² to 11 J/cm², as shown in figure 4. This figure presents only two peaks, the ZnO exciton emission at 379 nm and the Raman scattering of water at 364 nm with 3298 cm⁻¹ as energy difference from that of the excitation radiation, which matches the stated value of 3300 cm⁻¹ as being the Raman peak of water [23]. Accordingly, there is no increase in the band gap energy, which signifies that we are dealing here with large particles with radius much bigger than the Bohr radius.

In fact, increasing the fluence means delivering more energy that implies ablating larger amount of material. And this fact was also observed while monitoring the ablation process. Actually, we can clearly see a plasma plume directly on the surface of the target and a cloud of ZnO colloids formed in the liquid. As we increase the laser energy and by consequence the fluence, the plasma plume becomes more intense and the ZnO colloidal particles cloud becomes denser. Most likely, this means that bigger particles will be present due to longer growth time and to the high probability of cluster aggregation. In other words, atoms and nanoscale clusters ablated under laser radiation tend to aggregate during and after the laser pulse [17]. This fact leads to creation of larger particles [2] that becomes more prominent when the density of the ZnO clusters increases further with increasing the fluence, as clearly suggested by figure 2.
3.2. *Ablation in ethanol*

Laser ablation was also carried out in pure ethanol. Figure 5(a) stands for the AFM representation of ZnO particles of about 4 nanometers synthesized at 3 J/cm² and 5000 shots, while figure 5(b) expresses their size distribution.

![AFM image](image1)

![Size distribution](image2)

**Figure 5.** AFM image (a) and size distribution (b) of ZnO nanoparticles prepared in ethanol C₂H₅OH at 3 J/cm² and 5000 shots.

Figure 6(a) represents a spherical monocrystalline nanocluster of ZnO, where atomic planes are clearly distinguished. This picture is done by the high resolution transmission electron microscope on the same sample prepared in ethanol and at the same conditions, which are 3 J/cm² as fluence and 5000 as number of pulses. The plot of the corresponding particle size (diameter) distribution, exposed in figure 6(b), certifies the occurrence of a mean ZnO particles size of 4 nanometers. Thus, we can assume that performing TEM measurements outcomes with results that show fair correlation with measurements performed with AFM in what concerns the average particle size. However, if we compare the two size distribution plots belonging to AFM analyses (see figure 5(b)) and TEM analyses (see figure 6(b)), we notice that for analysis with TEM the size dispersion is relatively narrower than that given by AFM. Probably, this difference can be explained by partial convolution of the tip and particles of smaller size when operating in contact mode. Therefore, analyses done by the transmission electron microscopy (TEM) are much more reliable.

![HRTEM image](image3)

![Size distribution](image4)

**Figure 6.** HRTEM image (a) and size distribution (b) of ZnO nanoparticles prepared in ethanol C₂H₅OH at 3 J/cm² and 5000 shots.
However, if we increase slightly the laser fluence to 4 J/cm² keeping the same number of laser shots, two populations of nanoparticles appear, as realized by TEM and shown in figure 7. These distributions are fairly described by two Gaussian functions with two maxima centered at 4.25 and 10 nm with dispersion of 2.45 and 7.2 nm, respectively. So, we found a distribution at 4.25 nm that equals the one found with a fluence of 3 J/cm². In addition, another distribution at 10 nm appears suggesting that the growth mechanism depends on the fluence. So a slight increase in fluence leads to increase in the size of ZnO nanoclusters, as already shown when ablating in water. In fact, the presence of the first less dispersed population can be qualified as the consequence of pure radiation of the femtosecond laser ablation followed by the coalescence mechanism in the liquid medium. Whereas, the target heating by the plasma as well as its erosion by the collapse of formed bubbles were suggested to be responsible of the formation of the second highly dispersed population with larger nanoparticles [16-17].

![Figure 7. HRTEM size distribution of ZnO nanoparticles prepared in ethanol C₂H₅OH at 4 J/cm² and 5000 shots.](image)

![Figure 8. HRTEM image of ZnO nanoclusters synthesized at 3 J/cm² at 5000 shots in solution of dodecanethiol in ethanol](image)

### 3.3. Ablation in solutions of do- and octa-decanethiol

Analyses done by AFM of ZnO nanoparticles ablated in dodecanethiol show that the average particle size is 1.4 nm. Whereas when analyses were performed by HRTEM for the same sample, the particles were estimated to be about 7 nanometers. The remarkable difference in size evaluation may outcome from the fact that the AFM is unable to locate the zero level, above which the scanning can be achieved. This can be possibly explained by the presence of large dodecanthiol molecules surrounding the ZnO particles. Thus, it seems mandatory to rely on HRTEM results owing to its precision when dealing with thiol solutions being dodecanethiol (C₁₂H₂₅S) or octadecanethiol (C₁₈H₃₇S).

Figure 8 shows selected HRTEM image of ZnO nanocolloids prepared, in the solution of dodecanethiol (2.8 10⁻⁴ mols/cm³), at the same laser fluence as that for the nanoparticles of the figure 6 that was prepared in pure ethanol.

From the figure 8, we can clearly see increase in the nanoparticle size. Close examination of the morphology of these particles reveals a formation of the well developed facets for the particles with dimension more than 15 to 20 nm. Facets are indicated by straight lines on the figure 8. This kind of morphology shows obvious change of the growth condition comparing with pure ethanol, which is probably related to the decrease of the growth rate due to partial decoration of the nanocrystals by thiol molecules that leads to slow diffusion of the metal and oxygen atoms from the thiol solution.
4. Conclusion

For the first time, in our knowledge, we proved the ability of femtosecond laser in ablating ZnO targets in liquid medium to create particles of a few nanometers. For samples prepared in deionized water at low laser fluence, photoluminescence measurements explicitly reveal the effect of quantum confinement which is directly linked to the presence of small particles whose radius is less than Bohr radius. Indeed, particles of about 1 to 2 nm were identified by AFM and TEM observations, which also unveil the increase in ablated particle size when raising the fluence.

Ablating in the thiol solutions (do- and octa-decanethiol) leads to slow cluster-growth manifested by the development of faceted particles, providing evidence of the graft of the thiol molecules onto ZnO nanoparticles. This result opens the way to further investigation concerning diverse molecule-grafting onto ZnO nanoparticles in order to produce inorganic-organic nanohybrids to be applied in bio-sensing technology.

References
[1] Mafuné F, Kohno J, Takeda Y, Kondow T and Sawabe H 2000 J. Phys. Chem. B 104 9111-7
[2] Mafuné F, Kohno J, Takeda Y, Kondow T and Sawabe H 2001 J. Phys. Chem. B 105 5114-20
[3] Mafuné F and Kondow T 2004 Chem. Phys. Lett. 383 343-7
[4] Simakin A V, Voronov V V, Shafeev G A, Brayner R and Bozon-Verduraz F 2001 Chem. Phys. Lett. 348 182-6
[5] Dolgaev S I, Simakin A V, Voronov V V, Shafeev G A and Bozon-Verduraz F 2002 Appl. Surf. sci. 186 546-51
[6] Anikin K V, Melnik N N, Simakin A V, Shafeev G A, Voronov V V and Vitukhnovskya A G 2002 Chem. Phys. Lett. 366 357-60
[7] Tsuji T, Iryo K, Watanabe N and Tsuji M 2002 Appl. Surf. sci. 202 80-5
[8] Liang C, Shimizu Y, Sasaki T and Koshizaki N 2003 J. Phys. Chem. B 107 9220-5
[9] Liang C, Sasaki T, Shimizu Y and Koshizaki N 2004 Chem. Phys. Lett. 389 58-63
[10] Liang C, Shimizu Y, Masuda M, Sasaki T and Koshizaki N 2004 Chem. Mater. 16 963-5
[11] Usui H, Shimizu Y, Sasaki T and Koshizaki N 2005 J. Phys. Chem. B 109 120-4
[12] Ozerov I, Arab M, Safarov V I, Marine W, Giorgio S, Sentis M and Nanai L 2004 Appl. Surf. sci. 226 242-8
[13] Wang Y and Herron N 1991 J. Phys. Chem. 95 525-32
[14] Tsuji T, Kakita T and Tsuji M 2003 Appl. Surf. sci. 206 314-20
[15] Kabashin A V, Meunier M, Kingston C and Luong J H T 2003 J. Phys. Chem. B 107 4527-31
[16] Kabashin A V and Meunier M 2003 J. Appl. Phys. 94 7941-3
[17] Sylvester J P, Kabashin A V, Sacher E and Meunier M 2005 Appl. Phys. A 80 753-8
[18] Lin K F, Cheng H M, Hsu H C, Lin L J and Hsieh W F 2005 Chem. Phys. Lett. 409 208-11
[19] Brus L 1986 J. Phys. Chem. 90 2555-60
[20] van Dijken A, Meulenkamp E A, Vanmaekelbergh D and Meijerink A 2000 J. Luminescence 90 123-8
[21] Senger R T and Bajaj K K 2003 Phys. Rev. B 68 045313
[22] Monticone S, Tufeu R and Kanaev A V 1998 J. Phys. Chem. B 102 2854-62
[23] Vallee P, Lafait J, Ghomi M, Jouanna M and Morthange J 2003 J. Mol. Struct. 651 371-9