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Study the Structure Properties of Metal Oxide Prepared by Laser Ablation in Liquid

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Abstract: numerous experiments for nanomaterial fabrication using pulsed laser ablation in liquid have been reported. Most studies have focused on the formation of metal oxide nanoparticles . This show review highlights the fabrication of metal oxidebased nanomaterials such as oxide and hydroxide nanoparticles, as well as layered nanocomposites, vi nanosecond pulsed laser ablation of metallic target materials in water and aqueous surfactant solutions. These crystallized oxide-based nanomaterials are formed through the ejection of ablated species with extremely high density and high kinetic energy followed by oxidation in the liquid. The titanium oxide nanomaterial was prepared by removing titanium in a liquid medium, the structural and optical properties of the resulting material were studied by using uv visible device, XRD device and SEM.

Introduction

Nanocrystalline TiO2NPs are attracting great attention due to their broad variety of uses, such as photocatalysis, photoelectric conversion process in solar cells, antibacterial coatings, and gas sensors, thus titanium dioxide considers an important topic of research [1, 2]. Surface characteristics of NPs play a critical role in modifying bulk physical properties at the nanoscale, so many of the aforementioned applications are based on crystallographic structure, crystalline structure, and shape of nanoparticles [3, 4].

Because of its high internal activity, TiO2 is among the first semiconductor photocatalysts to be examined and considers an active photocatalyst essential with the effect of ultraviolet radiation. Anatase (tetragonal), rutile (tetragonal), and Brookite (orthorhombic) are the three main distinctive primary crystalline phases of TiO2 (bulk or nanoparticles).

The rutile phase of TiO2 is generally stable, whereas the anatase and brookite crystalline phases are semi-stable and quickly has converted to the rutile phase when is heated of over 600 to 800 degrees Celsius [5]. The Eg of anatase is approximately 3.2eV and 3.0eV for rutile. The third crystal phase, brookite, is the rarest naturally found phase of titania and is difficult to obtain in pure form. Brookite, like other phases, is photo-catalytically active [6].

There are many different methods to produce TiO2 nanoparticles, such as sol-gel, chemical vapour deposition (CVD), spray pyrolysis, mechanical method (Milling), and laser ablation. Laser ablation is a unique technique of basic interest to fabricating TiO2 nanoparticles in the liquid phase, and also a promising technique for handling nonmaterial production by quick reactive quenching of ablated species at the interface of plasma-liquid.

The PLAL method for preparing nanoparticles from a solid target in a liquid medium has a number of advantages. Firstly, is the low cost of ablation environment-keeping devices. Secondly, it does not use chemical substances. Thirdly, it creates free-contamination nanoparticles without polluting the environment [7].

Many researchers have focused on the preparation of TiO2 nanoparticles, for instance; A. Singh, et al. [8] have used pulsed laser ablation to prepare TiO2 nanoparticles in water and reported the influence of laser power on generated TiO2NPs. They found that the generated TiO2 NPs showed an increase in the yield NPs with increasing laser power.

Also, V.A. Zuñiga-Ibarra, et al. [9] used pulsed Nd: YAG laser with a 532 nm wavelength in their study, black TiO2 nanoparticles were created by irradiating white TiO2 nanoparticles in water. Recently, Amir R. Sadrolhossini et al. [10] have used laser ablation techniques to create titanium oxide nanoparticles in an aqueous solution containing carbon quantitative points.

The prepared sample was utilized to detect sugar and the sample's sensitivity. Where glucose was detected more readily than other sugars. The detection limit was 0.01 parts per million. More, recently N. Pashazadeh Kan et al. [11] have prepared TiO2 nanoparticles in water using the PLAL method and investigated the effect of SDS incorporation. In the PLAL technique, a laser (in pulsed operating mode) irradiates a highly pure target immersed in a liquid to synthesis particles of different sizes.

Cavitation bubbles form due to the water optical breakdown via the pulsed laser, which the generation and growth of NPs carry out inside. Upon the breakdown of the cavitation bubble, such nanoparticles released into the surrounding solvent forming a suspension of NPs [12]. Due to the abundance of numerous lasers, no definite outcomes on the influence of the parameters of the laser, such as laser density and laser energy, on the product of the synthesis of TiO2 nanoparticles. The aim of this research is to satisfy this study gap by experimental examination of disparity in the synthesis yield of nanoparticles. In the current research, we determined how the laser energy affects the physical properties of the prepared TiO2 nanoparticles.

Laser-assisted synthesis of colloids emerged as a versatile approach to access a library of oxide nanoparticles and related nanostructures at room temperature and ambient pressure. This review provides a critical presentation of laser-based methodologies, of the various oxide nanoparticles achieved so far, and of their applications in catalysis, optics, biotechnology and further emerging fields.

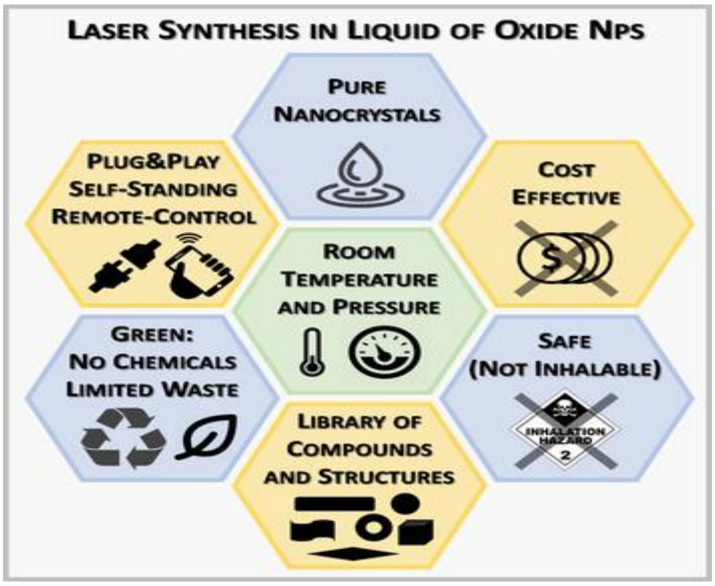


Fig 1.1

1.1 Metal oxide prepared

Oxide nanoparticles (NPs) are largely exploited for a variety of purposes, which embraces fields as different as, for instance, heterogeneous catalysis, biotechnology, medicine, photonics, solar energy conversion, microelectronics, automotive industry, pharmaceutics, and food additives[1, 2]. This variety of applications also comes with a vast number of distinct compounds belonging to the class of oxide nanomaterials. The synthesis of oxides with tailored properties requires a multitude of different synthetic procedures, including for instance the hydrothermal, calcination, mini-emulsion, spray pyrolysis, plasma-assisted and inert-atmosphere growth methods.[1-3]. Usually, these procedures allow high productivity but require sophisticated setups (autoclave reactors for the hydrothermal methods, furnaces for calcination, vacuum systems for plasma-assisted and inert atmosphere methods, pressure- and precursor-flow-controlled flame synthesis). Also tailored experimental conditions including high temperature and pressure (hydrothermal, calcination, spray pyrolysis) and chemical precursors and/or additives that potentially persist as contaminants in the final products (calcination, mini-emulsions, plasma-assisted chemical vapor deposition) are needed. The required precursors and their synthesis, as well as the post-treatment, often leads to toxic or pollutant waste, which poses the problem of their disposal[3]. Moreover, for some oxide cations, no precursors are available at all, limiting their flame spray synthesis. In the framework of the global efforts towards a circular and sustainable economy, it is therefore of utmost importance to develop synthesis routes running at room temperature and ambient pressure, which allows the cost-effective and green development of nanotechnologies based on oxides.

To this end, the laser-assisted synthesis of colloidal NPs, that is, the use of laser beams to generate a dispersion of NPs in a liquid environment, is emerging as a promising approach[4-7]. The oldest examples are dated back around 1991–1993,[8, 9] and are based on laser ablation in liquid (LAL)[10], where a laser beam is directed on a solid target immersed in a liquid solution, to generate a colloid through the ablation of the surface of the solid (Figure 1 A). In most cases, LAL is performed with pulsed lasers, and it is also called pulsed-LAL (PLAL). The synthesis of nanomaterials by LAL is sometimes called laser ablation synthesis in solution (LASiS)[11]. In 1997,[12] a variant of LAL appeared, where the laser beam is focused inside a liquid dispersion of micrometric or nanometric powders, to obtain their photo-fragmentation into smaller NPs, in a process known as laser fragmentation in liquid (LFL, Figure 1.2)[10, 13, 14].

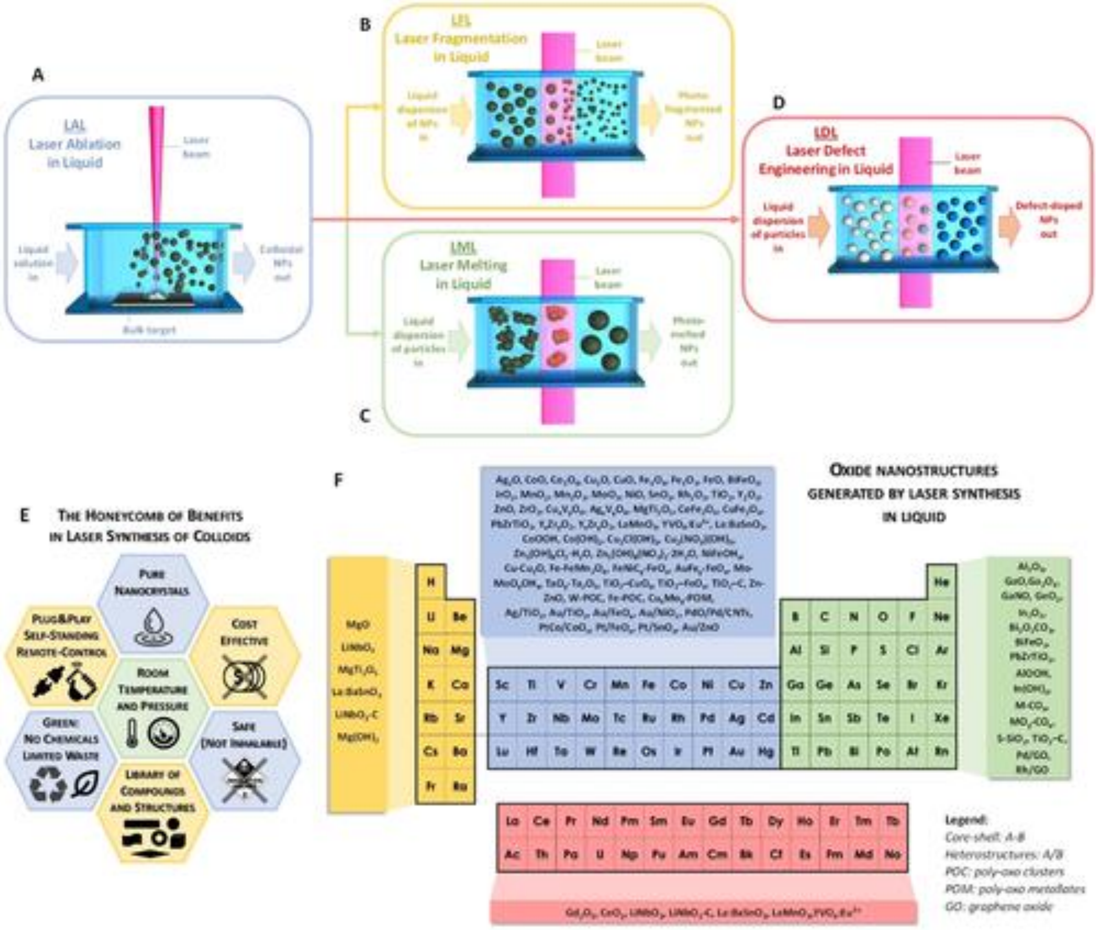


Figure 1.2

The landscape of laser synthesis of oxide nanoparticle colloids: Sketch of LAL (A), LFL (B), LML (C) and LDL (D). E) Honeycomb with frequently encountered advantages in laser synthesis of colloids. F) Overview of oxide nanostructures generated by laser synthesis in liquid in the literature.

Soon, LFL turned out to be also an effective way for the reduction of size and polydispersity of the colloids obtained by LAL. While performing LFL with laser pulse energy lower than the fragmentation threshold, it was observed that it is possible to obtain the photothermal fusion of aggregates of NPs into larger nanospheres,[11, 15] or the photothermal melting and vaporization of micrometric powders into submicron spheres,[16]through a process known as laser melting in liquid (LML) or pulsed-LML (PLML), (Figure 1.2 C).[10, 16] LML was also applied to the size increase of the colloids obtained by LAL. In fact, LAL, LFL, and LML can be combined for the production and the subsequent size control (reduction or increase) of colloidal NPs, as shown already in 2007.17 Using milder fluence regimes to irradiate a colloid with the intention mainly to change the atomic structure of NPs by introducing defects, while keeping the size unchanged, is called laser defect-engineering in liquid (LDL, Figure 1.2 D). Inspired by the first seminal reports in the field, a growing international community of scientists pursued the study of physical and chemical processes involved in laser synthesis of colloids[6, 10] They demonstrated several advantages of the method (Figure 1.2 E) and that colloids can be generated with peculiar features (e.g., metastable phases and doped nano-crystals) not present in NPs obtained by other procedures, as will be described in the following text[.6, 10, 18]

1. First of all, laser-generated colloids are highly pure, ligands-free and expose an uncoated surface, because no chemical precursors, chelating agents or coordinating molecules are required in the majority of cases[11, 19, 20]. Often, the absence of pollutant waste and the use of raw materials make laser synthesis compatible with the 12 principles of green chemistry,[11] offering new opportunities for the development of a green and sustainable nanotechnology, and for the integration of colloidal NPs in a circular economy.
2. The achievement of oxide NPs as a colloid does not expose the operator to airborne particle inhalation risks, thus allowing occupational safe and easy manipulation of the products, compared to dry nano-powders[21]. Besides, the effective interaction of NPs in a stable colloid with solid substrates and matrixes is facilitated by impregnation or mixing with the liquid phase[10, 19].
3. Another relevant advantage of laser-assisted synthesis methods is the access to a wide range of oxide (and non-oxide) nanoparticles in similar experimental conditions, all at room temperature and pressure,18 as shown in Figure 1.2 F on the basis of a literature overview. To clarify why laser synthesis falls under the "room-temperature and pressure synthesis" classification, on the one hand, the mechanistically relevant local (temporal and spatial) temperature and pressure profiles and on the other hand, the practically relevant global-extrinsic parameters have to be differentiated. It is worth specifying that locally and temporally, at the level of the matter interacting with the laser beam, extremely high temperatures and pressures are reached, but this is self-confined in a limited region of space coincident with the laser spot and the early explosive boiling volume. Molecular dynamic simulations coupled with the two-temperature-model were recently extended from the ultrashort-pulsed to nanosecond-pulsed laser ablation regime[22],where after short non-equilibrium phase the majority of nanoparticles are in thermodynamic equilibrium with their local environment at the end of the simulation (a few nanoseconds).

These predictions are backed by experimental findings on binary, partly immiscible nanoparticle systems, where both a kinetic control and thermodynamic contribution of the particle formation dynamics are concluded[23-25]. Hence, on the one hand, highly non-equilibrium conditions are pointing at a kinetic control of the synthesis at the very early, sub-nanosecond formation time regime[26]. Later, the whole system quickly reaches and remains in equilibrium with ambient conditions. Globally, there is no need for strategies for heat or pressure regulation, which is a big advantage compared to gas-phase (pressure), hydrothermal (pressure, temperature), or sol-gel (temperature) synthesis, and wet chemical co-precipitation or reduction (temperature). Even with high repetition rate lasers (>kHz), liquid flux simultaneously works for draining the colloid and cooling the synthesis environment macroscopically keeping a steady state of temperature and pressure.

This means that laser synthesis does not require unit operations for in-process-heating/cooling or pressure control, which makes laser synthesis systems easily implemented in laboratories. Overall, laser synthesis mechanistically benefits from accessibility to metastable nanoparticle crystal structures or compositions via temporal, pulsed, non-equilibrium condition that is confined in a microscopic volume, at the same time macroscopically continuously operating in steady state, at room temperature and pressure.

2.2 Preparation

2.1. Basics of laser ablation in liquids

In this section, the general processes occurring during PLAL of solid bulk targets are briefly described. A more detailed description can be found, for example, in Ref. [6].

Initially, laser ablation models that describe the process of absorption of the radiation by the target, its explosive vaporization with the formation and diffusion dynamics of plasma and the radiation interaction with plasma have been developed for the case of ablation in the gas phase. Our primary interest is in the description of the ablation process under the action of nanosecond laser pulses. In contrast to the very short (fs) pulses where the processes of excitation (isochoric heating) and further thermodynamic behavior of the system can be divided, more long (ns) pulses lead to the simultaneous course of these processes, making it difficult to describe them. In this case, the ablation is described well enough by the modern thermal model [9], which takes into account the absorption of radiation by plasma and uses a movable boundary of evaporation and evaporation obeying the Hertz-Knudsen law. This model works well not only near the ablation threshold but also when there is a large pumping over the threshold where a dense plasma plume appears.

The main differences between ablation in liquids and ablation in gas phase/vacuum are as follows. Firstly, ablation occurs at the boundary between the solid and liquid phase. Secondly, the formation and distribution of the plasma plume occurs in the liquid environment. Because the liquid has a much higher density and thermal conductivity than gas, this environment significantly affects the thermodynamic characteristics of the process. Thirdly, a large number of chemical transformations are possible in liquid. In characterization of the ablation in liquids, an approach described in Ref. [10] seems to be effective. It describes the process mechanisms, aggregate states and phase transitions depending on the pulse duration in temperature-density coordinates.

From the practical point of view, ablation in liquids leads to the following consequences. First of all, the threshold for ablation in liquids is higher than in gas and the material of the target removal rate, i.e., the productivity of obtaining nanoparticles, is much lower. Secondly, a vapor plasma plume that is much denser (up to 1023 cm^{-3}) is formed. At flame temperatures of 4000–5000 K, its pressure reaches 10 GPa and higher. This leads to efficient chemical transformations, as well as to the possible formation of metastable phases. Moreover, because the plasma is limited and is held by the dense liquid, its expansion occurs adiabatically at supersonic speed with the formation of a powerful shock wave.

In terms of practical use of PLAL in NPs synthesis, the use of ns excitation sources is the most promising. The greatest efficiency in the synthesis of large quantities of nanoparticles is observed exactly when nanosecond laser pulses are used. When short (femto- and picosecond) pulses are used, the productivity at the beginning of the process can be higher than for nanosecond pulses, but with the increasing of the particles’ concentration in the solution, the efficiency of the process decreases sharply. This happens, for example, due to the secondary interaction of laser radiation with particles in solution that leads to its strong attenuation and scattering. In addition, the cost of a sufficiently powerful picosecond laser suitable for PLAL is several times higher and femtosecond (oscillator-amplifier) more than 10 times exceeds the cost of the usual nanosecond Q-switch Nd:YAG laser. In conjunction with the complexity of the operation and relatively low resources of such short-pulse lasers, the cost of synthesis of meaningful quantities of nanoparticles (except for scientific research and a number of high-tech biomedical applications) will not be justified.

The use of longer μs pulses significantly reduces the efficiency of the ablation process. This is connected with the higher threshold for ablation in liquids compared to gas/vacuum systems, as well as with the strong screening effect of the plasma for microsecond pulses. Besides, a large energy contribution to the media leads to the heating of the liquid that limits the power of lasers used. In addition, when long pulses (from several tens of ns to hundreds of μs) are used, other ablation mechanisms take place [11], which will not be covered in this chapter.

The scheme of the ablation process is presented in Figure 2.1. Figure(2.1 a) shows the formation of a plasma cloud, Figure 1b shows interaction of plasma with radiation, Figure 1c shows chemical processes in plasma and Figure 1d shows the result: nanoparticles in liquid and surface erosion.

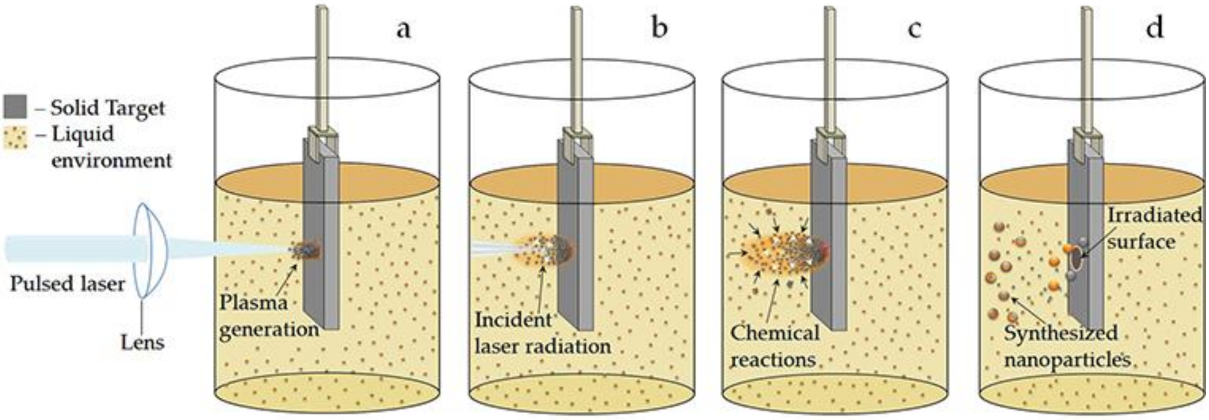


Figure 2.1

Nanosecond-pulsed laser ablation in liquids: (a) the formation of a plasma plume resulting from the absorption of laser pulse, (b) the evolution of the laser plasma in liquid during the nanosecond pulse and its interaction with radiation, (c) the further evolution of the plasma after the pulse and the chemical reactions inside the plume and at the border and (d) clusters (nanoparticles) in liquid and a crater on the surface of the target after the process.

There are three significant moments that should be noted:

1. Interaction of a plasma cloud with the liquid that limits it and with laser radiation leads to the formation of powerful shock waves in the environment.
2. Heated dense plasma cloud stimulates several types of chemical reactions inside the plasma and on the interface between three components: the target material, clusters (particles) that are formed and the solvent molecules.
3. Generated particles remain in the liquid in the path of laser radiation and participate in a secondary interaction with the laser beam at long pulse-periodic irradiation of the target influencing the processes of plasma formation, diffusion dynamics and chemical reactions.

3.2. General experimental technique of PLAL

Experimental technique for nanosecond PLAL is simple; that makes this method attractive for laboratory applications. To start the process of ablation, it is enough to focus the radiation of a nanosecond laser source on the target surface submerged in the liquid. At the same time, to obtain high-quality nanocolloids with reproducible properties, a variety of experimental procedures are required.

There are two variants of introducing radiation into the reactor: from above, across the air/liquid border and sideways through the transparent window/side wall reactor. From the point of reproducibility of the experiment and control of the focus conditions, the second option is preferred. When the radiation is introduced to the reactor from above, there are difficulties related to the control of the liquid layer over the target and the formation of bubbles during ablation that leads to scattering and bad focusing. In addition, when the thickness of the layer of liquid above the target is small, the spraying of the liquid takes place and contamination of focusing elements and protective windows may occur. When the radiation is introduced through the side wall of the reactor, these obstacles do not appear. But in this case, the main point is the radiation resistance of a window or transparent reactor wall that is affected by the laser beam. To minimize the power density of radiation in the window or wall of the reactor, one has to use short-focus lenses. In practice, the focal length of the lenses in such experiments is $F = 25–50$ mm.

As a result of the PLAL process, a thin layer of the material is removed from the surface of the target. After repeated multiple irradiation of the same place on the surface of the target, a crater appears and then a through-hole is formed. For uniform irradiation and to prevent crater formation, scanning of a laser beam on the surface of the target is used. To do this, one can either redirect the laser beam or move the target itself. There are two common methods for moving the target. For cylindrical targets, the rotation around their axis with a slow linear displacement is preferable. Most often, however, the target is a parallelepiped and in this case, scanning in the XY plane orthogonal laser beam is used.

The removal of the nanoparticles obtained by PLAL from the optical path of the radiation occurs either naturally through the convection or by the agitation of the liquid in a reactor, for example, using a magnetic stirrer. To produce large amounts of colloidal solutions with a concentration of nanoparticles of 10–50 mg/l, it is advisable to use flow reactors with the control of concentration in the synthesis process. Possible ways of technical implementation of such methods are considered, for example, in our work [12].

To obtain concentrated dispersions for further use and preparation of the nanocrystalline powders, it is better to carry out the optimization of synthesis conditions (considered below) instead of using flow reactors.

4.2. Effect of thermophysical parameters of the target on the PLAL process targets

One of the fundamental factors that determine the efficiency of ablation is a combination of thermophysical characteristics of the target material: melting point and evaporation temperature, heat capacity, heat of fusion and boiling and thermal conductivity. The dependence of ablation threshold and the thickness of the removed layer from the thermal characteristics of the target can be easily seen on the example of chemically inert materials, such as noble metals. For targets made of chemically active metals, this dependence may be more complicated. This is connected with the formation of oxides and other compounds on the surface of the target and these compounds' thermophysical characteristics differ from those of the target material. On the other hand, during the frequency pulse-periodic irradiation, the thickness of the modified layer on the surface is very thin and the thermodynamic characteristics of the PLAL are mainly determined by the properties of the target material. An additional factor, particularly for relatively refractory metals (Ti, Fe, etc.), is the decomposition of organic solvents on the surface of the target and formation of carbides, nitrides and other compounds.

5.2. Application

The scope of application of metal oxide NPs is extremely wide and varied. However, for the oxide nanoparticles obtained by PLAL, there are two most promising applications: scientific research and biomedicine. In both cases, there is no demand for large quantities of nanomaterials and the disadvantage of the PLAL connected with the relatively low productivity is immaterial. Instead, the important advantages of PLAL are express preparation of a wide range of nanomaterials in laboratory conditions for scientific research and "pure" nanoparticles directly in the form of colloidal solutions for biomedicine.

Thus, in our laboratory, oxide nanoparticles obtained by PLAL are used in the study of catalytic processes for searching for the structure and composition of the most effective catalysts for various chemical and photochemical processes. In Ref. [25], the results of the study of catalytic CO oxidation reaction for CeO_2-Pd composites obtained by PLAL of Ce and Pd targets in various solvents are presented. The change of the synthesis parameters of PLAL allows control of the size, chemical composition and superficial properties of obtained particles and hence modification of the catalytic properties. In addition to the cerium dioxide, we used Al_2O_3, SnO, SnO_2, CuO and CuO obtained by PLAL as carriers and catalysts. Composites based on zinc oxide, titanium dioxide and copper oxide nanoparticles were used for the study of photocatalytic processes.

Nanocolloids obtained by PLAL are suitable material for the study of the influence of nanomaterials on the environment. On the one hand, inert enough particles of noble metals can be used to define their migration paths in different ecosystems and, on the other, to investigate the toxicity. Authors of Ref. [26] used several types of nanoparticles including particles obtained by PLAL to study their influence on different aquatic organisms.

3.1 Experimental Setup

The formation of TiO2 nanoparticles is fabricated via pulsed laser ablation of the corresponding TiO2 metal plate (99.99%) of 3 mm thickness and its dimensions 1.5 × 1 cm2 immersed into the liquid as shown in Fig. 1. The TiO2 plate was thoroughly washed with ethanol and deionised water to remove organic contamination and placed at the bottom of a glass vessel filled with 2.5 ml of an aqueous solution of deionized water. The TiO2 metal plate was kept at 1 mm below the liquid surface. Pulsed Q-Switched laser Nd:YAG type (HUAFGI), (λ = 1064 nm, pulse width of 10 ns, repeating frequency of 1 Hz, and energy (120) mJ with 100 pulses was used as showing in Fig (1). The laser beam was focused by a plano-convex lens with focal length of 5 cm. The ablation process was typically done at room temperature. The surface morphology, particle size distributions and root mean square of roughness of TiO2 layer prepared under various conditions were analyzed using Scanning electron microscope (SEM) and XRD.The optical absorption spectrum of the solution was measured with UV-Vis spectrophotometer.

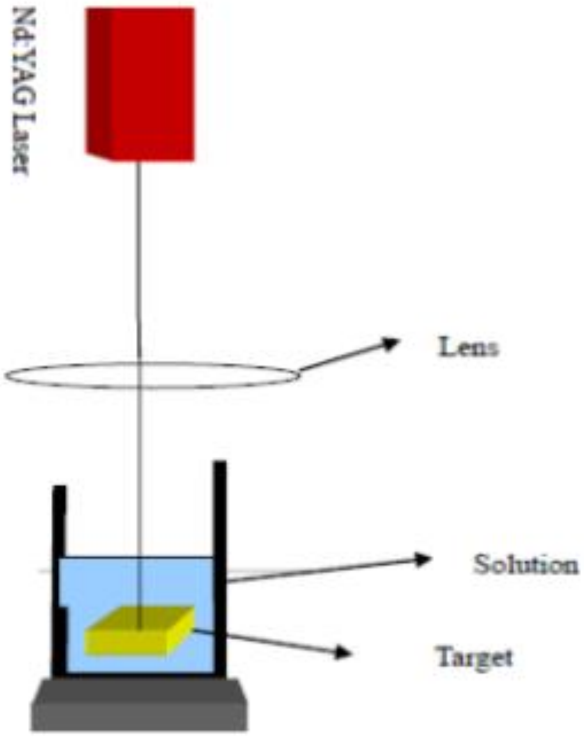
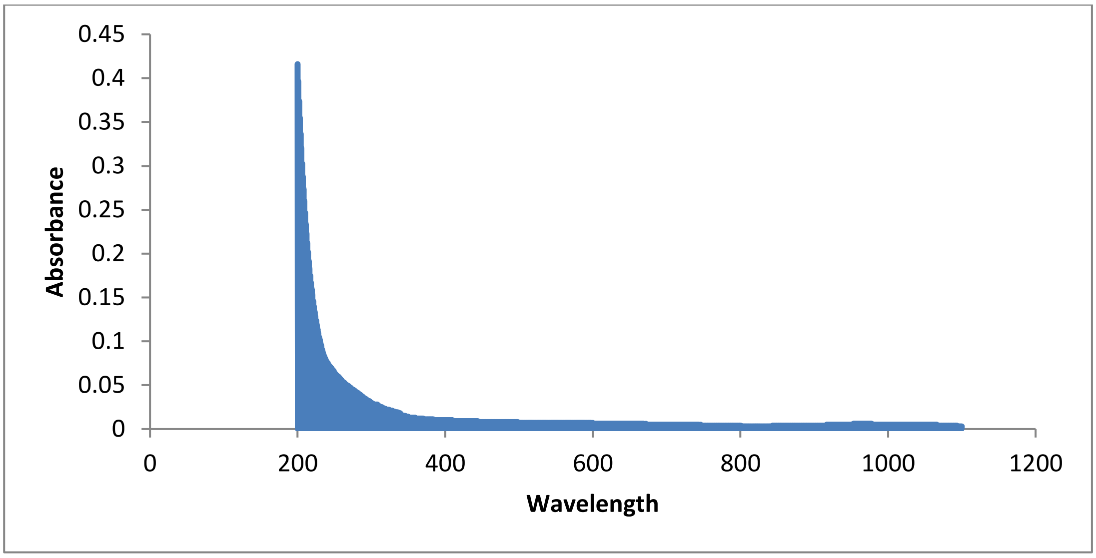


Figure (1). Schematic diagram of experimental setup

4.1 Results and Discussion

Optical properties results Optical properties of Titanium oxide nanoparticles were studied by UV-vis measurements of Titanium colloids. According to the Mie theory, metal nanoparticles with spherical shape had a light absorption due to scattering of light by small particles. The optical absorption spectra of Titanium nanoparticles in the range 250 nm were shown in Fig. 4.1. Bandwidth of optical extinction is related to the size distribution and the agglomeration of nanoparticles [13].



Figure(4.1). The absorbance spectrum of Titanium oxide nanoparticles prepared in deionized water at laser energy (20 J/cm^2).

Figure 4.2 explains the XRD pattern of Titanium oxide nanostructure material prepared at the laser energy of 20 J/cm^2. In general, there are one peak at $2\theta \approx 25^o$ conforming to (111) planes. This refers to cubic Titanium oxide nanoparticles. Also notice that the intensity of these peaks about 600 during the ablation process.

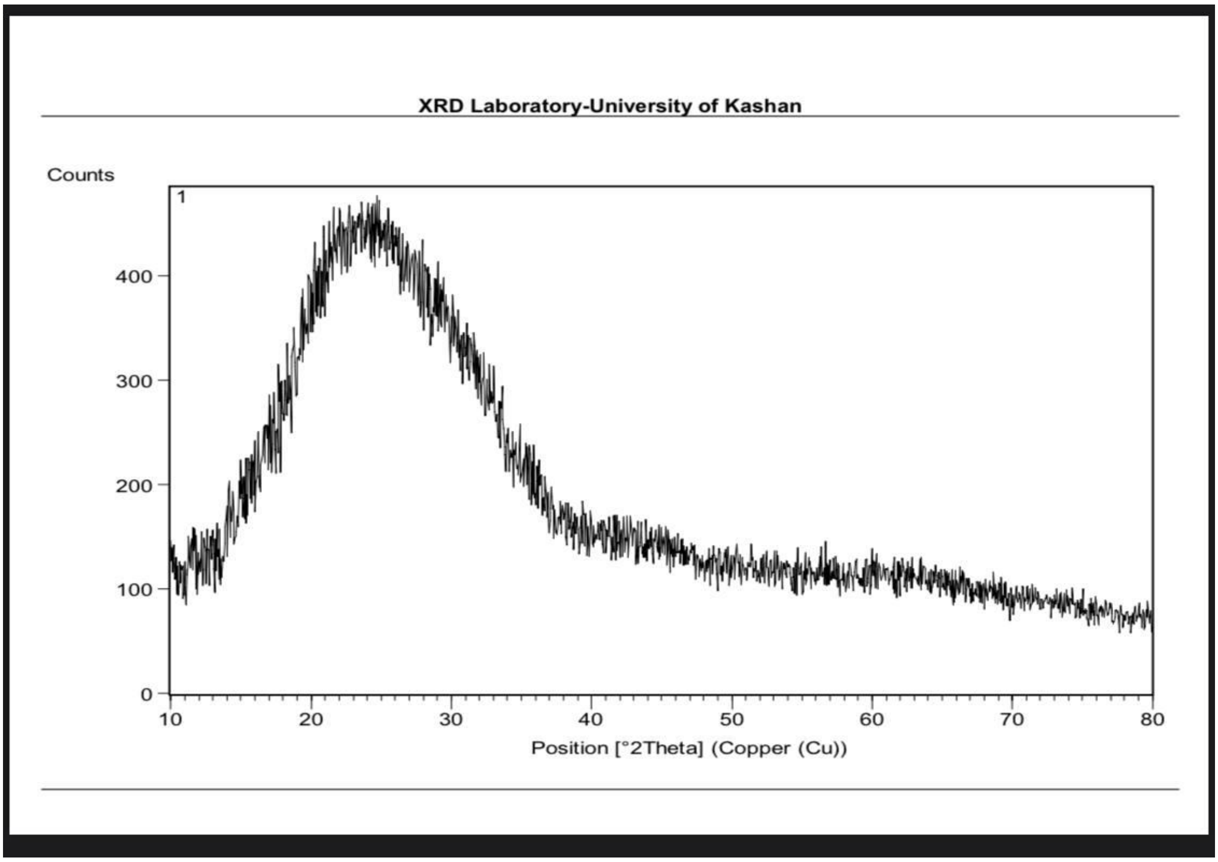


Figure 4.2 XRD pattern of Titanium oxide nanoparticles producing with 20 mJ laser power energy

image of Titanium oxide synthesized with 1064 nm laser wavelength and 20 mJ laser power . The morphology was a mixture of spherical and cylindrical nanoparticles due to the nature of laser-particle interaction and hydrodynamic expansion.[16] When the laser pulses hit the Titanium oxide surface, it will be absorbed and results in melting, vaporization and ionization. A consequence of plasma formation, a shock wave produced and plasma plum expands causing the quenching and formation of Titanium oxide[17] .

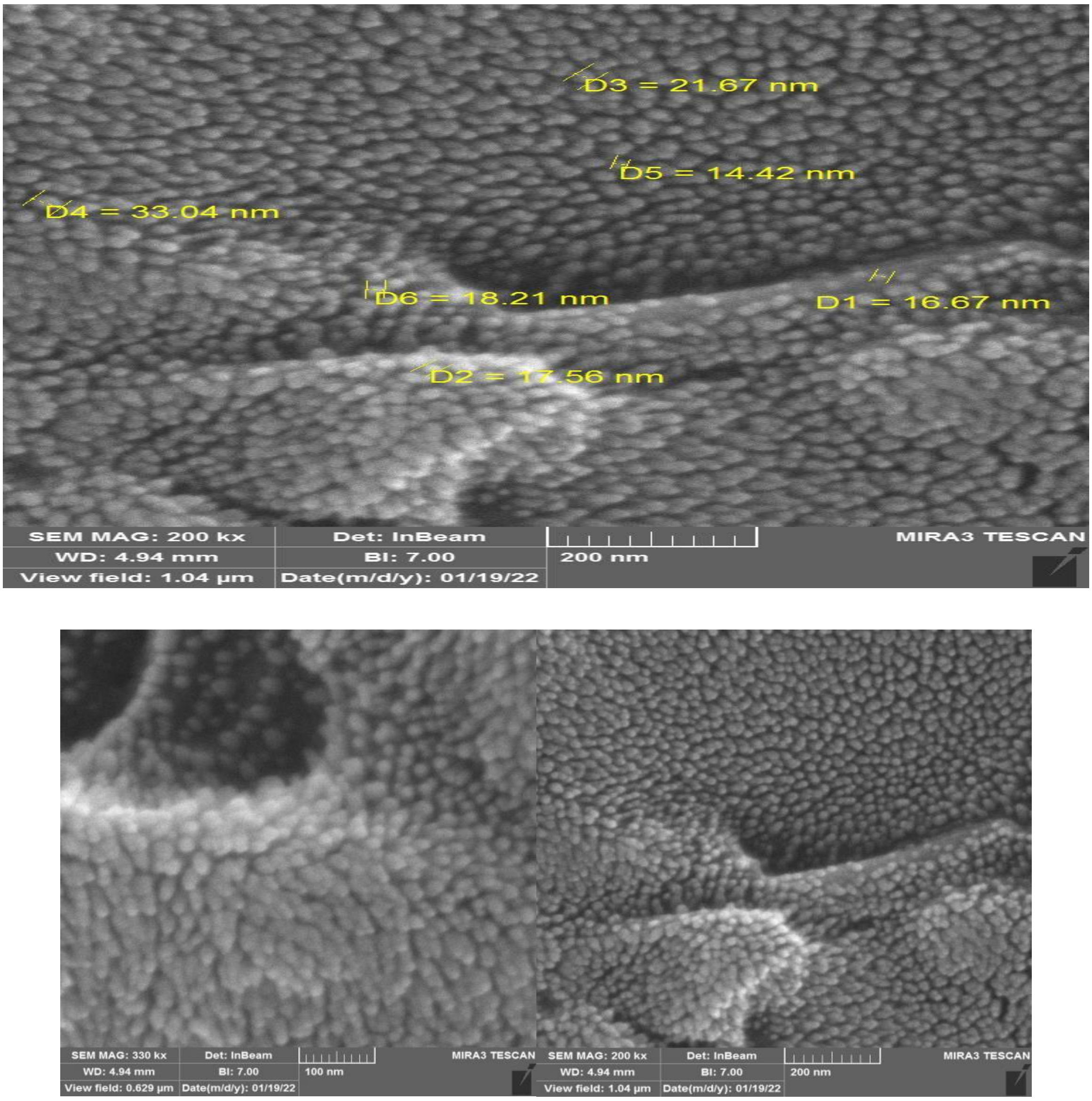


Figure 4.3 SEM images of Titanium oxide NPs prepared by 20 mJ laser power energy

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