Preparation and application of nanomaterials

2 -1Introduction

During the last ten years, nanoscience and nanotechnology have advanced rapidly in many aspects such as preparation and application of nanomaterials. A broad range of nanomaterials has been developed for varieties of applications ranging from microelectronics circuits, food science, medicines to aerospace exploration.

1. Laser ablation in liquid

Nanostructures such as particles, wires, and tubes have become the focus of intensive research owing to their unique applications in microscopic physics and chemistry and fabrication of nanoscaled devices. Therefore, to obtain various nanometer sized building blocks, a lot of self–assembly and synthesis processes have emerged in recent years. Similarly, laser ablation of solids in liquids opened a unique route to synthesize nanostructures. As a result, there has been rapid growth of studies on the formation of nanostructures by this technique in recent years.

Laser ablation has been known since the invention of laser in 1960 as materials-processing technique. It was firstly developed after the invitation of ruby laser[26]. The last decade showed many experimental and theoretical investigations of laser ablation technique[27]. Laser ablation in liquid of solid targets conceders as new method that firstly presented in 1993[28]. Laser ablation in liquid top-down method described as the manufacturing of nanostructures with various sizes, compositions, and morphologies. Many types of targets such as (metals, alloys, oxides, carbides, hydroxides, etc.) and several surface structures (nanoparticles, nanotubes, nanorods, nanocomposites, etc.) can be applied as a precursor.[29]

The ablation of the target material by laser irradiation considered as a complex process. The ejected species of materials from the target surface induced by the interaction of short (~ nanoseconds – picoseconds), intense (~10^{6} to 10^{14} W/cm2) laser pulses at the surface. This probably useful in vacuum, gas, and liquid, providing that the gas or liquid does not strongly attenuate laser energy and the light intensity on the solid surface.[30]

Laser ablation in liquid accomplished as a high power laser focused at the surface of the target material, which is immersed under laying a chosen liquid. The laser target interaction vaporized the surface and creates an ablation plume [31]. Atoms, ions, and clusters produces in the producing plume have the ability to travel in a high speed with high kinetic energy. The species that ejected from the solid target containing in the plume can react with molecules of the certain ambient liquid, making new structural material involves atoms from the original target and the liquid.[32] The combination effect of high intensity laser ranging in nanosecond, instant elevated temperatures and pressures within the reaction volume could thousands of K at tens of GPa [33]. This special condion of pressure, temperature, and laser parameters have the ability to produce a " brute force". This force define as a method of building new material that was incredible so far using techniques more moderate, and more traditional[32]. Figure(2-1) show a simple schematic of laser ablation in liquid.

Fig.(2-1) illustrated laser ablation in liquid. [26]

3. Laser ablation Mechanism:

The initial step of laser ablation in liquid (LAL) process is the reaction of the laser light with the surface of the target material. The chemical reactions take place between the species in the plume and with Liquid environment molecules cause to collide, producing new compounds [1]. The results are naturally nanoparticles consist of atoms from the target and the liquid that suspended in the liquid. The aggregation accrues to the nanoparticles in the solution manufacturing a colloidal solution. Series reactions may occur with the laser radiation due to the colloidal solution, leading to further changes in the result structure, size and to the surface structure [34].

The plasma creates and restricted in the liquid, it expand adiabatically at supersonic velocity producing a shock-wave in front of it. This in turns will induce an additional, immediate pressure when it passes through the liquid. The temperature increasing in the plasma is the result of ‘ laser-induced pressure’. According to local high temperature a small quantity of the neighboring liquid is vaporized creating bubbles inside the liquid. As evaporation of the material increased, and a bubble tends to expand, until the combination reaches certain critical temperature and pressure, the bubbles collapse [31] [27].

At the room temperature, when the localization pressure in the ambient liquid could not reach the vaporization pressure, the cavitation formed. It could be represented as a dynamic phenomenon which has an important role in producing nanoparticle. The cavitation caused by the elevated plasma pressure and directed towards balance pressure between in and outside the bubble. Figure (2-2) illustrated the generation of shock wave, cavitation bubble, and high-pressure plasma plume. [35]

Fig. (2-2) Sketch of the laser plasma plume formation induced by LAL at different stages: (1) initial, (2) expansion, and (3) saturation.[35]

The laser ablation process was discussed in details in figure (2-3). The creation of the spherical shock wave noticed in 0. 7µs after irradiating with Nd: YAG laser pulse. The shock wave propagate in the sound speed and the initial cavitation bubble creation noticed in figure (2-3 a). Temperature and pressure begun to increased, and cavitation bubble expanded with time. A significant phenomenon can be detected in Fig. 2-3b after 26 µs. It was the ejection of tiny bubbles from the main bubble. In figure (2-3 c) the bubble size reach to its maximum size after 90 µs, then cavitation bubble begun to collapse with time. The creation of a second shockwave was observed at around 186 µs as shown in figure (2-3 d), which was induced by the shrunk of the first bubble. The production of the second shockwave submits the raised up in temperature and pressure at the breakdown of the cavitation bubble. Then, the generation of another cavitation bubble as illustrated in figure (2-3 e) follows the production of the second shock wave. The expansion and contraction of the bubble is not standardized after a long period (> 250 µs), and was not a hemispherical shape. The final form of the bubble is spherical completely as seen in figure (2-3 f), which was perceived at 2. 4 ms.[36]

Fig.(2-3) Time-resolved shadowgraphs at different delays after the laser pulse superimposed with images of laser light scattering[36].

2-4. 1 The advantage of Liquid phase laser ablation

By comparison with traditional physical methods such as chemical vapor deposition and pulse laser deposition, etc. with laser ablation in liquid technique take high attention according the following characteristics:

- Any target material could be applied in LAL.[29]
- The intense laser pulse has the ability to reach the target material as the liquid is transpired to the laser.[37]
- Good crystalline nanoparticles presented in one–step process without graduated heat–treatments.[38]
- The ablated materiel can be atoms and ions in highly excited states being able to emit light. [29]
- The presence of liquid generated high pressure which produced high confinement to the particles in small sizes and high density are probable in the initial of the ablation.[39]
- The low cost and simple because of the absence of any vacuum equipment.[40][41]
- Simplicity gathering nanoparticles after the synthesis according to nanoparticles are kept as a colloidal result in liquid-phase laser ablation.[42]
- Using the colloidal production as a precursor for another chemical reaction, especially in the formation of the nano-particles.[43]
- Structure, size and form, and design of the manufactured nanostructures can easily control by changing laser parameters and practical supports.[44]

- The nanoparticles production applicable to use in optoelectronics, and medical application [45]

2-4. 2 Limitations of liquid-phase laser ablation

Despite of the unique features of laser ablation in liquid there are limitations. A problem of liquid-phase laser ablation is the difficulty method for controlling plasma properties [36]. The size distribution of the NPs prepared by this technique tends to be broadened due to agglomeration of nanoclusters and to the possible ejection of the relatively large target fragments during the laser ablation process [43]. Relatively low product yield is one of the main disadvantages associated with LAL. [26]

5. parameters affected on laser ablation

Many parameters can effect on laser ablation technique, some of them related to the solution such as: transparency and liquid depth. Other parameters related to laser: energy, time, and wavelength.

2-5. 1 laser parameter

It is found that for a certain laser energy applied and the ablation time increased the ejection particles decreases. For enlarging the ablation time, the growth of absorption intensity is observed. This behavior is related to the existence of scattering phenomena that reduce the essential absorption according to the increased concentration of nanoparticles per unit volume. Fig.(2-4) show the absorption peaks of indium oxide prepared by laser ablation in liquid at fixed laser flounce 3J/cm ^{2} and different laser ablation (10, 30, 60, 120) min.[46]

Fig.(2-4) UV–vis absorption spectra of the indium oxide at the fixed laser fluence of 3 J. cm $^{-2}$ in 10, 30, 60 and 120 min. [46]

This is occur due to the decreasing the transparency of the solution and the particles absorb the laser energy. Another factor affected on the laser ablation method at high laser fluence in LAL must be the absorption of the laser light through NPs suspension produced by LAL [37]. Figure (2-5) explain a simple schematic of colloidal absorption in the LAL process causing reduction in the size and formation efficiency.

Fig.(2-5) Schematic illustration of colloidal absorption in the LAL process.[37]

Another important laser parameter is the laser wavelength. It seems that the shorter wavelength laser such as UV-laser it gives lower ablation threshold of the flounce due to high absorbance. The long wavelength laser such as IR-lasers efficiently excites more free electrons in the plasma plume, so improve the ablation process [47].

The ablation process can be affected by the laser energy. Increasing the laser energy leads to a broader range of particle size can be obtained. This broad range because of increasing laser energy supplied more energy to the target that drives the material removal by process satisfied by melting. The interaction between laser beam and the melting material makes the droplets to fragment and quenching rapidly produced large nanoparticle [48].

To obtain accurate information about the size distribution of nanoparticles, fig.(2-6) show TEM images of InN-NCs obtained with a laser pulse energy of 8 mJ range from 5. 9 to 25. 3 nm (inset, Fig. 2-6a), the sizes of InN-NCs obtained with a laser pulse energy of 12 mJ range from 5. 4 to 34. 8 nm (inset, Fig. 2-6b), and the sizes of InN-NCs obtained with a pulse energy of 16 mJ range from 3. 24 to 36 nm (inset, Fig. 2-6c). It should be noted that increasing laser energy leads to obtain more smaller particles.[20]

Fig. 2-6 TEM images of the laser-generated InN-NCs under laser pulse energy values of 8 mJ (a), 12 mJ (b), and 16 mJ (c) with corresponding particle size distributions (insets). [20]

2-5. 2 liquid parameter

This parameter can effect on liquid phase laser ablation technique and its efficiency. The solution must be transparent to the laser wavelength in the case of vertical side irradiation. Even high purity water can absorb 20% of the overall laser energy at 1 cm depth. That means if the target placed very deep in the solution, the laser energy reaching the target could be very low [37].