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**Study on Fabrication of $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles by Laser
Ablation in Liquid**

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Chapter 1. General Introduction

1.1 Basics of lanthanide luminescence

1.1.1 Photoluminescence (PL)

Electrons with energies above a certain value are referred to as conduction electrons, while electrons with energies below a certain value are referred to as valence electrons. The gaps between the conduction and valence electron states are the so-called energy gaps, which existed in all the solids. Normally, the electrons are located in valence states. If the electrons absorb enough energies (greater than band gap), the electrons will be excited from the valence states to the conduction states. The electrons in conduction states are not stable, they will fall back down to the valence states. In this process, part of energies is lost and changed to thermal energy as non-radiative relaxation. The left energies release as luminescence photons, as shown in Figure 1-1. The process of photon excitation followed by photon emission is called photoluminescence (PL) [1].

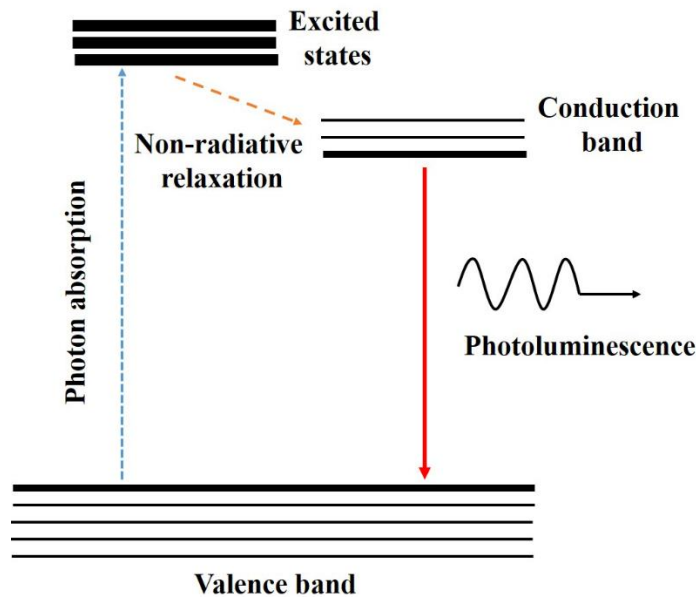


Figure 1-1. Photoluminescence process.

1.1.2 Lanthanide doped phosphors

Luminescent materials are defined as the solids, which are able to absorb and emit light radiation. The lanthanide doped luminescent materials are also named phosphors. In phosphors, Ln ions usually exist as trivalent cations, which refer to elements from La^{3+} (atomic number 57) to Lu^{3+} (atomic number 71). The ground state electronic configuration of Ln^{3+} is $[\text{Xe}]4f^n$ ($n = 1-$

14), as shown in table 1-1. As can be seen from the table, ions from Ce^{3+} to Yb^{3+} have partially filled 4f orbitals, while the 4f orbital is empty in La^{3+} and fully filled in Lu^{3+} .

The energy levels of 4f electrons are not affected so much by the ligand ions in host matrix since 4f electrons are shielded by the outer $5s^2$ and $5p^6$ electrons. Therefore, Ln^{3+} except La^{3+} and Lu^{3+} are able to exhibit different sharp fluorescent emissions via intra-4f transitions owing to their various and numbers of f-orbit configurations. This is the key to spectroscopic properties of Ln^{3+} ions.

$^{2S+1}L_J$ is defined as electronic states, where S, L, and J are the spin angular momentum, orbital angular momentum, and total angular momentum, respectively. L represents S, P, D, F, G,....., when L is equal to 0, 1, 2, 3, 4, 5....., respectively. Table 1-1 also shows the electronic properties of Ln and Ln^{3+} ions [2].

Table 1-1. Electronic properties of Ln and Ln^{3+} ions

Ions	Ln	Ln^{3+}
La	$4f^0 5d 6s^2 (^2D_{3/2})$	$4f^0 (^1S_0)$
Ce	$4f 5d 6s^2 (^1G_4)$	$4f (^2F_{5/2})$
Pr	$4f^3 6s^2 (^4I_{9/2})$	$4f^2 (^3H_4)$
Nd	$4f^4 6s^2 (^5I_4)$	$4f^3 (^4I_{9/2})$
Pm	$4f^5 6s^2 (^6H_{5/2})$	$4f^4 (^5I_4)$
Sm	$4f^6 6s^2 (^7F_0)$	$4f^5 (^6H_{5/2})$
Eu	$4f^7 6s^2 (^8S_{7/2})$	$4f^6 (^7F_0)$
Gd	$4f^7 5d 6s^2 (^9D_2)$	$4f^7 (^8S_{7/2})$
Tb	$4f^9 6s^2 (^6H_{15/2})$	$4f^8 (^7F_6)$
Dy	$4f^{10} 6s^2 (^5I_8)$	$4f^9 (^6H_{15/2})$
Ho	$4f^{11} 6s^2 (^4I_{15/2})$	$4f^{10} (^5I_8)$
Er	$4f^{12} 6s^2 (^3H_6)$	$4f^{11} (^4I_{15/2})$
Tm	$4f^{13} 6s^2 (^2F_{7/2})$	$4f^{12} (^3H_6)$
Yb	$4f^{14} 6s^2 (^1S_0)$	$4f^{13} (^2F_{7/2})$
Lu	$4f^{14} 5d 6s^2 (^2D_{3/2})$	$4f^{14} (^1S_0)$

The phosphors consist of host lattice and activators (Ln^{3+}). The host lattice sometimes not only holds the Ln^{3+} ions but also acts as a sensitizer. Many host materials such as oxy-sulfide,

fluoride, phosphate, and vanadate have been widely used. For instance, Eu^{3+} doped YVO_4 ($\text{YVO}_4:\text{Eu}^{3+}$) absorb adequate energy and transfer the energy from VO_4^{3-} group to Eu^{3+} ions lead to the strong red luminescence. There are two types of excitation processes: direct excitation (Ln^{3+} directly absorb the energies) and indirect excitation (host lattice first absorbs energies and transfers them to Ln^{3+}). For the latter one, it is widely applied to use abundant host lattice for the desired luminescence properties. The host lattices provide a chemical environment for the Ln^{3+} emitters, giving the various luminescence color from the ultraviolet (UV) to infrared (IR) region upon excitation [3]. Depending on the differences of mechanism, the luminescence of Ln^{3+} consist of down-conversion (DC) and up-conversion (UC) emissions. The DC and UC processes can be accomplished by doping different Ln^{3+} ions. The former one obeys Stokes' law.

1.1.3 Applications of phosphors

The conventional bulk phosphors play a vital role in light-emitting diodes (LED) [4], display monitors [5], lasers [6] and scintillation [7]. In recent years, growing endeavors are devoted to the nanoscale phosphors mainly for applications in biological field such as bio-imaging [8, 9], photodynamic therapy [10, 11] drug delivery [12, 13], and so on. Here, part of above applications is introduced in detail as follows.

A) White LED

S. Nakamura invented the white LED by combining a blue LED chip and a yellow emitting phosphor in 1993 [4]. In this case, the cerium doped yttrium aluminum garnet ($\text{YAG}:\text{Ce}^{3+}$) was used as the phosphor materials. Figure 1-2 displays the mechanism to generate a white light: a GaN-based blue LED chip is coated with the $\text{YAG}:\text{Ce}^{3+}$ phosphors. In this system, the simplest combination is a yellow phosphor and a blue LED chip, which is called one-phosphor-converted (1-pc) white LED. When the phosphor is excited by the blue light, it emits the yellow light. Therefore, the mixing of the light from the blue LED chip and phosphor finally generate the white light. However, 1-pc white LED usually is unable to be tuned in color temperature because of the lack of red and green color, resulting in high color temperatures (cold/blue light). With the advancement of phosphor technology, new generation of phosphors such as nitride phosphors are obtained much attention because of its high chemical stability and small thermal quenching [14]. Furthermore, the phosphors with different emission color are also very popular to compensate the color temperature in white light for applications in some cases. For instance, the green emitting

$\text{MSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ (M: Ca, Sr, Ba) [15], red emitting $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ (M: Ca, Sr, Ba) [16], yellow emitting $\text{CaAlSiN}_3:\text{Ce}^{3+}$ [17] and Ca- α -sialon: Eu^{2+} [18] are often used as the phosphor candidates for white LED.

In near future, white LED are proposed to take the place of conventional light sources for common illumination because of its huge energy savings [19]. Therefore, Ln ions such as Eu and Ce will be extremely important for illumination in the worldwide.

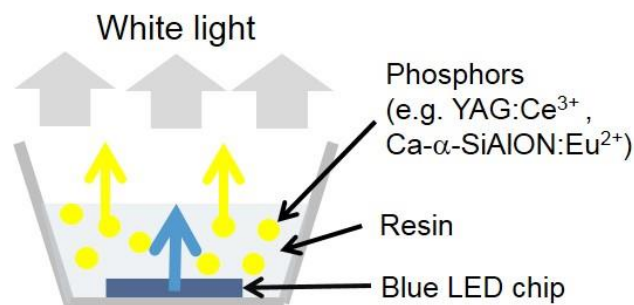


Figure 1-2. The mechanism to generate white light in LED.

B) Scintillator

Scintillators are materials that are able to absorb X-ray, α -, β -, γ -ray and efficiently convert the radiation energy into visible light. $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$ is regarded as a cathode-ray phosphor in flying-spot scanners [20] and $\text{Y}_2\text{SiO}_5:\text{Tb}^{3+}$ as a green cathode-ray phosphor [21]. $\text{Gd}_2\text{SiO}_5:\text{Tb}^{3+}$ is regarded as an X-ray phosphor [22]. $\text{Gd}_2\text{SiO}_5:\text{Ce}^{3+}$ and $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ are reported as an efficient scintillator [23, 24]. Scintillators are usually used in medical diagnostics, X-ray security, computed tomography and positron emission tomography and particle detector. For instance, in medical diagnostics, the scintillators emitted the light after excitation of the X-ray, the emission light is used as the image; K. Wisshak et al [25] used certain scintillator to discriminate γ -photons and charged hadrons by detecting different emissions, one with a shorter and one with a longer decay time.

C) Bio-imaging

Imaging techniques in single molecule scale is of quite important for cell and molecular biology and fundamental diagnosis. These applications are often limited by the optical properties of the available probes. There are several candidates for these applications such as the organic dyes, semiconductor fluorescent nanoparticles and Ln doped nanoparticles. The organic dyes such

as fluorescent protein used for protein labeling have their weakness for deeper application. For example, the tracking of membrane proteins labeled with organic dyes can provide its diffusion coefficients, but no information on the evolution of its organization. This is because the photo-bleaching occurs under the illumination within some seconds. The fabrication of semiconductor fluorescent nanoparticles extends the application range owing to their high photo-stability [26]. For example, in vitro assays, single protein labeling in living cells usually use these nanoparticles [27]. However, the fluorescence intermittency (blinking) and the potential cytotoxicity in vivo also limit their applications [28, 29]. With the advancement in this field, Ln doped nanoparticles are discovered for biological applications. There are many attractive advantages of these nanoparticles such as low cytotoxicity, high photo-stability, absence of fluorescence intermittency, narrow emission range and longer lifetime up to millisecond magnitude. Over the past decades, there were numbers of papers focused on these nanoparticles on imaging technologies. For instance, M. Nichkova et al [30] synthesized 120 nm DC $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ to target phenoxybenzoic acid (PBA) by a microarray immunoassay. In that case, the nanoparticles were modified by anti-PBA IgG. The detailed experimental imaging is described in refs [30].

Furthermore, UC nanoparticles have wider applications in bio-imaging, as they are excited in the NIR allowing deeper tissue penetration [31-33]. Upon NIR (980-nm) excitation, strong UC luminescence can be clearly observed in cells without auto-fluorescence [34]. For the application cases, there are many works published by scientists worldwide [3, 32, 34].

D) Photodynamic therapy (PDT)

Study on cancer therapy is of vital issue since millions of deaths it caused every year. The cancer therapy is so complicated owing to the high mutation rates. With development of technology, Ln doped nanoparticles are discovered to be an important material for cancer therapy. These nanoparticles are quite suitable for cell imaging as described above, and detecting the size and location of tumors [35-37]. Therefore, the combination of these nanoparticles and therapeutic agents is very useful to tumor-targeted therapies. Among the therapies, PDT is a typical one, which includes a photosensitizer, working as a light-sensitive drug. If the photosensitizer is exposed to an appropriate light source, it can be excited, and the absorbed energy will be transferred to the surrounding molecular oxygen to generate $^1\text{O}_2$, that can oxidize and kill cancer cells. Thus, when the photosensitizer is combined with UC nanoparticles, the photosensitizer will be excited by the emission light from UC nanoparticles using IR excitation light source. Then the $^1\text{O}_2$ can be released

from the photosensitizer to kill the cancer tumors [10, 38, 39]. The mechanism is simply described in Figure 1-3.

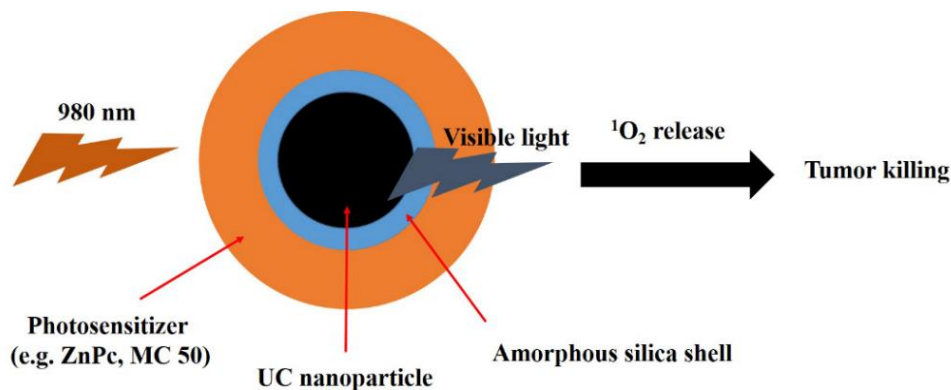


Figure 1-3. Simple schematic of photosensitizer combined with UC nanoparticle for PDT.

E) Enhanced permeability and retention (EPR) effect

The EPR effect is a quite unique phenomenon of tumors owing to its relation to anatomical and pathophysiological differences from the normal tissues [40]. Due to the applications of functionalized UC nanoparticles, the size of the nanoparticles is necessarily located in a range. EPR effect requires the particle size ranged approximately from 10 to 200 nm. When a nanoparticle with size lower than 10 nm, it can be eliminated by the kidney. If the size is larger than 200 nm, the nanoparticles can be captured in the liver by phagocytosis by Kupffer cells.

Owing to the EPR effect, the nanoparticles ranged from 10 to 200 nm can be gathered in the tumor cell. UC nanoparticles emit the visible light by the excitation of IR light. The UC nanoparticles are often used after functionalization to visualize and even kill the tumor cells [41]. UC nanoparticles are usually obtained by doping the activators such as Er^{3+} and sensitizers such as Yb^{3+} , YVO_4 [42, 43], Y_2O_3 [44, 45], and NaYF_4 [46, 47] are often used as the host materials. UC nanoparticles are attracted considerable attention since the IR excitation light has the minimal damage to the live tissues and cells owing to lowest absorption, which is named as the optical window [48].

1.2 Lanthanide doped YVO_4 phosphor

1.2.1 Crystal structure of YVO_4

Yttrium orthovanadate (YVO_4) crystal is a body tetragonal crystal having unit cell of $a = b = 0.7119 \text{ nm}$ and $c = 0.6290 \text{ nm}$ in the $D_{4h}^{19} - I4_1/amd$ space group [49]. This structure is xenotime type and quite similar with zircon [50]. There are four YVO_4 molecules in one tetragonal unit cell. The principal structural unit of YVO_4 is a chain of edge-sharing VO_4 tetrahedra and YO_8 triangular

dodecahedron [51]. Each isolated VO_4 tetrahedra is surrounded by YO_8 dodecahedron, and each YO_8 dodecahedron is connected an adjacent YO_8 dodecahedron by a shared edge, as shown in Figure 1-4. In a single YVO_4 crystal, it has a density of 4.3 g/cm^3 , Mohs 4 hardness and high chemical stability. Moreover, it is a birefringent uniaxial crystal ($n_o = 1.958$, $n_e = 2.168$ at $1.06 \text{ }\mu\text{m}$) with a high optical transparency from 40 to 5000 nm range [52].

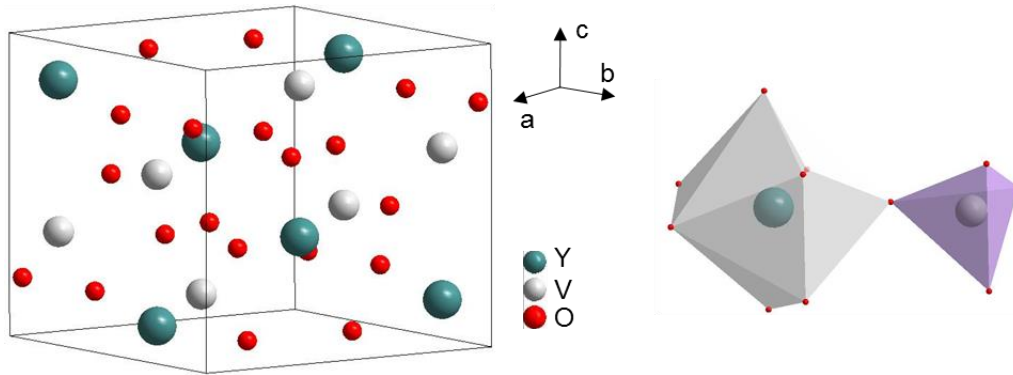


Figure 1-4. The crystal structure of YVO_4 . [53]

1.2.2 Luminescent properties of $\text{YVO}_4:\text{Ln}^{3+}$

The bulk YVO_4 crystal is one of the most excellent host lattices for doping Ln ions for various applications such as in display, luminescent lamps and solid state lasers [54]. Besides of the chemical and physical properties as mentioned above. This structure has an ionic lattice with the desirable property to provide the trivalent site. When YVO_4 is doped with a Ln ion, the Ln ion which enters the lattice substitutionally in yttrium sites is surrounded by eight oxygen atoms at the vertices of a tetragonal dodecahedron. The yttrium sites are quite suitable to provide Ln ions with trivalent sites, in which they can reside without the need for chemical charge compensation.

In this section, we give some examples based on Ln doped YVO_4 materials, and the corresponding applications.

A) $\text{YVO}_4:\text{Nd}^{3+}$

$\text{YVO}_4:\text{Nd}^{3+}$ crystal is one of the excellent laser crystals [55]. In 2000, the simultaneous operation at 1.06 and 1.30 μm in continuous-wave (CW) regime was firstly reported. The energy level diagram of $\text{YVO}_4:\text{Nd}^{3+}$ is depicted in Figure 1-5, the positions of the energy levels are referred from [56]. The CW laser emission at 1.06- μm ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ with a slope efficiency of 0.80 [57] was realized by using a Ti: Sapphire laser source at 0.88 μm excitation. Another wavelength of interest corresponds to 1.34- μm ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ transition. The output performance at 1.34 μm can

be increased by using in-band pumping at 0.88 μm directly into the $^4\text{F}_{3/2}$ emitting level. The laser radiation at 1.34 μm indicates the potential application in medicine, fiber optics and spectroscopy [56].

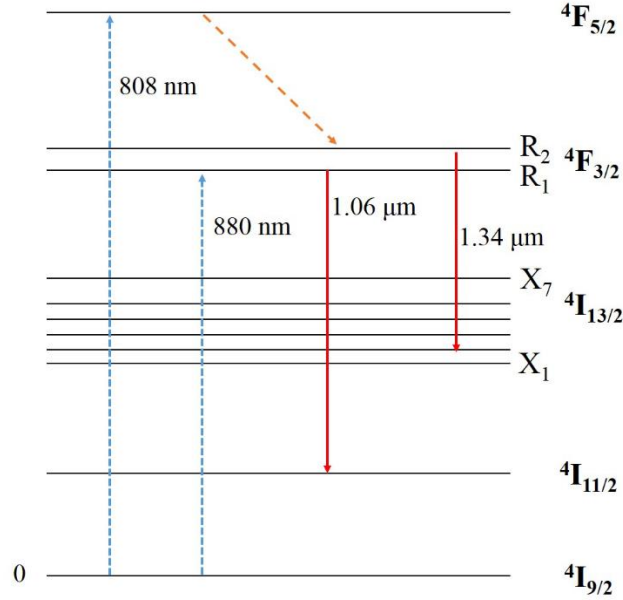


Figure 1-5. Energy level diagram of $\text{YVO}_4:\text{Nd}^{3+}$ with pumping wavelengths at 0.81 and 0.88 μm and of the mission wavelengths at 1.06 and 1.34 μm .

B) $\text{YVO}_4:\text{Eu}^{3+}$

The optical properties of Eu^{3+} has been of great interest over the past decades. The spectra of the Eu^{3+} doped luminescent materials mainly depend on the chemical environment of the matrix. When Eu^{3+} is doped into YVO_4 matrix, the dopant ions are surrounded by eight oxygen ions, in which has the local site symmetry of D_{2d} . Figure 1-6 shows the partial energy-level diagram of Eu^{3+} ion in YVO_4 matrix. YVO_4 possesses a valence band that mainly consists of O^{2-} 2p, and the conductin band mainly consists of V^{5-} 3d [58]. When the $\text{YVO}_4:\text{Eu}^{3+}$ is excited by proper UV light, charge transfer from O^{2-} to V^{5-} of VO_4^{3+} occurs. During a quite short time, the energy transfer to Eu^{3+} ions, resulting in the luminescence. The luminescence spectra will mainly be dominated by $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric-dipole transitions owing to the absence of an inversion symmetry at dopant lattice site (D_{2d} symmetry) [59]. Moreover, $^7\text{F}_2$ level consists of four levels splitted by crystal field, including three degenerate (A1, B1, B2) and one generate (E) [60]. Among them, B2 and E levels can be identified from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission, corresponding to 615.5 nm and 619.3 nm,

respectively [60]. The transitions from $^5D_0$ to the other two levels of the $^7F_2$ are optically forbidden. The $YVO_4:Eu^{3+}$ bulk phosphor is one of the most classical and popular phosphors in color television and cathode ray tubes owing to its high luminescence efficiency upon electron beam excitation [61] and high quantum yield (around 70%) [61]. $YVO_4:Eu^{3+}$ can be excited through the energy transfer from VO_4^{3-} , for which peak UV absorption occurs at 280 nm, or directly through the excitation of Eu^{3+} , which absorbs at 396, 466, and 537nm [62].

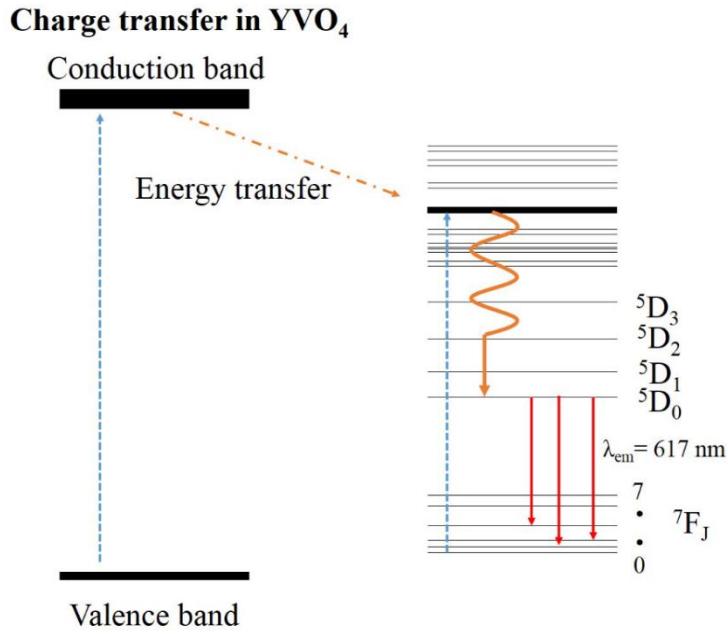


Figure 1-6. Partial energy-level diagram of Eu^{3+} ion in YVO_4 matrix.

Besides the applications of $YVO_4:Eu^{3+}$ bulk phosphor in display and lamps, the corresponding nanoparticles are also quite famous. In the latter case, the absorption coefficients depend primarily on the Eu^{3+} content in the matrix. D. Casanova et al [63] utilized $YVO_4:Eu^{3+}$ nanoparticles to measure the amount of generation of oxidants such as NO, H_2O_2 in living cells. J. Masson et al [64] labeled the toxins in membranes using $YVO_4:Eu^{3+}$ nanoparticles in Madin-Darby canine kidney (MDCK) cell and image the Na^+ channel in live cardiac myocytes of a frog.

C) $YVO_4:Er^{3+}, Yb^{3+}$

The UC process can emit a higher energy photon after absorbing two or more lower energy photons based on the sequential absorption and energy transfer [65]. This process can be divided into three classes as depicted in Figure 1-7: excited state absorption (ESA), energy transfer up-

conversion (ETU), and photon avalanche (PA) [3]. In case of ESA, one single ion absorbs the photons and be pumped to metastable level E1. A second photon promotes the ion from E1 to higher-lying state E2, resulting in the UC emission. ETU process is quite similar with the ESA process. However, ETU is realized through the energy transfer between two ions. Both ions absorb photons, promoting the ions from ground state to E1. The energy of one ion is transferred to another ion, promoting another ion to emitting state E2, while this ion relaxes back to ground state. The PA process was first discovered by Chivian and co-workers [66] in Pr^{3+} doped quantum counters. The PA process requires the pump intensity above a certain threshold value. This process is a combination of ESA and ETU. It starts with the population of level E1 by non-resonant absorption, then the ion is populated to upper lever E2 by resonant ESA. After the metastable E1 population is established, cross-relaxation energy transfer occurs between two ions: one ion relaxed back to E1, another ion is populated to E1, resulting both ions occupy level E1. This will exponentially increase level E2 population by ESA process, thus generating the UC emission as an avalanche process.

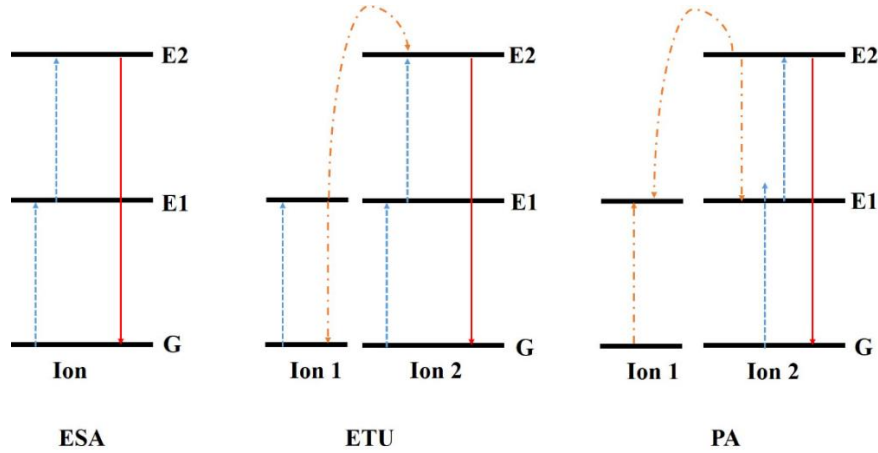


Figure 1-7. The principle UC processes for Ln doped materials.

To get the efficient UC luminescence, the compositions including the host matrix, activators, and sensitizers have to obey the strict criteria. Er^{3+} , Tm^{3+} , and Ho^{3+} ions are the most common activators used to generate UC luminescence under NIR (e.g. 980 nm) excitation. Correspondingly, Yb^{3+} ion is a quite particular sensitizer for activators mentioned above, since Yb^{3+} ion has a more sufficient absorption cross section around NIR than other Ln^{3+} ions and has quite suitable energy levels similar with activators, giving rise to the sufficient energy transfer to activators. Therefore, Yb^{3+} ion is usually codoped into the host lattice together with the activators.

In various host materials used for UC, YVO₄ crystals are of considerable interests and attract many attentions for UC luminescence [43, 67, 68]. Figure 1-8 shows the partial energy-level diagram of Yb³⁺, Er³⁺ ions co-doped in YVO₄ matrix. The UC luminescence for the ²H_{11/2}/⁴S_{3/2} — ⁴I_{15/2} green emission is efficient in YVO₄ matrix under excitation by a 975 nm laser diode [43]. The luminescence mechanism follows the ETU as described above. C. Thao et al [69] synthesized YVO₄: Er³⁺, Yb³⁺ with polymer as template and used it for bioimaging of Hela cells.

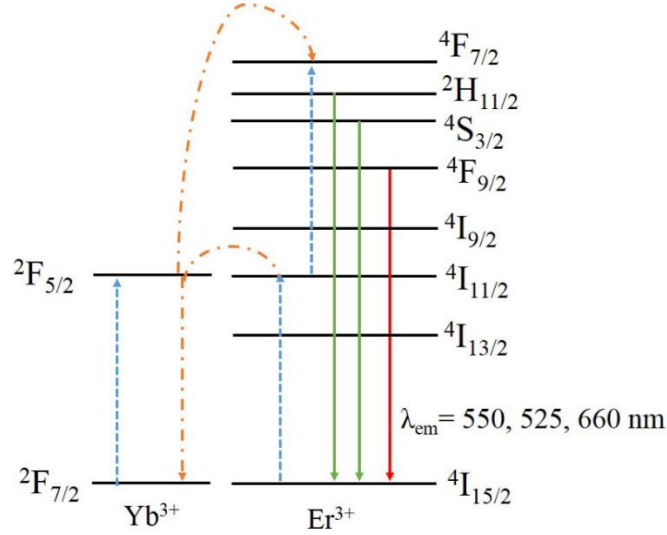


Figure 1-8. Partial energy-level diagram of Yb³⁺, Er³⁺ ion in YVO₄ matrix.

1.2.3 Conventional synthesis of YVO₄:Ln³⁺ nanoparticles

Over the past few years, there were various approaches for YVO₄:Ln³⁺ nanoparticle synthesis. Among them, vast majorities were focused on the chemical methods as part of these methods are list in table 1-2.

Table 1-2. Typical chemical synthesis methods of YVO₄:Ln³⁺ nanoparticles.

Synthesis methods	Refs	Additives
Sol-gel	[70]	Citric acid
Hydrothermal	[71]	EDTA
Precipatation	[72]	Sodium citrate
Liquid phase precursor	[73]	Cellulose
Microemulsion mediated	[74]	CTAB
Microwave irradiation	[75]	Acetic acid
Solvothermal	[76]	PVP, CTAB

Here, some conventional synthesis methods are briefly described as follows.

A) Sol-gel synthesis method [70]

During this reaction, the solution gradually evolved towards the formation of gel which consists of a liquid phase and solid phase. The metal alkoxides or chlorides were usually act as the precursors to form a colloid after the hydrolysis. In this process, the chelating agent is needed for the metal ions. For instance, it was reported that the citric acid can act as a chelating agent to prepare Ln^{3+} doped YVO_4 nanofibers. The poly(vinylpyrrolidone) was used to adjust the viscoelastic properties of the solution. The corresponding metal oxide and NH_4VO_3 acted as the reaction sources. After the reaction, the obtained solution was stirred for 4h to form a hybrid sol. Then, the sol was transferred to a furnace for a low temperature sintering (400 °C) and dried in the air. Finally, the YVO_4 based nanofibers were obtained.

B) Hydrothermal synthesis method [71]

This method describe that the materials can crystallized from controlled high-temperature and high-pressure in a steel antoclave. Using this method, the particle size from nanoscale to microscale can be obtained by tuning the pH values using orgainic molecules. For instance, the corresponding metal oxide and NH_4VO_3 acted as the reaction sources, which were mixed and dissolved in hot water to form a aqueous solution. The final mixture was transferred into a Teflon lined stainless autoclave for hydrothermal reaction. The pH value was adjusted by adding sodium hydroxide. EDTA or acetic acid were necessary for the reaction to quench the particle size. After the reaction, the autoclave was cooled in the air naturally, and the obtained product were washed with distilled water for several times, and dried in the air.

C) Precipatation synthesis method [72]

When a reaction occurs in the liquid solution, the directly obtained solid is usually named as precipitate. The precipitation can be occurred when the concentration of the compound exceeds its solubility. For instance, the $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles could be formed using this method. The $(\text{Y, Eu})(\text{NO}_3)_3$ and NH_4VO_3 acted as the reaction sources, the $(\text{Y, Eu})(\text{NO}_3)_3$ were mixed with sodium citrate, which subsequently led to a formation of a white precipitate. Then the precipitate was dissolved into NH_4VO_3 solution after adjusting the pH value at 8.4 using sodium hydroxide.

Finally, the solution was cooled and dialyzed against water. Water was removed using a rotary evaporator under mild conditions, leading to the nanoparticle powders.

One can see that, the organic chemicals are necessary to be added during the chemical reactions. Because the particle size quenching by the surfactant is one vital step in chemical method. However, there are some disadvantages which cannot be avoided in chemical methods. For instance, it needs lots of steps and complicated procedures, leading to the time consuming. More importantly, the organic additives are quite difficult to remove in final products. A. Huignard et al [72] reported that the residual of sodium citrate still existed in the nanoparticles proved by FT-IR characterization. X. Wu et al [61] reported the existence of CTAB in the nanoparticles by FT-IR characterization.

Therefore, exploring the novel approach is quite necessary to synthesize the clean nanoparticles without any ligands. In my research, one facile and green physical method named laser ablation in liquid is utilized to synthesize the Ln doped YVO₄ based luminescence nanoparticles. YVO₄:Eu³⁺ bulk materials are used throughout the paper, because the obtained nanoparticles with crystallinity, morphology and particle size will be same with other Ln doped YVO₄ nanoparticles, only the luminescence properties are different.

1.3 Laser ablation in liquid (LAL)

1.3.1 Background of laser ablation

The lasers have been used in various applications and technologies in worldwide since its invention in 1960 [77]. In 1965, the lasers were applied in vacuum chambers to obtain the thin films, this technique was subsequently referred to as pulsed laser deposition (PLD) [78]. The rough setup is shown in Figure 1-9. In this technique, the materials are vaporized from the target and form a plasma plume containing atoms, electrons, molecule clusters and so on. Therefore, the plasma has quite high temperatures and pressures, which will be deposited as a thin film on the surface of a substrate in the high vacuum environment. The PLD technique has been applied to fabricate numbers kinds of thin films with high crystallinity such as ceramic oxides, metals, and nitrides. Moreover, PLD method was also developed to fabricate the nanoparticles, such as Si [79] and carbon nanotubes [80]. However, the nanoparticle formation by PLD needs the post annealing, and aggregation are easily occurred. These nanoparticle films are also not easy functionalized for deeper application.

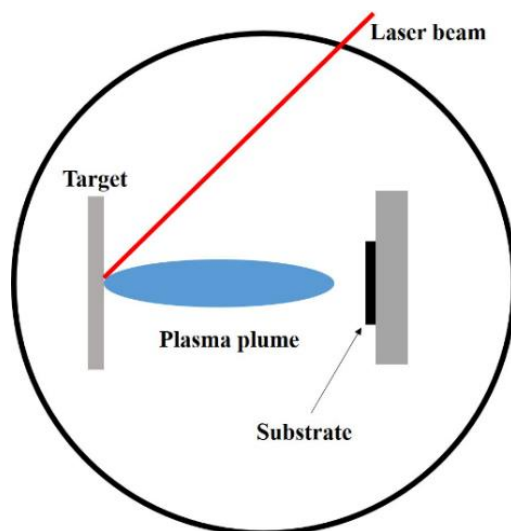


Figure 1-9. Schematic setup of pulsed laser ablation (PLD).

In recent years, with the rise of nano-science, LAL has been developed to fabricate nanoparticles. The utilization of LAL is different from that mentioned in PLD technique, here, the environment of laser ablation is performed in liquid media. This concept was first put forward by Fojtik and co-workers in 1990 [81]. Since then, LAL technique had been developed into an important method to fabricate nanoparticles including metals, ceramic oxides, semiconductors, and even polymers. LAL is totally different from PLD that operate in vacuum because the liquid not only act as a medium for collecting nanoparticles but also greatly affects the morphology and particle size of the final products. In fact, the LAL technique was really focused on since the work by F. Mafune in 2000 [82], and the paper publications rise very fast year by year. In that work, it was the first time to give an effective step to quench the particle size and make the nanoparticle uniformly dispersed in the liquid by irradiating the Au target. Table 1-3 lists some selected cases of nanoparticles fabricated by LAL in various liquids in the past few years. Looking backward respecting the LAL, one can see that LAL enjoys a great success upon fabricating the metal nanoparticles. However, there is a big lacking on fabricating the luminescent oxide nanoparticles, and also the existing reports are not deeper compared with the reports of metal nanoparticles.

Table 1-3. Selected cases of nanoparticles fabricated by LAL in various liquids.

Target	Liquid media	Target	Liquid media
Ag	Water, ethanol, SDS [82-84]	Si	Water, ethanol, SDS [85-87]
Au	Water, CTAB [88, 89]	Ni-Fe alloy	Water, cyclopentanone [90, 91]
Pt	Water, SDS [92, 93]	Ag-Au alloy	Water [94, 95]
Zn	Water, SDS, CTAB, LDA [96-98]	TiO ₂	Water, ethanol, cyclohexane [99]
Al	Water, ethanol [100, 101]	CdS	Water [102]
W	Water, ethanol [103, 104]	Y ₂ O ₃ :Eu ³⁺	Water, MEEAA [105, 106]
C (graphite)	Water, acetone [107, 108]	Y ₃ Al ₅ O ₁₂ :Ce ³⁺	Water MEEAA [106]

As the advancement of laser technique to produce particles. N. Koshizaki groups [109-111] proposed an approach to fabricate sub-micron spheres from the nanoparticles by laser irradiation at low fluences, which is different from LAL applied with high fluences for ablation. This process was defined as pulsed laser melting in liquid (PLML). During this process, the pulsed laser irradiates the colloid containing nanoparticles directly in a transparent vessel. The irradiated nanoparticles can be turned into the droplets after the energy absorption. The applied laser fluence usually below the ablation threshold. Then the formed droplets merge and coalenscent with their neighboring particles to generate the sub-micron particles. Since the difference with the mechanism of laser ablation in PLML, the authors [112, 113] developed the particle heating–melting–evaporation model when the particles absorb the energies from the pulsed laser. According to the model, this energy is totally spent for the particle heating-melting-evaporation process. If the amount of absorbed energy is rather small, the absorbed energy can be expressed as follows:

$$Q_{abs} = J\sigma_{abs} = \mathbf{m_p} \int_{T_0}^T c_p^s(T) dT = m_p(H_T - H_0) \quad 1-1$$

With more absorbed energy, melting occurs.

$$Q_{abs} = J\sigma_{abs} = \mathbf{m_p} \left[\int_{T_0}^{T_m} c_s^p(T) dT + \Delta H_m \right] = m_p [(H_{T_m} - H_0) + \Delta H_m] \quad 1-2$$

If the absorbed energy is even higher, the particle reaches the boiling temperature and starts to evaporate.

$$\begin{aligned} Q_{abs} = J\sigma_{abs} &= \mathbf{m_p} \left[\int_{T_0}^{T_m} c_s^p(T) dT + \Delta H_m + \int_{T_m}^{T_b} c_p^l(T) dT \right] \\ &= \mathbf{m_p} [(H_{T_m} - H_0) + \Delta H_m + (H_{T_b} - H_{T_m})] \end{aligned} \quad 1-3$$

Herein, c_s^p and c_p^l are the particle thermal capacities in solid and liquid state; m_p is the particle mass; T_0 is the particle initial temperature, T_m is the melting temperature, T_b is the boiling temperature, ΔH_m is the melting enthalpy. When the enough energy was absorbed by a particle, the melting will occur surrounding the particle surface. The authors used this model calculated the laser fluences needed for the different particle size when the melting occurred. Also the particle size can be adjusted by applying different laser fluence.

Therefore, laser ablation or melting in liquid has been recognized as a bottom-up and top-down method to fabricate the particles with different size.

There are also many other advantages of LAL to fabricate nanoparticles. First, the procedure of LAL technique is quite simple, it is almost one-step experiment to fabricate nanoparticles. The nanoparticles are very pure if only DI water is used, which is greatly superior to the chemical methods. Second, the conventional chemical methods usually need extra high temperature and high pressure to obtain nanoparticles. Then, contrast to those methods, the extra conditions are not needed while they can be created during the laser ablation process. Therefore, it is quite safe and moderate, excluding the potential of explosions. Last, the productivity problem is promising by solving the technical issues [114].

1.3.2 General mechanism of LAL

1.3.2.1 Basic process of LAL

In general, the experimental process is described as follows: a piece of target is put at the bottom of a beaker. The beaker is filled with some liquid media, and surface of the target is focused and irradiated by the laser beam, as shown in Figure 1-10. The nanoparticles are subsequently formed and collected in the liquid. LAL is famous for its non-equilibrium reaction process. Parameters of this process to synthesize the nanoparticles by LAL can be divided into two categories: material parameters such as the liquid media, system temperature and pressure, and the

target materials; laser parameters such as the wavelength, duration, repetition rate and fluence [115]. In material parameters, the liquid media have a big effect upon the fabricated nanoparticles: the DI water is used as the most common liquid, and the surfactant solutions are also investigated by many groups to quench the nanoparticle size, and list in table 1-3. If the target is different, the resulted nanoparticle morphology and size are also different owing to the difference of target properties. The system temperature can also influence the final products, for instance, Y. Ishikawa and coworkers [116] reported the formation of ZnO nanorod by laser ablation in neat water in a setup heated to 60–80 °C by an external sources. In laser parameters, variations in laser wavelength result in the different energy absorption, the repetition rate can influence the productivity of the obtained nanoparticles [114]. The laser fluence can affect the lifetime of cavitation bubble, which would further have effect on the nanoparticle growth [117].

Figure 1-10 shows the basic process of LAL. When the laser beam irradiates the surface of target in liquid medium, a plasma plume with high temperature, high pressure and high density is induced at the interface of solid and liquid [118]. And then it slows down by compressing the surrounding liquid. The cooling process occurs in a few microseconds with the energy exchange between the plasma plume and the adjacent vapor layer. Primary nanocrystals can be fabricated after the cooling down of the plasma plume. A cavitation bubble is subsequently induced from the vapor layer after the disappear of plasma plume, and the primary nanocrystals then move into the cavitation bubble and grow up inside. Finally, the formed nanoparticles are released after the cavitation bubble extinguishes [119]. Therefore, the cavitation bubble is filled with the water vapor and the species of the target materials. However, in the LAL process, one problem that have to face that the raw target particles are usually detached from the target owing to the shock wave caused by high laser power as shown in Figure 1-10.

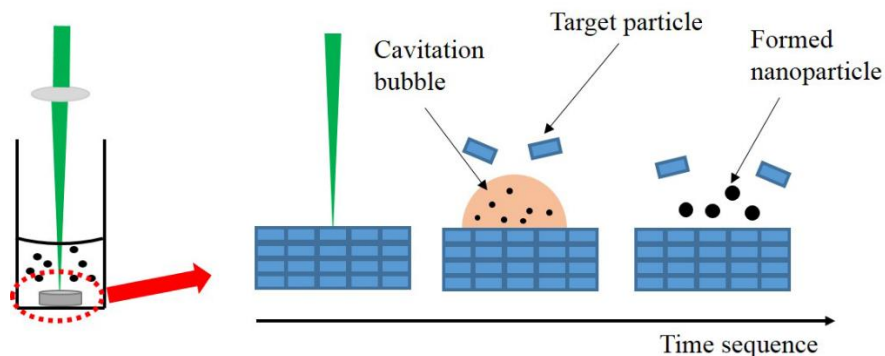


Figure 1-10. Schematic of basic process for nanoparticle fabrication by LAL.

Finally, in the research field of LAL to fabricate nanoparticles since 1992, scientists have devoted vast energies into investigating the mechanism of LAL using various technologies, such as the laser scattering, small angle X-ray to cavitation bubble, shadowgraph imaging and so on [120-124]. Up to date, the community gives the result that the primary nanocrystals are obtained from the quenching of the plasma plume and then grow up inside the cavitation bubble. Herein, some detailed studies about the dynamics of the cavitation bubble, and the investigation for particle growth inside bubble are described as follows.

1.3.2.2 Dynamics of the cavitation bubble

There are some popular models are used to study the dynamics of the cavitation bubble, which is of great importance to understand the growth behavior of the nanoparticles inside the cavitation bubble. It is known that high pressure and temperature are created at the collapse of the cavitation bubble. For the dynamics calculation inside the cavitation bubble, some models are introduced as follows.

A) Modification of Rayleigh-Plesset theory

The investigation of the dynamics of small bubbles or cavity can be dated from the work of Lord Rayleigh in 1917. Afterwards, Plesset modified the Rayleigh theory and developed it, and finally the Rayleigh-Plesset equation was formed to describe the oscillation behavior of a cavitation bubble in fluid as follows

$$\frac{P_B(t) - P_l(t)}{\rho_l} = R(t) \frac{d^2 R(t)}{dt^2} + \frac{3}{2} \left[\frac{dR(t)}{dt} \right]^2 + \frac{4\eta}{R(t)} \frac{dR(t)}{dt} + \frac{2S}{\rho_l R(t)} \quad 1-1$$

Where $R(t)$, $P_B(t)$, $P_l(t)$, S , η and ρ_l are the radius of cavitation bubble, the internal pressure, the liquid pressure, surface tension of water, the kinematic viscosity, and the density of water. Therefore, the bubble pressure $P_B(t)$ can be deduced that [125]

$$P_B(t) = P_V(T_B) + P_{G0} \left(\frac{T_B}{T_0} \right) \left[\frac{R_0}{R(t)} \right]^{3\gamma} \quad 1-2$$

Where $P_V(T_B)$ is the vapor of surrounding liquid at T_B temperature. T_0 is the temperature of the liquid at a long distance from the bubble, γ is the ratio of the specific heat. P_{G0} and R_0 are pressure and bubble radius existed by the formation of cavitation bubble induced by laser ablation, which can be expressed as [125]

$$P_{G0} = P_0 - P_V(T_0) + \frac{2S}{R_0} \quad 1-3$$

Where P_0 is the liquid pressure at a long distance from the cavitation bubble. The vapor pressure at T_B , $P_V(T_B)$ can be found by the Clausius-Clapeyron relationship [126]

$$P_V(T_B) = P_0 \exp \left[\frac{H_V m}{R_g} \left(\frac{1}{T_0} - \frac{1}{T_B} \right) \right] \quad 1-4$$

Where H_V is the latent heat of vaporization per unit mass, m is the mass of water vapor molecule, R_g is the universal gas constant. Assuming the expansion of the cavitation bubble is adiabatic, therefore, the temperature inside the bubble can be expressed as [127-129]

$$T_B(R) = \frac{T_0 R_0^{3(\gamma-1)}}{(R^3 - a^3)^{\gamma-1}} \quad 1-5$$

Where a is the hard core radius of the bubble contents, which can be expressed as $a = R_0/8.86$ [130, 131].

The liquid pressure $P_l(t)$ outside of the cavitation bubble is estimated by Bernoulli's principle, which can be expressed as [132]

$$P_l(t) = P_0 - \frac{\rho_l}{2} \left[\frac{R(t)^2}{r^2} \frac{dR(t)}{dt} \right]^2 \quad 1-6$$

Therefore, the pressure and temperature can be estimated according to the above calculation. However, the above theory is based on the cavitation bubble in fluid, and the shape of the cavitation bubble is a sphere. In the case of the laser ablation to a target surface in liquid, a hemisphere shaped bubble is produced, and the effect of contact angel $\theta(t)$ is different, and modified as follows [133, 134]

$$\cos \theta(t) = \cos \alpha - \frac{S}{\sigma} \frac{1}{R(t)} \quad 1-7$$

Where α and σ are a constant and the linear tension of water, respectively.

Therefore, the authors modified the Rayleigh-Plesset equation due to these differences. And the pressure and temperature are estimated as detailed described in refs [132], the results show that the pressure can reach up to 70 GPa, and temperature can reach up to 10^4 K at the collapse moment.

J. Lam [135] et al also modified the Rayleigh-Plesset equation, which is different from that described in refs [132]. In this case, the viscous and surface tension items are neglected since the authors claimed the little influence to the final calculated results. Their corresponding results also showed that the calculated pressure and temperature are in the same order of magnitudes with that

obtained in refs [132]. The detailed calculation in this case will be described and shown in chapter 5. This model is also the one we used in this research.

B) Hard core van der Waals model

A.De Giacomo [123] et al calculated the dynamics of the cavitation bubble using the hard core van der Waals model, which expressed as follows for pressure

$$P_B(t) = (P_\infty + \frac{2\sigma}{R(t)}) \left[\frac{R_\infty^3 - h^3}{R(t)^3 - h^3} \right]^\gamma \quad 1-8$$

And temperature is expressed as

$$T_B(t) = T_\infty \left[\frac{R_\infty^3 - h^3}{R(t)^3 - h^3} \right]^{\gamma-1} \quad 1-9$$

Where P_∞ and T_∞ are pressure and temperature of the liquid, $R(t)$ is the radius function of the cavitation bubble, R_∞ is the radius inside bubble, at which the pressure equal to the liquid pressure, σ is the surface tension of the liquid (water), $h = R_\infty/9.174$ is the actual radius that taking into account the water molecules covolume, γ is the ratio of the specific heat. According to the calculation result, the pressure can reach up to $10^7 - 10^8$ Pa, and temperature can reach up to 1000 K [123]. This result is quite similar with the result calculated by J. Lam et al. The relationship between the bubble collapse time and bubble lifetime can be estimated by [136]

$$R_{max} = \frac{t_{collapse}}{0.915\sqrt{\rho/(P_\infty - P_v)}} \quad 1-10$$

Where R_{max} is the largest bubble radius during expansion, ρ is the liquid density, $t_{collapse}$ is the collapse time, P_∞ is the liquid pressure, and P_v is the vapor saturation pressure inside the cavitation bubble. Authors also reported the relationship between laser fluence, the maximum bubble radius, and the collapse time using equation 1-10. A higher laser fluence usually result in a bigger bubble radius, and a longer bubble lifetime. This would be the possible reason why some groups found the bigger particle size when applying higher laser fluence since the longer growth time in the cavitation bubble [82, 137].

1.3.2.3 Growth of nanoparticles inside cavitation bubble

Over the past decades, there was one question, which attracted much attention in generating nanoparticles by LAL: where and how the nanoparticles grow up? To answer this question, many groups devoted considerable efforts to get the answer. The difficulty to explore the mechanism

mainly due to the complexity of the laser ablation process. When the solid target was ablated by a laser beam, many physical and chemical phenomena occurred, such as the ultrafast laser light absorption and electron-phonon coupling process [138, 139], the energy dissipation in target and surrounding liquid [140, 141], the plasma and cavitation bubble formation. The lifetime of plasma usually in a few ns [142]. Therefore, it is difficult to explore the growth behavior of the nanocrystals. Recently, some groups used some unique techniques to investigate this research and gave some plausible answers as described in following.

A) Small angle X-ray scattering (SAXS)

SAXS technique is able to detect the the electron density modulation from the nanometer to sub-nanometer scale [143, 144]. L. Lavissee [145] et al successfully detected two species in laser ablation in ambient air, which had the size of 20 and 180 nm simultaneously. S. Ibrahimkuty [146] et al used SAXS technique detected the species inside cavitation bubble induced by laser ablation in liquid media. The SAXS signals were recorded by time-gated detection. Figure 1-11 shows the schematic illustration of this technique to detect the species inside the cavitation bubble. According to their results, there were two species were detected, one was small primary nanoparticles with a mean size of 8–10 nm. Another species was the agglomerated particles with a mean size of 45nm. Moreover, the larger nanoparticles were not detected close to the target surface, but accumulated in the middle site of the cavitation bubble. These results demonstrated that the primary nanocrystals were grown inside the cavitation bubble. The results also detected that the agglomerated nanoparticles did not penetrate the bubble interface, and effectively limited inside the cavitation bubble.

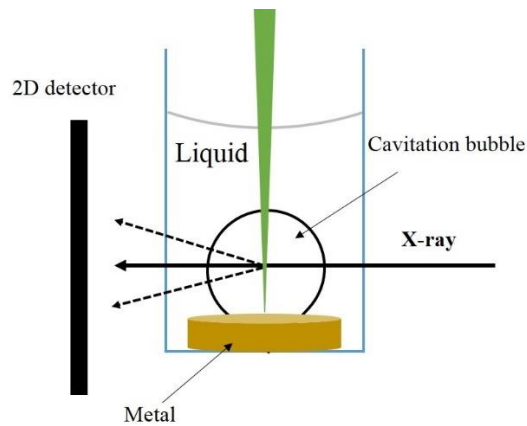


Figure 1-11. Schematic of SAXS technique to detect the species inside the cavitation bubble induced by laser ablation in liquid to a metal target.

B) Laser scattering

W. Soliman [121] et al utilized a imaging system combined with a laser-light scattering to get the location information of cavitation bubble and the nanoparticles. After the laser ablation to a Ti target in water, another laser beam at a delay time illuminated the area in front of the target surface. And a flash lamp was used to illuminate the ablation space in a different direction to get the shadowgraph imaging simultaneously. The images of laser light scattering and shadowgraph were taken by a ICCD camera. Through observing the scattering light information at different delay time, the position of the nanoparticles could be taken. The results showed that the scattered laser light was detected inside the cavitation bubble in the region near the boundary of the interface between the water and cavitation bubble. The authors also reported the scattered light was detected after the collapse of the first bubble. This scattering is from inside the rebounded second cavitation bubble, confirming the existing of the nanoparticles inside the rebounded cavitation bubble. To confirm the scattered light was from the scattering of nanoparticles, the authors also did the comparison experiment. When the probe laser illuminated the same space without the target, no scattering signals were detected, confirming the scattered light inside the cavitation bubble was from the scattering of the nanoparticles. One unique result which was different from the SAXS was that the upper side out of the cavitation bubble could lead to the laser light scattering. This phenomenon indicated a small part of the nanoparticles were transported from the cavitation bubble towards the liquid during the bubble expansion. But most portions of the nanoparticles were still limited inside the cavitation bubble. Furthermore, the scattered light was even detected at a delay time of 0.2 μ s, indicating the faster growth speed of nanoparticles in gas-phase laser ablation. This would be due to the higher particle density confined by the surrounding liquid media.

The above fundings and the dynamics of the cavitation bubble confirm that the nanoparticles are formed after the quenching of the plasma plume, and then transferred into inside the cavitation bubble. The nanopartilces can grow up inside the bubbles since it has high temperature and high pressure. However, there are still some questions which are still unsolved. For instance, how do the nanoparticles grow up inside the cavitation bubble in different materials; how and when the surfactant molecules influence the growth of the nanoparticles. Therefore, there is still a long way to go to explore these unknown areas. As the advancement of the technology, I believe that all these questions will be answered in the future.

1.4 Objectives

First, the objective of this research is to synthesize the YVO_4 based nanoparticles by the green physical method: laser ablation in liquid. $\text{YVO}_4\text{:Eu}^{3+}$ will be investigated throughout the research. The liquid media are very important and have clear effect on the final nanoparticles.

Chapter 2 mainly focuses on the nanoparticles in water based solution including pure DI water, and surfactant solution to adjust the particle morphology and size. The anionic surfactant SDS and cationic surfactant CTAB were used to investigate their effect on the formation of nanoparticles

Chapter 3 focuses on the fabrication of nanoparticles in ethanol to investigate the liquid properties on the particle morphology, size and crystallinity.

In chapter 4, a free liquid reactor is utilized, in which a liquid filament can be formed and irradiated by the laser to investigate the effect of laser irradiation on the nanoparticles. This is quite different from the experiment in chapter 2 and 3, while chapter 2 and 3 are focused the attention on the irradiation on target materials, not on nanoparticles.

Second, another important objective is to explore the mechanism of laser ablation in liquid to synthesize the nanostructures. The particle formation mechanisms are put forward according to the experiment results. Furthermore, the dynamics of the cavitation bubble is studied to explore the nanoparticles' growth condition inside the cavitation bubble.

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Chapter 2. Effect of Water Based Solution on $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles Formation by Laser Ablation in Liquid

2.1 Introduction

There are many merits of the laser ablation in liquid (LAL) as described in chapter 1. Among them, one of the most important advantages is the ultra-purity of as-obtained nanoparticles if only pure water as the reaction liquid medium. In this chapter, effect of laser fluence on the final products was investigated, the laser fluence was set at 1.7 J/cm^2 , 3.2 J/cm^2 and 8.9 J/cm^2 . F. Mafune [1] et al. reported the increase of nanoparticle size with increasing laser fluence. More importantly, the ovoid-like nanoparticles were formed directly by LAL in DI water, which was never reported before. G. W. Yang group [2] fabricated the spindle-like CuO nanocrystals by laser ablation in electrical field. GaOOH and ZnO nanocrystals were also spindle-shaped by laser ablation in surfactant solution (CTAB) [3, 4]. As far as we know, this was the first time to report $\text{YVO}_4\text{:Eu}^{3+}$ ovoid-like nanoparticles without any assistances by LAL. The mechanism of nanoparticle formation is further discussed.

Using surfactant is one of the most effective approaches to quench nanoparticle size. The basic theory is to adsorb surfactant molecules of nanoparticles during laser ablation. F. Mafune [1] et al. reported that particle size distribution of silver shifts towards smaller sizes when using the anionic surfactant sodium dodecyl sulfate (SDS, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{-Na}$). After this very first report, many groups focused on the surfactant effect on nanoparticle size. H. Usui [5] et al. have succeeded in preparation of ZnO nanoparticles by LAL in solutions of cationic surfactant cetyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{N-Br}$) and lauryl dimethylaminoacetic acid betaine (LDA, $\text{C}_{16}\text{H}_{33}\text{NO}_2$).

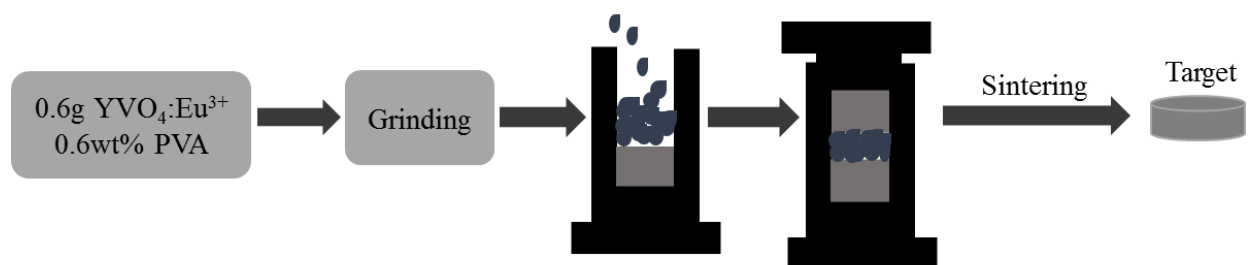
Therefore, in this chapter, the DI water was used as the working liquid medium, and the morphology, crystallinity, optical properties, elemental composition and productivity of as-obtained nanoparticles were investigated in detail. After that, the effect of SDS and CTAB on particle size of as-obtained nanoparticles is studied.

Moreover, the laser parameters were also investigated in this research. However, the laser wavelength, repetition rate and duration time did not influence the particle morphology and size. Therefore, the laser parameters were not focused in this chapter. Partial results obtained by changing laser parameters were shown in appendix data 2.

2.2 Experimental

2.2.1 Target preparation

$\text{YVO}_4:\text{Eu}^{3+}$ powder was purchased from Tokyo Kagaku Kenkyusho Co. Ltd. The powder was mixed with PVA (0.6 wt%) then moved into a compacting model to shape a pellet. The pellet was 10 mm in diameter. The procedure to obtain a pellet was described in Scheme 1. The obtained pellet was then transferred to muffle for sintering (1100 °C, 4 h) to obtain the final $\text{YVO}_4:\text{Eu}^{3+}$ target for LAL. The picture of the target is shown in Figure 2-1.



Scheme 1. The procedure to make a target for laser ablation by pressing commercial powder.



Figure 2-1. Picture of $\text{YVO}_4:\text{Eu}^{3+}$ target for laser ablation.

2.2.2 Laser setup

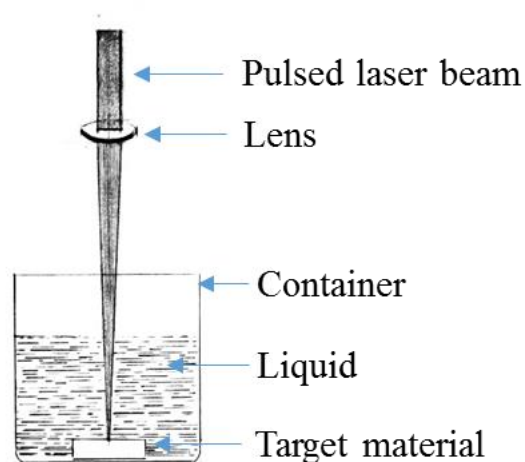


Figure 2-2. The process illustrator of LAL.

The target was placed at the bottom of the beaker that was filled with 4 ml DI water. The Nd:YAG laser (Spectron Laser Systems Ltd., SL8585G) was used for ablation (wavelength: 532 nm, repetition rate: 10 Hz, pulse width: 13 ns). A burning paper was used to determine the spot size of the focused laser beam. The laser fluence was calculated from the ratio of laser power and spot size, which located from 1.7 J/cm^2 to 8.9 J/cm^2 . Finally, the whole solution was lyophilized in order to collect powders for XRD characterization.

The anionic surfactant $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{-Na}$ (SDS) and cationic surfactant $\text{C}_{19}\text{H}_{42}\text{N-Br}$ (CTAB) were used to replace the DI water. The concentration of SDS surfactant was adjusted at 0.1, 1, 4, and 8.5 mM. And the concentration of CTAB surfactant was adjusted at 0.05, 0.1, and 0.25 mM. The concentration of the surfactant did not increase any more after characterizing the properties of the nanoparticles since the results were pessimistic when continued to increase the concentration of surfactant.

For the investigation of optical properties of nanoparticles obtained in DI water, the nanoparticles were dropped onto the surface of a glass slide. Then the glass slide loaded with the nanoparticles were sintered in an electromagnetic oven for 300, 400, 500, and 600°C for 24 h. Then, the obtained nanoparticles were measured with a photoluminescence spectrophotometer.

2.2.3 Characterization

The phase of the obtained nanoparticles was characterized by X-ray diffractometer (XRD, Bruker, D8 discover, Germany) with Cu- α_1/α_2 ratio of 0.514 radiation at 55kV and 22mA. Scanning electron microscopy (SEM, Hitachi High-technologies, S-5500, Japan) and transmission electron microscopy (TEM, JEOL, JEM-2010F, Japan) were used to investigate particle morphology, size distribution, and crystallinity. Luminescent properties of the colloidal nanoparticles were investigated by photoluminescence spectrophotometer (PL, Hitachi High-technologies, F-7000, Japan) with a 150V Xe lamp at room temperature. The obtained nanoparticles were filtered using 0.22 μ m pore-size filter for characterization except for X-ray diffraction analysis. Colloidal nanoparticles were collected through freeze drying; the same procedure was repeated for 5 times. Then the collected nanoparticles were used for X-ray diffraction. Energy-dispersive X-ray spectroscopy (EDS, Horiba, ENERGY EX-250, Japan) was utilized to quantitatively measure the content of the elements in the final nanoparticles after LAL.

2.3 Results and discussion

2.3.1 Morphology of as-obtained nanoparticles

Figure 2-3 displays the SEM results of YVO₄:Eu³⁺ raw particle (target) and the nanoparticles obtained with different fluences. The raw particles have irregular shape with around 1-5 μ m size, as shown in Figure 2-3a). The nanoparticles fabricated by laser ablation clearly show an ovoid shape with long axis of 90-120 nm (Figure 2-3b)). Effect of laser fluence on nanoparticle morphology was investigated, as shown in Figure 2-3c-e). Note that the fluence threshold detected to fabricate nanoparticles in this experiment is 1.7 J/cm². The fluence was increased to 3.2 J/cm² and 8.9 J/cm² to check the effect. The nanoparticles obviously aggregated at 8.9 J/cm² due to the melting at higher laser fluence. When using the high laser fluence, the lifetime of the cavitation bubble became longer than at low fluence, and more amount of the nanoparticles were fabricated. Therefore, it is possible for nanoparticles further aggregated inside the cavitation bubble. T. Nunokawa [6] et al reported the Y₂O₃:Er,Yb nano-strings, which showed the aggregation and connection of the nanoparticles. Figure 2-4 shows the raw particles co-exist with the nanoparticles, which were removed using the filter as described in experimental part.

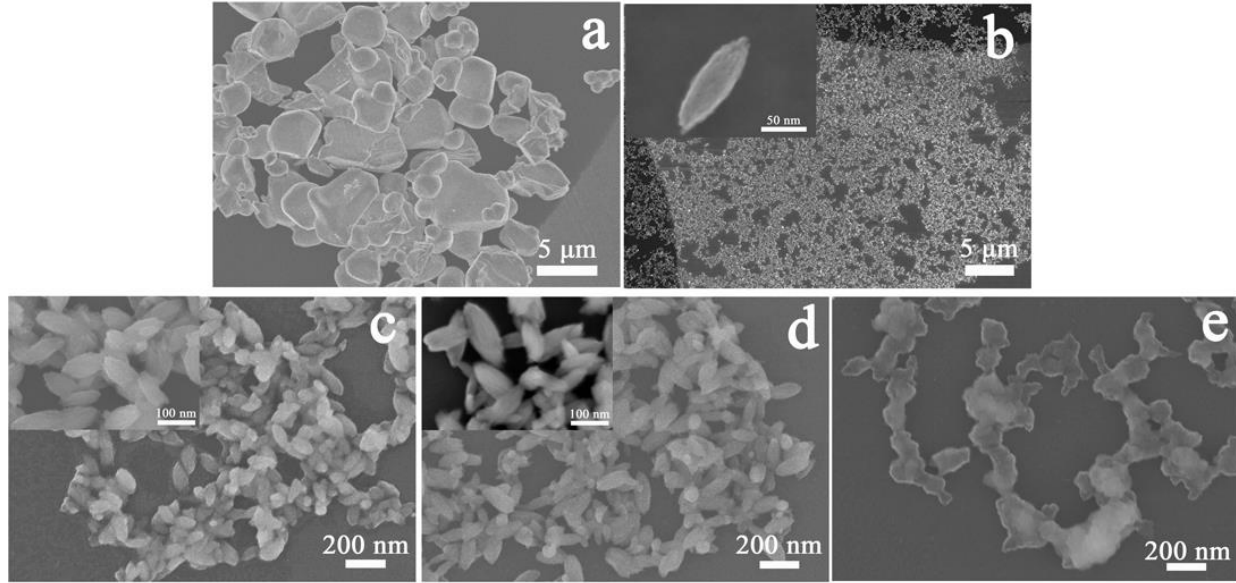


Figure 2-3. SEM images of a) the targets and b) the nanoparticles obtained at 1.7 J/cm^2 at low resolution while no filters were applied. Images c-e) were filtered (0.22 μm pore-size) nanoparticles obtained at fluences of 1.7 J/cm^2 , 3.2 J/cm^2 and 8.9 J/cm^2 with $\times 60\text{k}$ magnification, respectively. Inset image of b) was taken at $\times 600\text{k}$ magnification, while insets of c-d) were taken at $\times 250\text{k}$ magnification. [7]

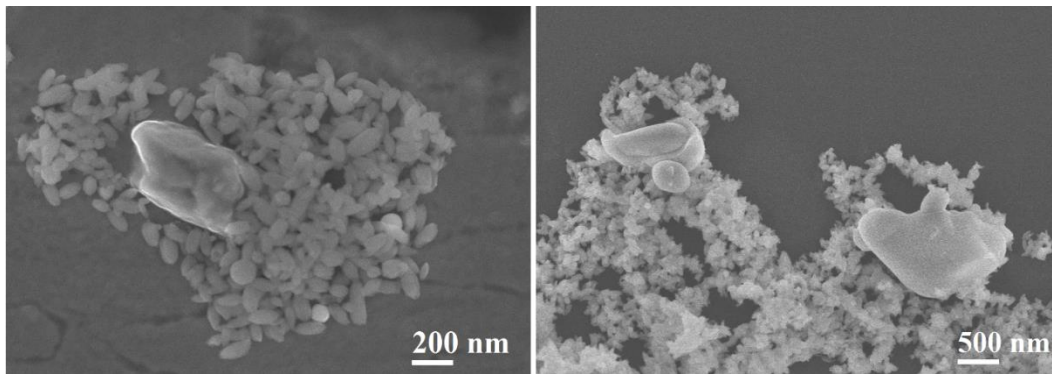


Figure 2-4. Laser-induced micron-sized particles without using 0.22 μm pore size filter. [7]

Figure 2-5 shows the size distribution diagram of the nanoparticles obtained at fluences of 1.7 , 3.2 and 8.9 J/cm^2 . As can be seen that, the mean size of the nanoparticles obtained at 1.7 J/cm^2 was about 94 nm , while that obtained at 3.2 J/cm^2 and 8.9 J/cm^2 were around 108 nm . The increase of the mean size with the laser fluence, reported by several teams [1, 8], was more difficult to observe in this research. This would be caused by the different crystal growth mechanism in various material structures. D. Amans et al [9] also reported the similar result.

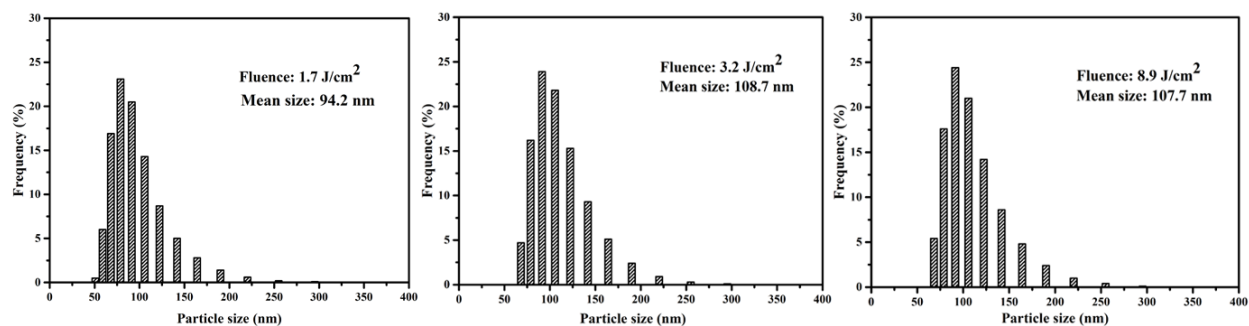


Figure 2-5. Size distribution diagram of the nanoparticles obtained at fluences of 1.7, 3.2 and 8.9 J/cm².

2.3.2 Crystallinity of as-obtained nanoparticles

The crystal phases of the target and obtained nanoparticles were determined by XRD (Figure 2-6). The diffraction peak positions for target and nanoparticles were completely consistent with the YVO₄ tetragonal structure (PDF No.17-0341), indicating the purity of the obtained products without any impurities. Furthermore, the XRD peaks of obtained nanoparticles were obviously broadened by their nano-size compared with that of the target. However, due to the broadening of the peaks, some planes did not shown such as plane (400). The nanocrystallite size could be calculated by Debye-Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad 2-1$$

D is the mean size of the ordered (crystalline) domains; K is a dimensionless shape factor, with a typical value of about 0.9; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM); θ is the Bragg angle (in degrees). After calculation, the result showed that the average crystallite size is around 7.9 nm. Herein, the products for XRD measurement were not filtered using 0.22 μ m pore-size filters. Therefore, micron-particles were co-existed with nanoparticles. Thus, the HR-TEM was utilized to characterize the detail structure of one single nanoparticle.

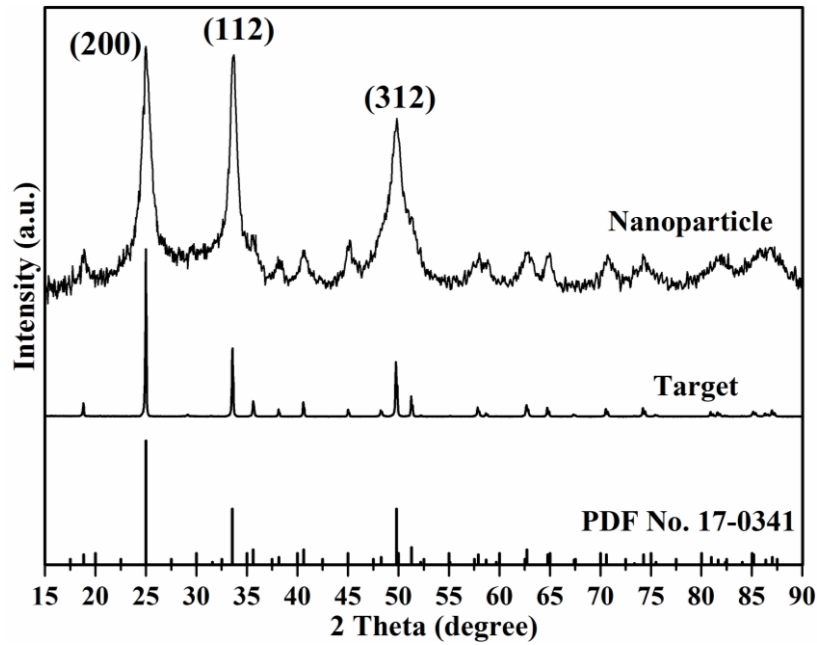


Figure 2-6. XRD patterns of the $\text{YVO}_4\text{:Eu}^{3+}$ target and nanoparticles. [7]

Figure 2-7 shows high resolution TEM (HR-TEM) of one ovoid-like nanoparticle. One can see that the particle had poly-crystalline phase and consists of smaller nanoparticles. This result was consistent with the crystallite size estimated from the XRD pattern. The measured lattice spacing of 0.356 nm and 0.268 nm were consistent with planes (200) and (112) of YVO_4 tetragonal structure, respectively. The measured angle, 67.7° , was also matched well with the theoretical value.

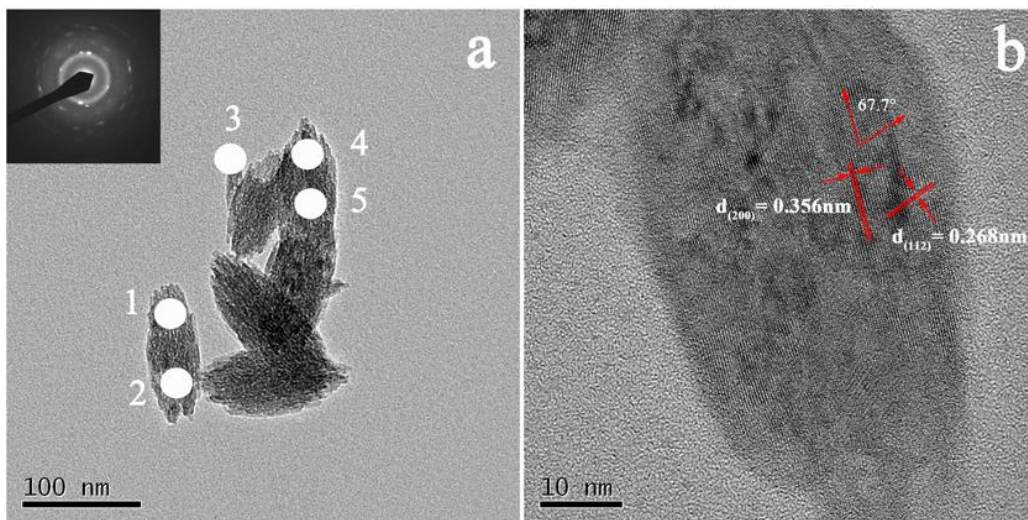


Figure 2-7. a) TEM and b) HR-TME images of as-obtained nanoparticles by laser ablation. The inset is the selected area electron diffraction pattern. [7]

2.3.3 Optical properties of as-obtained nanoparticles

Figure 2-8 shows the UV-vis absorption properties of as-obtained nanoparticles by LAL at different laser fluences. A strong absorption band between 250 and 280 nm was shown in all samples. This band could be attributed to the charge transfer from oxygen to vanadium atom in VO_4^{3-} groups [10, 11]. This result also confirmed that by-products were not produced after LAL. Insets in Figure 2-8a) present the transparent colloids obtained at 1.7, 3.2 and 8.9 J/cm^2 after filtration by 0.22 μm pore-size filter. The concentration of the colloidal solution was related to the absorbance according to Beer-Lambert's law:

$$A = \varepsilon cl \quad 2-2$$

where A is absorbance, ε is molar extinction coefficient, c is concentration, and l is path length. As ε and l are constant, the absorbance was directly proportional to the colloidal concentration. Therefore, the intensities of absorption band increased along with the increase of laser fluence, which could be due to the higher nanoparticles amount obtained at higher fluence. Figure 2-8b) presents a luminescent picture of as-obtained nanoparticles excited by 266nm UV light. The nanoparticle concentration was around 0.5 mg/ml obtained by performing the experiment for 6 cycles (20 min for 1 cycle) at fluence of 1.7 J/cm^2 .

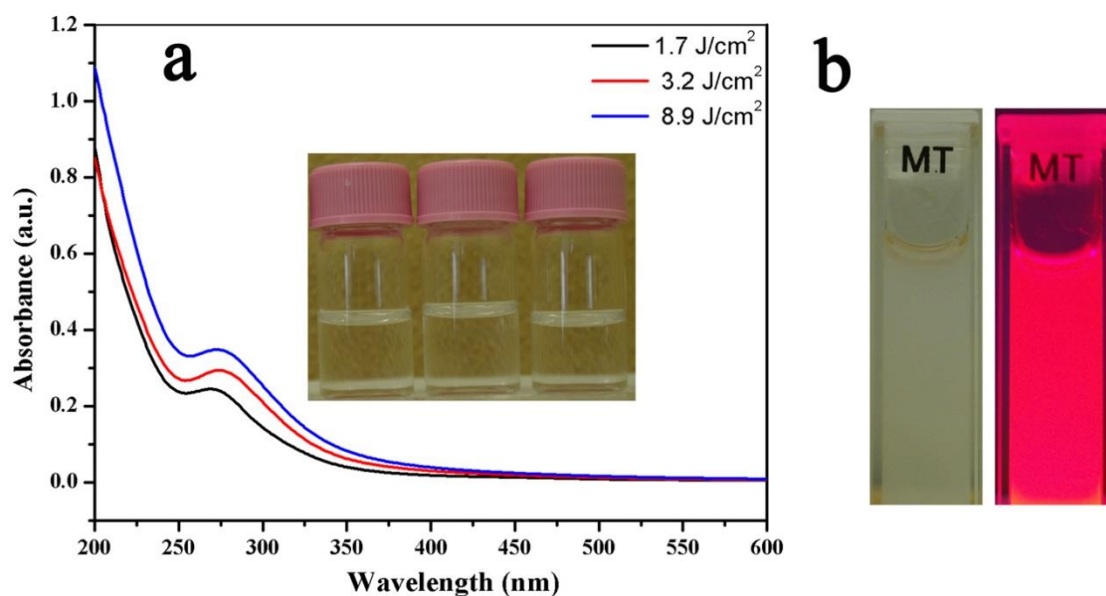


Figure 2-8. a) The UV-vis properties of $\text{YVO}_4:\text{Eu}^{3+}$ colloidal nanoparticles at different fluences; b) As-obtained colloidal nanoparticles (0.5 mg/ml) at 1.7 J/cm^2 before(left) and after (right) UV excitation. [7]

The luminescent properties of the obtained nanoparticles are presented in Figure 2-9. One can see that the PL spectra were dominated by the transitions $^5D_0-^7F_{2,4}$ (electric-dipole transitions) from Eu^{3+} ions, resulting from the absence of an inversion symmetry of Eu site (D_{2d} symmetry) [10, 12]. The magnetic dipole transitions $^5D_0-^7F_{1,3}$ were also observed. The enhanced PL intensity along with the increasing of laser fluence could be due to the higher nanoparticles amount, which was consistent with UV-vis absorbance spectra. The PL spectra presented the obvious intensity difference between the raw particles and colloidal nanoparticles. This difference could be ascribed to the luminescence quenching from the surface of nanoparticles. Because of the higher specific surface areas for nanoparticles, there existed more amount broken bonds on the surfaces of nanoparticles than that of the target. In addition, the reaction process was performed in water. Therefore, the nanoparticle surface might be covered with some species to quench the luminescence such as the hydroxyl groups [10].

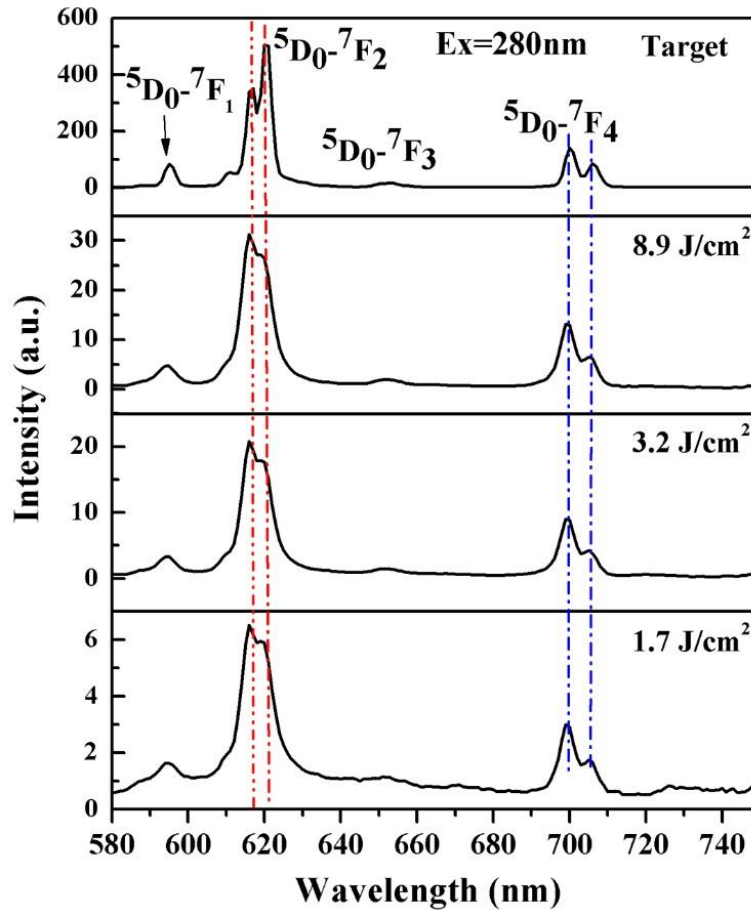


Figure 2-9. Photoluminescence spectra of $\text{YVO}_4:\text{Eu}^{3+}$ colloidal nanoparticles at different fluences ($\text{Ex} = 280\text{nm}$). [7]

However, one distinct difference had to be pointed that the ratios of $I_{615\text{nm}} / I_{619\text{nm}}$ and $I_{700\text{nm}} / I_{706\text{nm}}$ that belong to $^5D_0-^7F_{2,4}$ altered significantly as shown in Figure 2-9, indicating the symmetry changes around the europium ions, which further affected the crystal fields around europium ions. When the particle size was reduced to the nano-scale, the crystal lattice would have distortions because of the increasing effect of the surface [13]. In other words, the difference of peak ratios was due to the poor crystallinity of as-obtained nanoparticles. In order to verify this claim, the obtained nanoparticles were dropped onto the surface of a quartz glass slide and dried in air. Then, the glass slide was annealed at 300°C, 400°C, 500°C, and 600°C for 24 h to get better crystallinity of the nanoparticles.

Figure 2-10 presents the PL spectra of the nanoparticles after annealing treatment at different degree temperatures for 24 h. One can see that the peak ratios of nanoparticles recovered close to the PL peak ratio of the raw particles (target) when increasing the annealing temperature. This indicated that better crystallinity of the nanoparticles leads to better PL performance. Intensity of PL also obviously increased after annealing treatment.

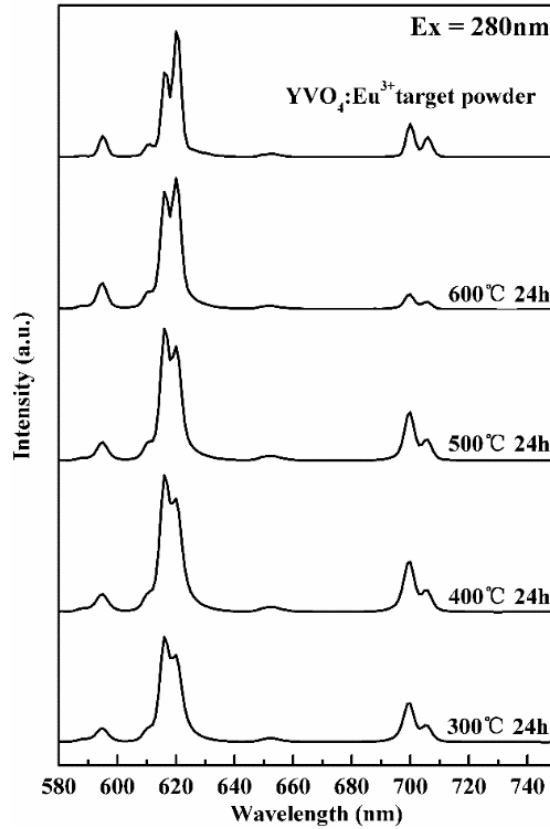


Figure 2-10. PL spectra of $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles annealed at different temperatures ($\text{Ex} = 280 \text{ nm}$). [16]

Figure 2-11 presents the HR-TEM results of the nanoparticles before and after annealing treatment. The nanoparticles directly obtained after LAL clearly showed defects and crystal boundaries. The observed crystal size from HR-TEM image was almost agree with the XRD results (8 nm). Small crystals and defects were due to the growth process. As mentioned, the nucleation and crystal growth occurred in ultra-fast periods during the cooling process of the plasma plume. As a result, small crystals with defects could be created with a high possibility in this process. LAL was regarded as a far-from-equilibrium process, where the metastable structures and impurities might be produced in the final products [14, 15]. However, YVO_4 with zircon structure was produced in this study fortunately. One possible reason for this result was the fact that natural YVO_4 stable existed only in zircon structure. Therefore, the pure phase could be preserved if the elemental composition was preserved.

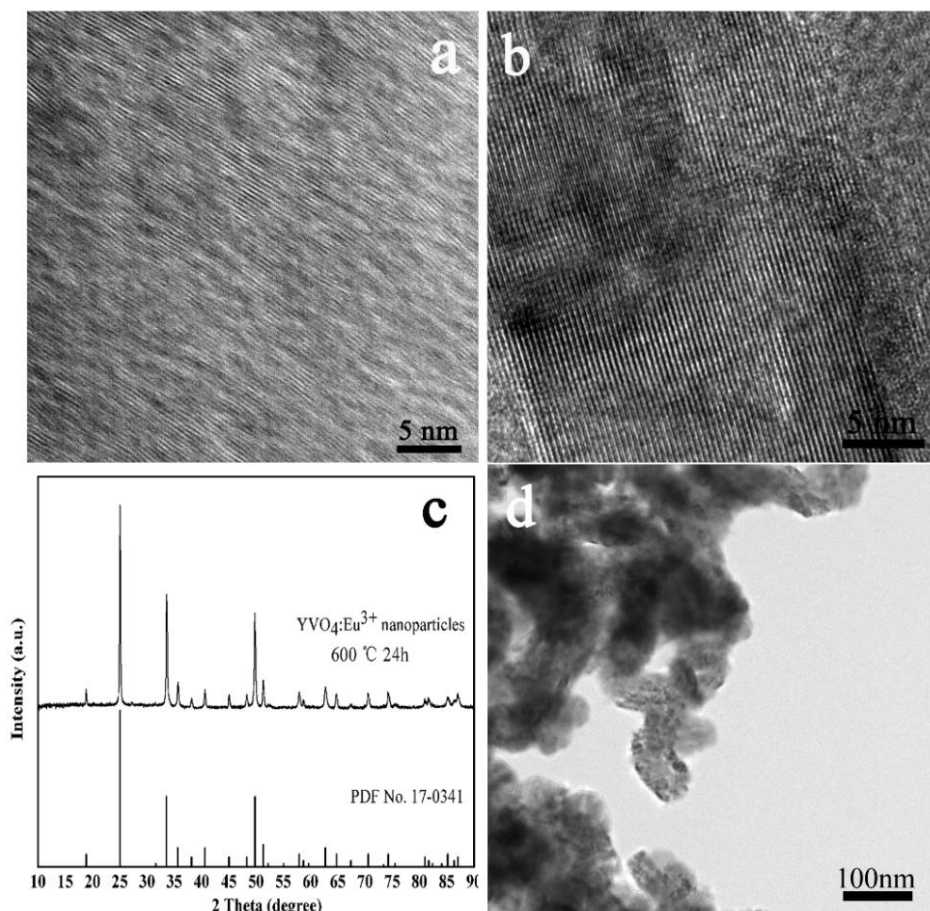


Figure 2-11. HR-TEM images of $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles a) before and b) after annealing at 600 °C for 24 h. c) XRD pattern of $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles after annealing at 600 °C for 24 h. d) TEM image of $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles at low magnification. [16]

2.3.4 Compositions of as-obtained nanoparticles

Over the past decade, the technique of LAL was mainly applied to fabricate noble metals and alloys nanoparticles. However, this technique suffered from the problem of elemental composition in nanoparticles for alloys and compounds [17-19]. In this research, the quantitative analysis of the dopant element (Eu^{3+}) in YVO_4 after reaction was characterized by SEM-EDS (area-mode). Ten different areas for nanoparticle and five areas for target were investigated (Figure 2-12). The ratios of Eu^{3+} in the $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles and raw particles were resulted to be $2.14 \pm 0.25\%$ and $2.16 \pm 0.16\%$, respectively. The result indicated the dopant ions concentration was well kept after laser ablation. Considering the laser ablation process of ultrafast cooling rate and nucleation leading to the poly-crystallinity of ovoid-like nanoparticles, the TEM-EDS (point-mode) was performed as shown in Figure 2-7. The result is shown in Table I. The atomic ratio of Eu^{3+} for nanoparticles and raw particles were $2.8 \pm 1.2\%$ and $3.0 \pm 0.3\%$, respectively.

The deviation of the data could be caused by the measurement of point-mode. As described above, the ovoid-like $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles were polycrystalline, and it was very likely containing different amounts of nano-crystallites for different point analyses. Large quantities of broken chemical bonds existed in crystal boundaries. It would result in the differences of different element contents between the crystal boundary and inside.

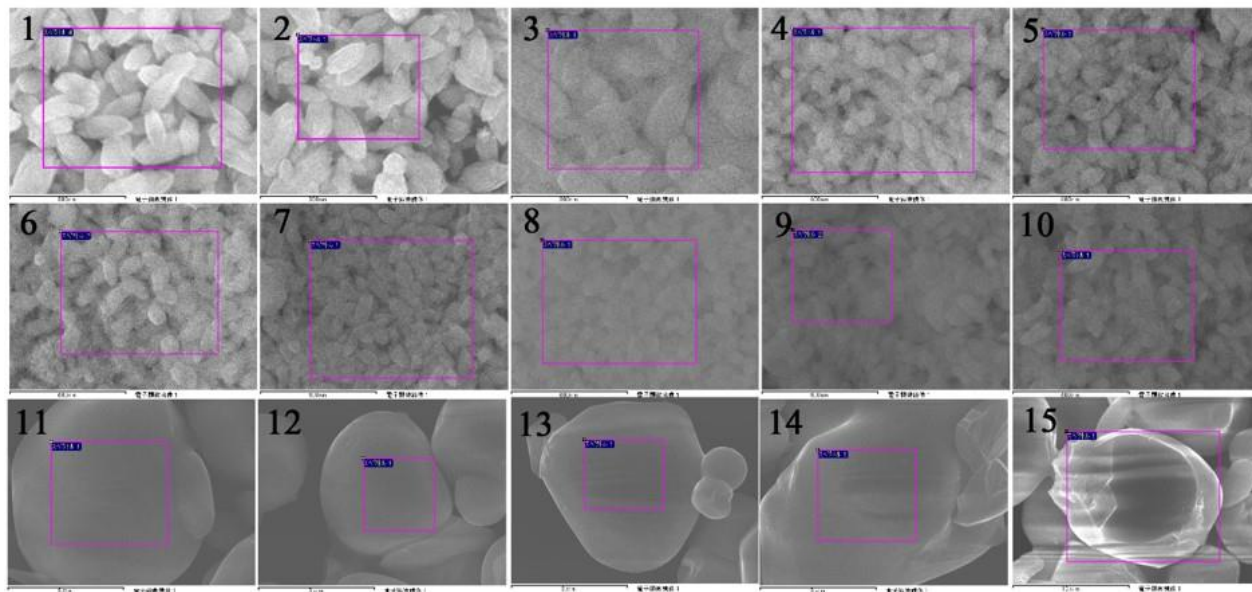


Figure 2-12. (1-10) SEM images of nanoparticles and (11-15) that of target with EDS-area analysis (purple square). [16]

Table I. Atomic ratios of Eu³⁺ in YVO₄ matrix.

EDS (Point-mode): Composition in Atom%	
Area	Eu ³⁺
1	2.4
2	2.4
3	3.9
4	1.2
5	4.1
Average	2.8 ± 1.1
Target (Average of 5 particles)	3.0 ± 0.3

2.3.5 Mechanism of nanoparticle formation

The final formation of ovoid-like nanoparticles is divided into two stages. The first stage is the formation of primary nanocrystal, while the second stage is the self-assemble of primary nanocrystal into an ovoid-like nanoparticles. G. Yang [14] et al. described the most possible nucleation and growth of nanoparticles in the process of LAL. While the surface of target is irradiated by the laser beam in liquid, numbers of elemental species form in a plasma plume with high temperature, high pressure, and high density. Liquid environment limits the expansion of plasma plume. During this process, the vapor layer is formed after the energy exchange between the plasma plume and surrounding liquid, and further a cavitation bubble is developed from the vapor layer. The primary nanocrystals is obtained from the quenching of plasma plume and released into the cavitation bubble. The nucleation thermodynamics can be explained by classical nucleation theory and the following assumptions are based on: i) nuclei are perfectly spherical and ii) nuclei are mutually non-interactive:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \sigma \quad 2-3$$

Where ΔG is the sum of a bulk term, r is the volume of a nuclei, Δg is the difference in free energy per unit volume between the thermodynamic phase nucleation is occurring in, and the phase that

is nucleating. There is a least-probable nucleus occurs, i.e., the one with the highest value of ΔG where

$$\frac{dG}{dr} = 0 \quad 2-4$$

Therefore, the critical radius of nuclei is calculated as

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad 2-5$$

Where r^* is critical nuclei radius, γ is surface energy per unit area, and ΔG_v is the change of Gibbs free energy per unit volume. Finally, energy barrier ΔG^* can be obtained as follows:

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \quad 2-6$$

According to this equation, high concentration favors the formation of nuclei. In other words, large amount of small nuclei is formed in the plasma plume.

The second stage is the formation of ovoid-shaped nanoparticles. The mechanism of ovoid-shape of $\text{YVO}_4:\text{Eu}^{3+}$ polycrystals could be explained as follows. As mentioned above, the primary crystals obtained from the quenching of plasma plume and then moved into inside the cavitation bubble for further growth. Herein, this process is composed of two different growth mechanisms: “Ostwald ripening” and “oriented attachment”. The former one described that the smaller nanocrystals dissolve and redeposit onto larger particles owing to the reduction in the driving force of surface energy with decreasing particle size [20]. In this experiment, “Oriented attachment” would be mainly occur during the growth of primary nanocrystals. This concept was proposed by Penn et al [21] in 1998. This mechanism described that the adjacent primary nanocrystals are self-assembled through sharing a common crystallographic orientation. In this process, the attachment typically occurs on crystal planes with high-surface energy [22, 23]. In the final obtained particles, the crystalline lattice planes of each nanocrystals are almost aligned in the same direction. However, defects in the resulting particles are formed owing to the dislocations at the contact areas between the adjacent particles. The basic process can be simply illustrated in Figure 2-13.

In addition, some groups reported the similar $\text{YVO}_4:\text{Eu}^{3+}$ morphology by ultrasound irradiation [24]. The particle morphology in our results is consistent with the above papers. Therefore, one possible reason for this result is that the “oriented attachment” would occur under the help of the acoustic wave. In fact, X. Lin [2] et al. reported the formation of CuO nanoparticles by LAL based on the mechanism of “oriented attachment”.

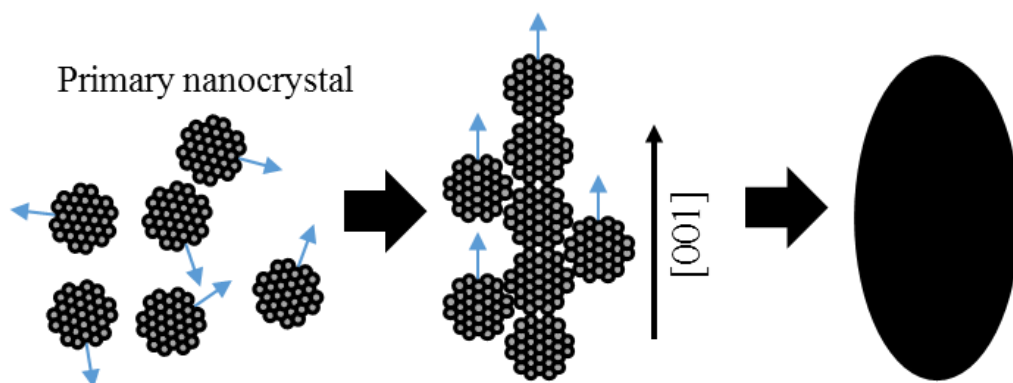


Figure 2-13. The scheme illustration of “oriented attachment” process.

Figure 2-14 presents the schematic diagrams of the formation process of $\text{YVO}_4\text{:Eu}^{3+}$ polycrystalline. A plasma plume containing Y, V, and O clusters is formed with high temperature and high pressure in water, and the acoustic wave is also induced at the same time. Then the $\text{YVO}_4\text{:Eu}^{3+}$ primary nanocrystals are fabricated during ultrafast quenching of plasma plume. After that, primary nanocrystals rapidly grow up and self-assemble with each other to form an ovoid-like particle, which could be attributed to the “oriented attachment”, as shown in Figure 2-13.

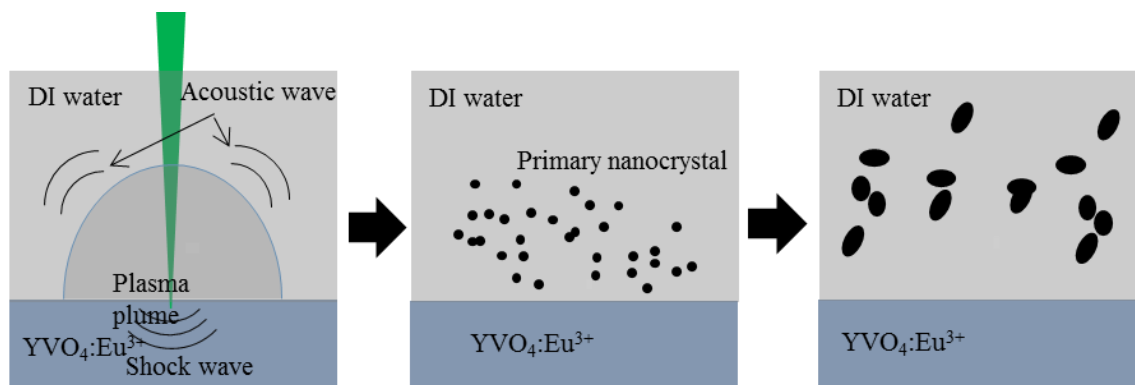


Figure 2-14. Schematic of the $\text{YVO}_4\text{:Eu}^{3+}$ ovoid-like nanostructure upon laser ablation in DI water.

2.3.6 Productivity of as-obtained nanoparticles

Generation of a high amount of colloidal nanoparticles was well established by conventional chemical methods. In terms of purity, it is necessary to investigate the scale-up of nanoparticles by LAL. Therefore, the factors on productivity of $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles were basically investigated.

Figure 2-8 shows effect of laser fluence when other factors was set as constant. From UV-vis spectra, one can see that the intensities of absorption band increased along with the increase of laser fluence indicating the higher nanoparticles amount obtained at higher fluence. T. Ishigaki [25] et al. also reported the similar results in $Y_2O_3:Eu^{3+}$. Figure 2-15 presents the difference between low and high laser fluence: when the laser beam irradiates the target surface, thermal energy accumulates from the target surface to inside. Higher laser fluence leads to bigger ablation volume bulk. C. Sajti et al. [26] reported the linear relationship bewteen nanoparticle productivity and laser fluence in Al_2O_3 case. However, the fluence factor was not studied more further owing to the limit of laser equipment. In addition, more higher laser fluence would induce more energy to break the pressed pellet. Using higher laser fluence is an effective approach to improve the productivity of nanoparticles, especially for metal nanoparticles.

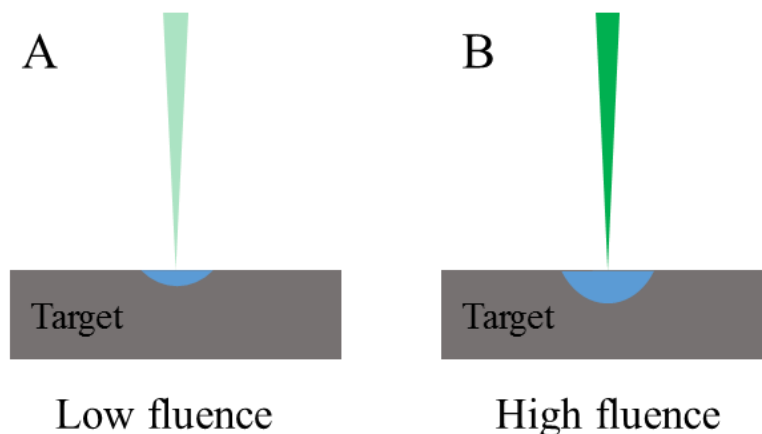


Figure 2-15. The effect of laser fluence on the target surface.

Figure 2-16 shows the as-obtained colloids at 1.7 J/cm^2 after laser ablation with various ablation time. It clearly showed the turbidity increase along with the continuous ablation time, indicating the productivity increase when prolong the continuous ablation time. Figure 2-17a) shows the dependence between the weight of as-obtained nanoparticles and continuous ablation time. As can be seen that the weight of as-obtained nanoparticles increased obviously and then the increase rate decreased. This change was caused by the turbidity of the colloid after ablation for several minutes. Figure 2-18a) shows the colloid after ablation for 2 min and b) 40 min. The increased turbidity of the colloid clearly decreased the laser fluence into the target surface. Figure 2-17 b) shows another method to collect the nanoparticles. The collect frequency was set at 10 min.

In other words, the laser ablation was performed every 10 min and collected for 8 times. One can see that the weight of nanoparticles increased obviously compared with panel a). Finally, around 1.12 mg was collect after 80 min laser ablation, while just 0.16 mg was collected after continuous ablation for 80 min in panel a). Figure 2-18 gives the reason of this change.

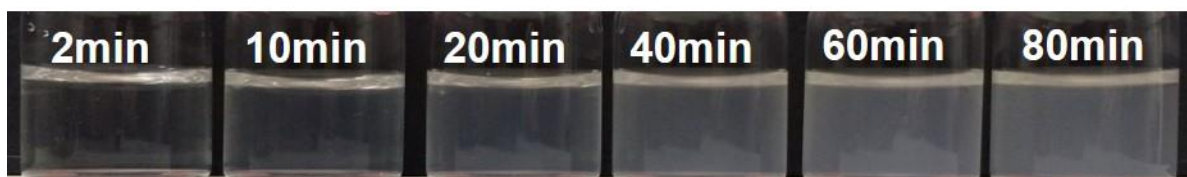


Figure 2-16. Turbidity of the colloidal nanoparticles obtained by LAL at different ablation time.

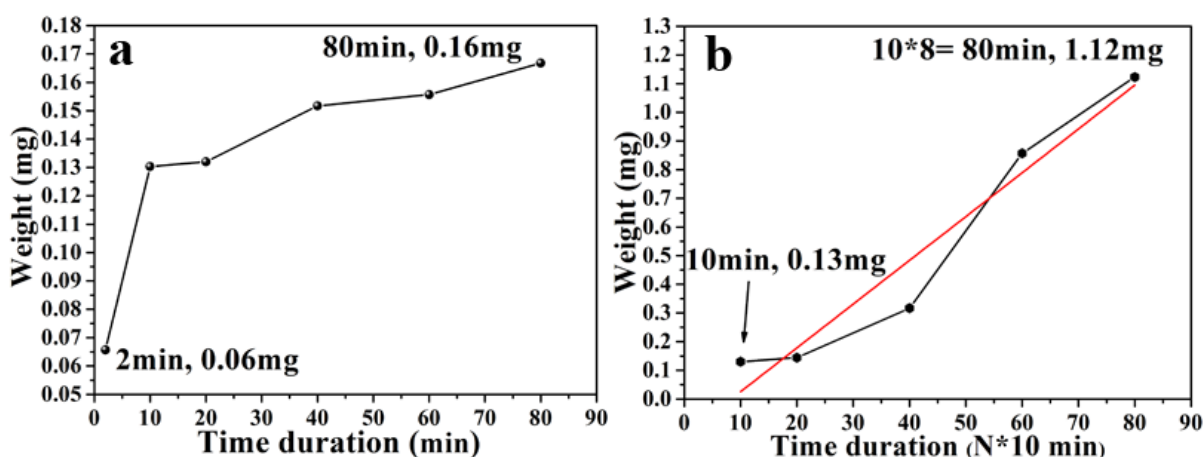


Figure 2-17. a) Dependence between the weight of as-obtained nanoparticles and continuous ablation time and b) segmented time for collection frequency (N) for every 10 min.

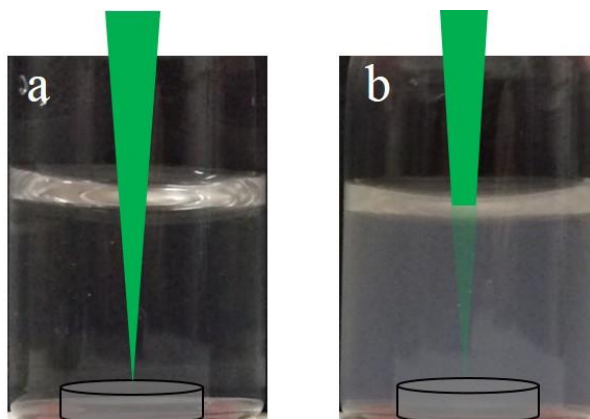


Figure 2-18. The effect of laser ablation time on laser pulse energy. a) is the colloid after ablation for 10 min and b) 40 min.

2.3.7 Effect of surfactant addition on as-obtained nanoparticles

In this part, effect of anionic SDS and cationic surfactant on nanoparticle crystallinity, morphology and size distribution will be presented. The concentration of SDS solution was set at 0.1, 0.5, 1, 4 and 8.5 mM. According to the SEM results, the nanoparticles that obtained in 0.1, 0.5 mM solution did not show any differences with the nanoparticles obtained in DI water. Figure 2-19 shows the SEM image of nanoparticles fabricated by LAL at 0.1, 1, 4, 8.5 mM SDS solution. One can see that the particles were quite similar with that obtained in water when SDS concentration was 0.1 mM. The morphology was slightly changed when SDS concentration increased to 1 mM. It showed that the long axis of the ovoid-like nanoparticles was shorten, and some nanoparticles became nearly sphere. Then the SDS concentration was increased to 4 mM. It showed that nearly spheres were clearly presented. Figure 2-20 shows the SEM images of nanoparticles obtained in 4 mM SDS solution at lower magnification, indicating the uniformity of the morphology. We can also see that the surface of the nanoparticles was more rough than the nanoparticles obtained in DI water. Figure 2-21 shows the size distribution nanoparticles fabricated in 4 mM SDS solution. We can see that the mean size of the nanoparticles located in around 55 nm. This result was obviously smaller than the size of nanoparticle fabricated in DI water. Then, the SDS concentration was increased to 8.5 mM. However, the particle size did not decrease any more. This result was consistent with that concluded by F. Mafune: the surfactant concentration should not too low or too high [1].

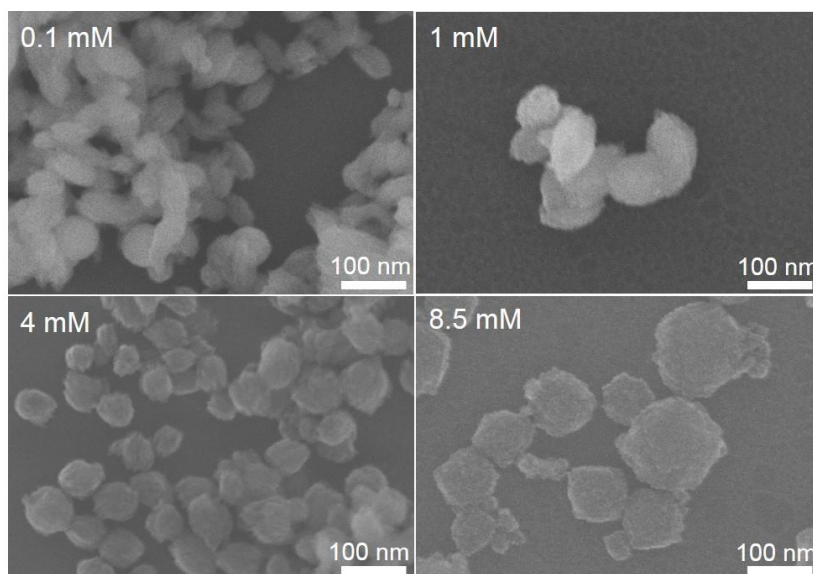


Figure 2-19. SEM images ($\times 200k$ magnification) of nanoparticles obtained by laser ablation in different SDS solution.

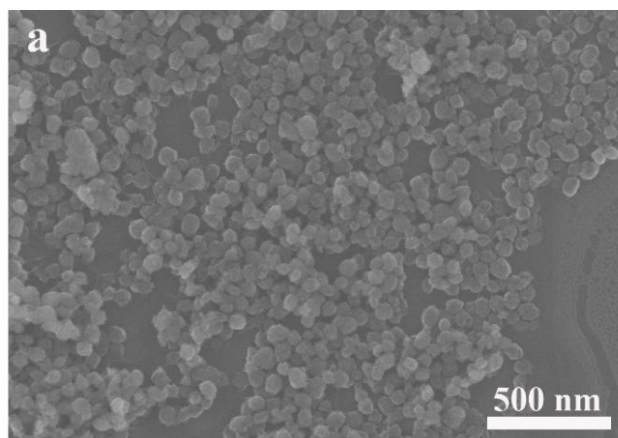


Figure 2-20. a) low $\times 50k$ and b) higher $\times 200k$ magnification SEM images of nanoparticles obtained by laser ablation in 4 mM SDS solution. [16]

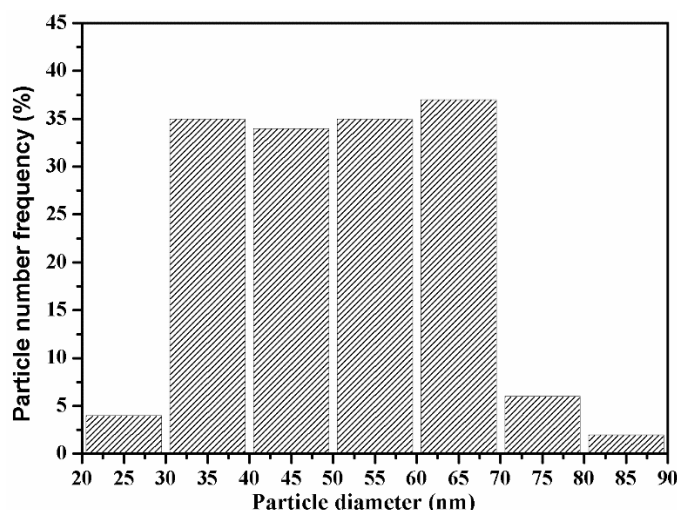


Figure 2-21. The size distribution of the nanoparticles obtained in 4 mM SDS solution. [16]

The phase of nanoparticles was determined by HR-TEM, as shown in Figure 2-22. The lattice spacing was measured to be 0.354 and 0.260 nm, which corresponded to plane (200) and (112) of tetragonal YVO_4 structure. The measured angle, 66.7° , was consistent with the theoretical value, indicating that the YVO_4 with tetragonal phase were successfully fabricated. FT-IR was used to investigate the chemical bonds adsorbed on the surfaces of nanoparticles. The obtained colloids in SDS solution were centrifuged at 10,000 rpm. The precipitates were washed with DI water to remove the residual SDS for several times. Figure 2-23 shows the FT-IR results of the nanoparticles after LAL in 4 mM SDS solution and DI water. It was shown that a strong signal at

830 cm^{-1} were observed for all samples. This band was the characteristic IR band of VO_4^{3+} group [27]. The broad absorption band peaked at 3445 and 1639 cm^{-1} corresponded to the $-\text{OH}$ groups in water molecules. The peak band at 2345 cm^{-1} was related to the CO_2 from air. The spectra of the nanoparticles obtained in SDS solution exhibited five bands at 2977, 2927, 2852, 1384, and 1045 cm^{-1} . These signals could be assigned to the $-\text{C}-\text{H}$ stretching and bending modes of SDS molecules [28]. The FT-IR results indicated the successful adsorption of SDS onto surfaces of nanoparticles. As a result, the size decrease of nanoparticle was caused by modification of the SDS molecules.

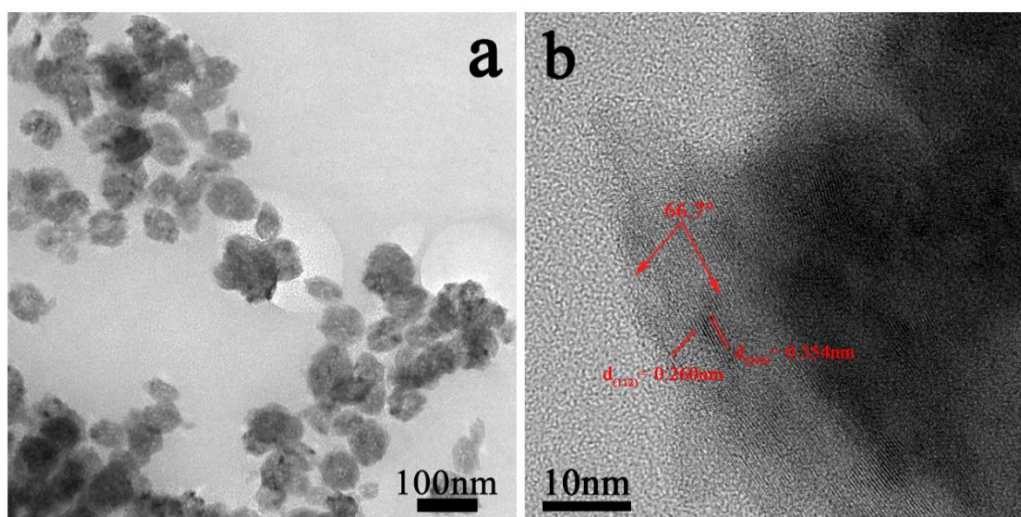


Figure 2-22. a) TEM and HR-TEM images of the nanoparticles obtained in 4 mM SDS solution. [16]

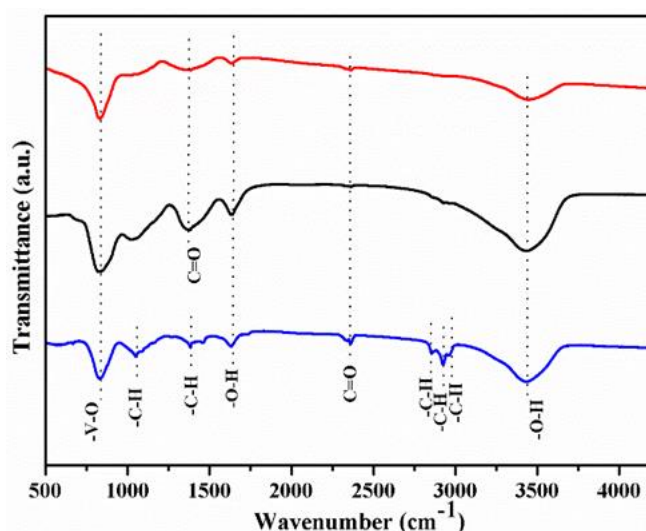


Figure 2-23. FT-IR spectra of $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles by laser ablation in 4 mM SDS solution (blue line) and DI water (black line). The red line shows the nanoparticles annealed at 600 $^{\circ}\text{C}$ for 24 h after laser ablation in DI water. [16]

Besides the anionic SDS, the effect of cationic surfactant CTAB was also investigated. Figure 2-24 shows the SEM images of the nanoparticles obtained at CTAB solution with 0.05, 0.1, and 0.25 mM. As clearly be seen that the nanoparticles aggregated severely even at 0.05 mM concentration. It also showed the same trend when increasing to 4 mM. Besides the aggregation of the nanoparticles, the morphology of nanoparticles also changed. The nanoparticles obtained at all concentration showed some sphere shape, indicating that the CTAB surfactant could effectively affect the particle formation by laser ablation in liquid.

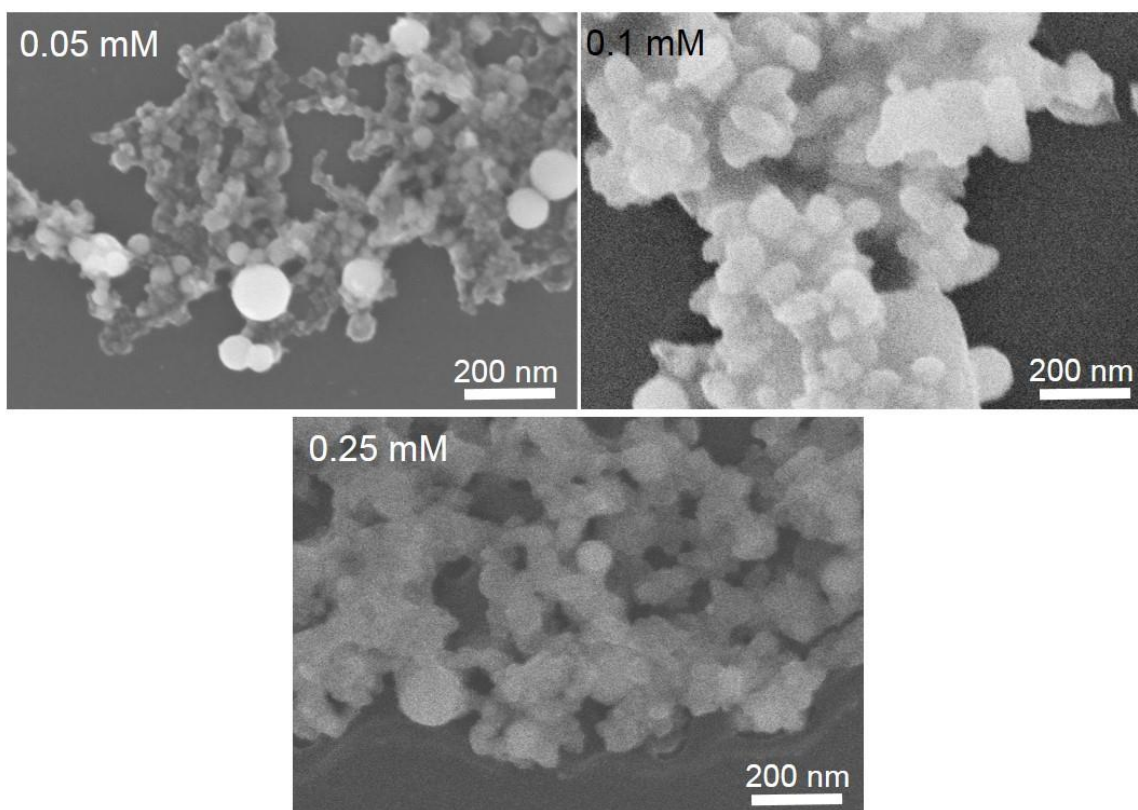


Figure 2-24. SEM images of the nanoparticles obtained by laser ablation at CATB solution with different concentration. The inset is the SAED pattern of image b).

Figure 2-25 shows the TEM images of the nanoparticles obtained by laser ablation in 0.25 mM CATB solution. As shown that the as-obtained nanoparticles aggregated severely, which was consistent with the result of SEM. And no smaller nanoparticles could be observed. Importantly, as more as we could observe, most nanoparticles were amorphous phase as indicated in SAED pattern in the inset. Furthermore, the cationic surfactant was very easily adsorbed onto the nanoparticles surfaces, and the thickness of the capping surfactant was far more than the length of

CTAB molecule (≈ 2 nm) as indicated in Figure 2-25b), indicating that the CTAB molecules were very easily adsorped onto the surface of the nanoparticles.

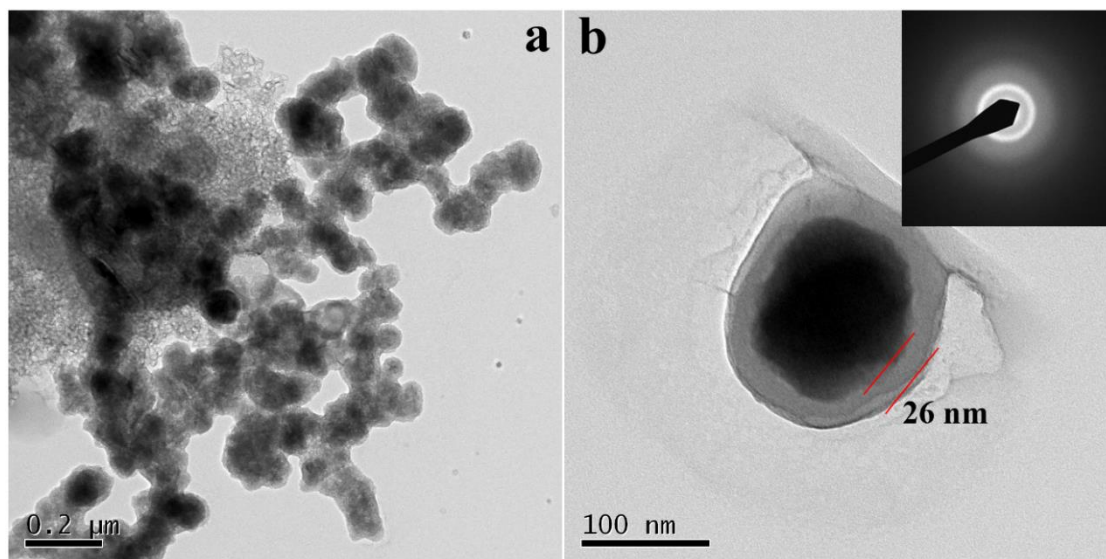


Figure 2-25. TEM images of the nanoparticles obtained by laser ablation at 0.25 mM CATB solution. The inset is the SAED pattern of image b).

Figure 2-26 shows the PL properties of nanoparticles obtained at by laser ablation at 0.25 mM CATB solution. However, we found the the PL intensity is quite low, even at the same level with the background of the measuring signals, indicating the YVO₄ crystal phase were not formed in CTAB solution. This result was consistent with the HR-TEM and SAED observations. In other words, we deduced that the cationic surfactant was pessimistic for the formation of YVO₄ based nanoparticles.

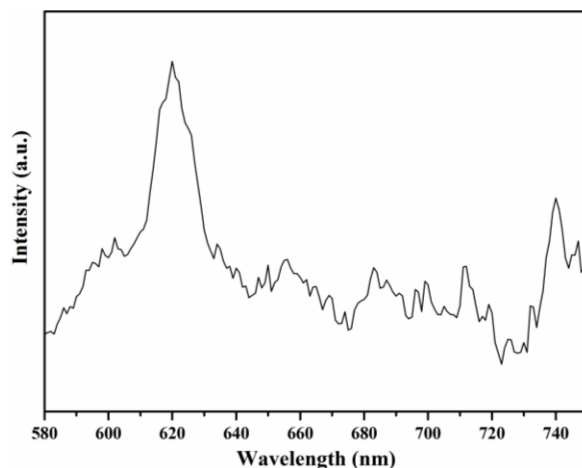
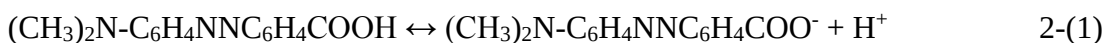


Figure 2-26. PL properties of nanoparticles obtained at by laser ablation at 0.25 mM CATB solution.

The adsorption mechanism are explained as follows. Figure 2-27 shows that the ζ -potential of the nanoparticles obtained in DI water is -38 mV, indicating the nanoparticles were negatively charged and very stable against aggregation. When enough cationic CTAB was added, CTA^+ rapidly attaches on the surface of the formed nano-crystallines, and hence, it neutralized the particle charge. When number the CAT^+ ions equaled the number of negative charge sites on nanoprticles surfaces, the nanoparticle would be completely neutralized. Therefore, the particles began to aggregate in water. In this case, the ζ -potential of the nanoparticles would be near zero. This would be the reason that aggregation occurred when we use 0.25 mM CTAB. H. Muto et al [29] reported the similar phenomenon in Au nanoparticles by laser ablation in CTAB solution.

On the contrary, SDS dissociating into Na^+ and $\text{C}_{12}\text{H}_{25}\text{OSO}_4^-$ in water modified the nanoparticles in a different manner. H. Muto et al [29] reported that the ζ -potential of the negatively charged nanoparticles in various SDS solution stayed almost unchanged. Then, the question was “Why the negatively charged nanoparticle can be modified by the anionic surfactant”. Ahmadi et al [30] reported the dissociation of methyl red in various SDS solution:



They described that negative DS^- could weaken the dissociation rate of methyl red: the above equilibrium shifted to the left side especially above the cmc of SDS. Therefore, it was very likely that the DS^- ions were able to cover the $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles after the surface charge had been neutralized in the SDS solution.

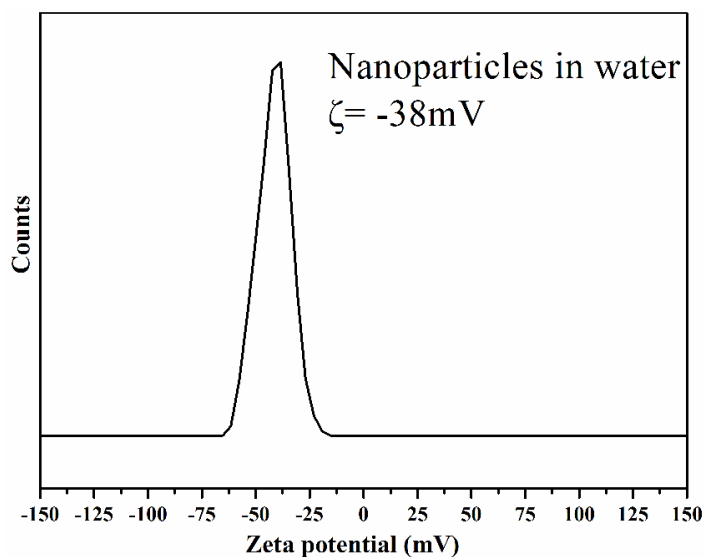


Figure 2-27. ζ -potential of the nanoparticles obtained in DI water.

2.4 Conclusions

In this chapter, $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles were successfully synthesized by LAL. According to the experimental results, the conclusions were summarized as follows:

- I. The laser fluence was altered to investigate its effect on morphology and particle size. The particle size in 1.7 J/cm^2 was around 94 nm, and it increased to around 108 nm when increasing laser fluence to 3.2 and 8.9 J/cm^2 . The morphology of as-obtained nanoparticles showed the ovoid shape. However, the ovoid-like nanoparticles aggregated at 8.9 J/cm^2 .
- II. The $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles with pure phase were fabricated by LAL in DI water, proved by XRD, and the ovoid-like nanoparticles were poly-crystalline which consisted of many primary nano-crystallines, proved by XRD and HR-TME analysis.
- III. EDS area-mode and point-mode were used to characterize the elemental composition, The results showed that the concentration of Eu^{3+} ions in nanoparticles was consistent with that of the raw particles.
- IV. The nanoparticle formation mechanism could be ascribed to “oriented attachment”, in which the overall energy in one nanoparticle could be reduced by the combination of primary nanoparticles at a crystal plane with high-surface energy.
- V. The productivity was studied in this study. When increasing laser fluence, ablation time, the weight of as-obtained nanoparticles was increased. The turbidity of the colloid could influence the productivity of producing nanoparticles.
- VI. The nearly spherical nanoparticles was formed in SDS solution. The as-obtained nanoparticle size was around 54 nm, which was clearly reduced compared to that obtained in DI water. The crystal structure of nanoparticle was confirmed by HR-TEM, and the particle formation mechanism was proposed.

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Chapter 3. Effect of Ethanol on $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles Formation by Laser Ablation in Liquid

3.1 Introduction

The basic process and mechanism of laser ablation in liquid (LAL) were introduced in chapter 1 and chapter 2. Controlling the morphology and size of nanoparticles is still a challenge by LAL up to date. As described in above chapters, experimental parameters having effects on the final fabricated products can be divided two categories: laser parameters such as wavelength, duration, fluence and material parameters such as bulk target, liquid medium, system temperature and pressure [1]. Among the above mentioned parameters, a liquid medium is very important in controlling the particle morphology, structure and size. Z. Yan [2] et al. reported the ZnO_x hollow nanoparticles by LAL of a bulk Zinc in ethanol. D. Werner [3] et al. reported that the smaller particle size distribution of silver was achieved in some alcohols by laser ablation, and also the liquid media had effect on the nanoparticles stability and yield. S. Yang [4] et al. reported the $\text{W}_2\text{C}@\text{C}$ core-shell nanoparticles by LAL of a bulk Tungsten in ethanol. Therefore, it is quite necessary to investigate the effect of the liquid medium as it had aroused substantial changes on the final products [5-7].

Chapter 2 introduced the traditional laser ablation in water based solution. In this chapter, we extended the research by investigating the effects of changing the liquid media. Herein, the water-ethanol mixtures worked as the liquid media, and the properties of as-obtained $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles were characterized. Interestingly, it was found that the morphology of as-obtained nanoparticles could be adjusted by changing the ethanol volume fraction. The possible particle formation mechanism was also discussed. It was the first time to investigate effect of the liquid medium on the $\text{YVO}_4\text{:Eu}^{3+}$ particle formation by LAL.

3.2 Experimental

The same laser set-up as chapter 2 was used. Herein, the DI water was replaced by water-ethanol. The nanoparticles obtained in various water-ethanol mixtures with ethanol volume fraction of 0%, 10%, 30%, 50% and 100% were named as 0%E, 10%E, 30%E, 50%E and 100%E respectively. After laser ablation, 3 ml supernatant was collected for various characterizations. After that, one drop of the supernatant was dropped onto the copper grid.

The characterizations used in this chapter was same with that described in chapter 2.

3.3 Results and discussion

3.3.1 Morphology of as-obtained nanoparticles

Figure 3-1 shows SEM results of the effect of ethanol contents on particle morphology fabricated by LAL. One can see that the ethanol addition in liquid medium clearly altered the particle morphology. The nanoparticles fabricated in DI water exhibited an ovoid-like shape. However, the as-obtained products from 10%E, 30%E, and 50%E contain both spherical and ovoid-like nanoparticles. When only using pure ethanol as working liquid medium (100%E), the obtained nanoparticles clearly presented the sphere shape. Furthermore, one can see that the particles obtained in water-ethanol mixtures (10%E, 20%E and 50%E) aggregated easily, whereas the particles obtained in DI water (0%E) and ethanol (100%E) were more clear and non-aggregated.

In addition, the sizes information of nanoparticles obtained from DI water, ethanol and SDS solution were also compared. Figure 3-2 shows the box plot distribution of particle size in water, ethanol and SDS by directly counting a number of particles in SEM images. The mean size of obtained from sample 0%E and 100%E are 97.6, 89.6 and 50.6 nm, respectively. The particle size obtained in ethanol in 25% — 75% of the specimen statistics was much broader than that obtained in water and SDS solution.

In this research, an important point was the formation mechanism of sphere morphology and the crystallinity of the nanoparticles. The morphology changes in Figure 3-1 were believed to be resulted from chemical and physical properties of the liquid media. Besides the obvious changes of liquid properties, one should keep in mind that ethanol molecules could have acted as a surface modifier and passivate forming nanoparticles [8]. When the DI water was used as the liquid medium, the obtained ovoid-like particles could be explained by the mechanism of “oriented attachment” process, as described in chapter 2. The passivation of ethanol molecules on nanoparticle surface could affect the preferred growth of $\text{YVO}_4\text{:Eu}^{3+}$ primary nanocrystals. Therefore, the resulting particle morphology should be ascribed to the competition between growth rate of primary nanocrystals and surface passivate speed of ethanol molecules. Finally, the sphere shaped nanoparticles were fabricated to maintain the minimum energy of the system. As shown in SEM images, the particle morphology had an obvious dependency upon the ethanol content since higher ethanol content could lead to the higher passivate speed and larger molecule amount on particle surface, at last inducing the sphere shape in 100%E.

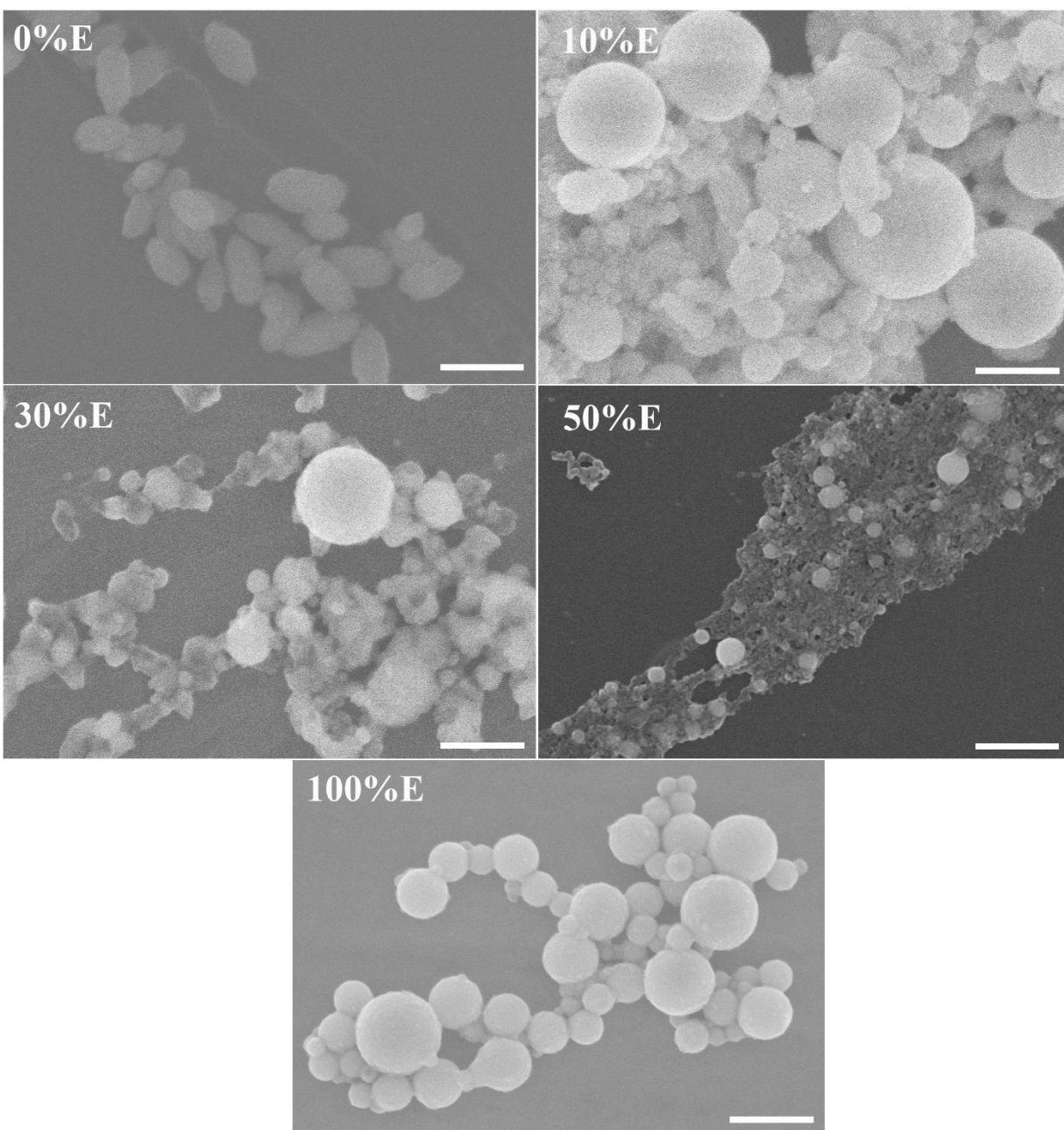


Figure 3-1. SEM images of nanoparticles fabricated by laser ablation in various water-ethanol mixtures. Scale bar in all images denotes 200 nm.

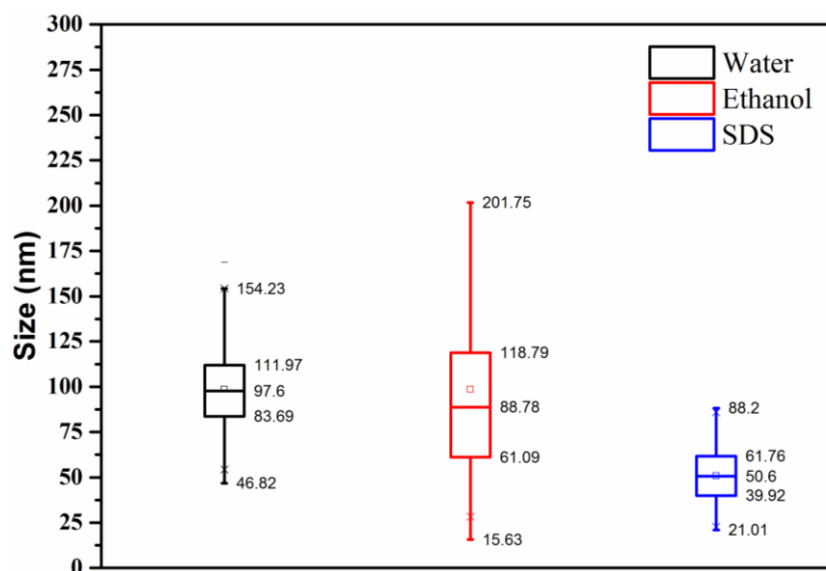


Figure 3-2. The box plot distribution of particle size fabricated in DI water (0%E), ethanol (100%E) and SDS solution.

3.3.2 Crystallinity of as-obtained nanoparticles

The HR-TEM analysis was used to investigate the effect of the ethanol content of liquid medium on the particle crystallinity. In chapter 2, the crystallinity of ovoid-like nanoparticles obtained in DI water was analyzed. The XRD and HR-TEM results showed that the ovoid-like nanoparticles had tetragonal YVO_4 phase, and one single particle was composed of many primary nanocrystals. Herein, TEM image of nanoparticles fabricated in 100%E was presented in Figure 3-3. The result indicated that the spherical nanoparticles were polycrystalline since several differently oriented crystalline lattices were distinguished in one sphere particle. More clear images and fast Fourier transformation (FFT) results (Figure 3-3c-d)) showed that the lattice fringes were consistent with the (301), $(\bar{1}23)$, (112) and $(2\bar{1}\bar{1})$ of zircon phase of YVO_4 (PDF No.17-0341), and the direction between the fringes can be matched each other (zone axis $[\bar{1}, \bar{5}, 3]$). FFT pattern showed the detailed indices of the crystal plane. However, we found that not all particles are crystals after performing the same characterization on randomly selected nanoparticles, the result was shown in Figure 3-3e). Some particles did not show lattice fringes and diffraction pattern (Figure 3-3f)), indicating the amorphous phases. In Figure 3-3a), the red arrow marked nanoparticles showed the clear lattice fringe and we found that almost 50% of nanoparticles crystallized into a sphere by observing several TEM images for a number of particles.

More TEM and selected area electron diffraction (SAED) results were presented in Figure 3-4. One can see that particle 1 was polycrystalline while particle 2 showed amorphous pattern.

Figure 3-5 showed the TEM and SAED patterns of the nanoparticles obtained in sample 10%E. Figure 3-5b) showed SAED pattern of red circle in Figure 3-5a), indicating the crystallinity of as-obtained nanoparticles. In sample 10%E, we found that all the ovoid-like nanoparticles were amorphous phase as far as we observed in several HR-TEM images as indicated by halo rings (Figure 3-5d)), and in this case the spherical nanoparticles are easier crystallized than the ovoid-like nanoparticles. However, not all the spherical particles were crystals, which was similar to that obtained in 100%E.

Furthermore, the crystallinity rate of as-obtained nanoparticles in DI water is the highest as reported in chapter 2. Approximately 50% of nanoparticles obtained in pure ethanol crystallized, whereas crystallinity rate of nanoparticles obtained in water-ethanol mixtures is the lowest according to our observation through SAED results of many particles. We attempted to correlate these results with various physical properties of the solvents, such as viscosity, density, thermal diffusivity, and so on. Qualitatively, we found an interesting relationship to some extent only for liquid viscosities. As is well-known, the viscosity of DI water is 1.002 mPa·s, which increase to 2.705 mPa·s when ethanol content is 70 vol. % in water-ethanol mixture [9]. However, the viscosity decreased clearly when ethanol content continually increasing and at last to be 1.187 mPa·s (100 vol. %) [9]. As described the crystallinity rate of obtained nanoparticles in DI water is quite high and it decreases obviously when increasing the content of ethanol, and finally the crystallinity rate of nanoparticles obtained in pure ethanol increases, proved from SAED and HR-TEM result for a number of particles. This variation would have relationships with the liquid viscosity. Furthermore, the liquid viscosity also would influence the aggregation of nanoparticles, as the nanoparticles obtained in water-ethanol mixtures are more easily aggregated than the nanoparticles obtained in DI water and pure ethanol. The amorphous phase of the nanoparticles of the $\text{YVO}_4\text{:Eu}^{3+}$ could be due to the rapid quenching in water-ethanol [10]. Many oxide compounds form amorphous phases under cooling rates as fast as 10K/s in air, and laser process in liquid media might provide an even greater heat exchange environment to preserve such metastable phases [10]. As described above, the liquid viscosity showed some relationships with the particle crystallinity. However, to the best of our knowledge, the mechanism of particle formation by LAL is not fully understood yet [11]. For example, various liquid viscosities and densities can influence the

expansion of the cavitation bubble; thermal conductivity of the liquid could have an effect on the decay process of the pressure and temperature of the cavitation bubble; the liquid transparency also has effect the peak value of the pressure and temperature of the cavitation bubble [12]. All these parameters may together influence the nucleation and growth process of the nanoparticles.

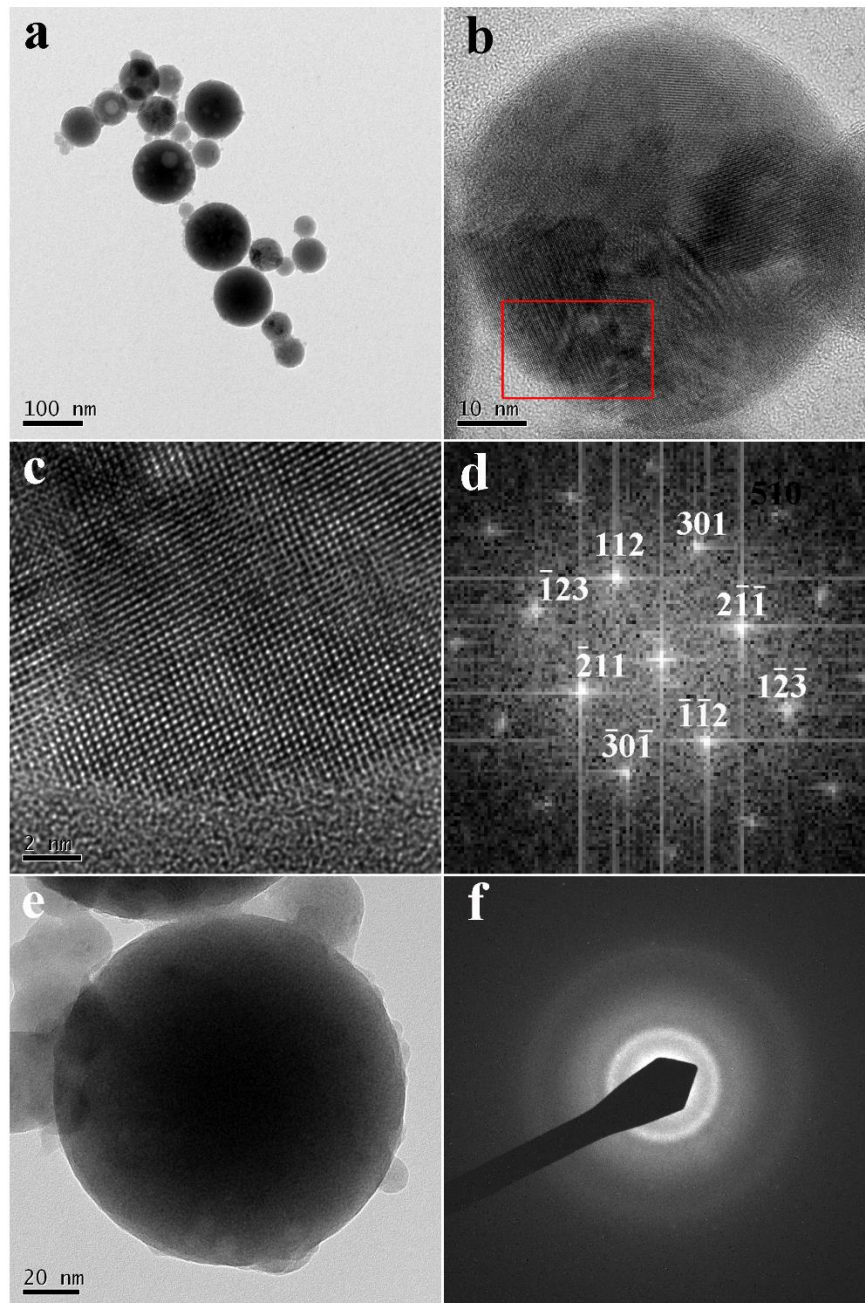


Figure 3-3. TEM analysis of nanoparticles fabricated in sample 100%E. a) TEM image, b-c) HR-TEM images and d) FFT result of image c). e) HR-TEM image and f) corresponding SAED pattern.

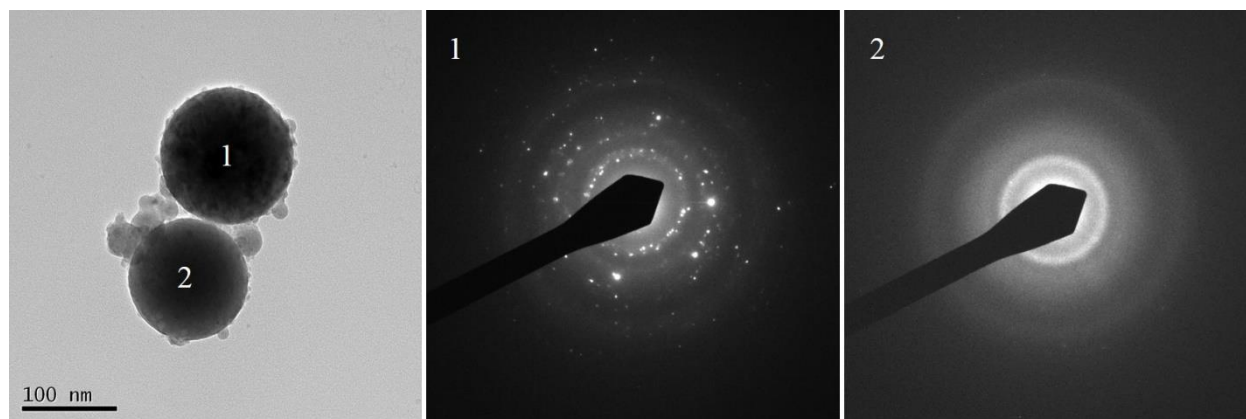


Figure 3-4. TEM image and corresponding SAED pattern of the nanoparticles in sample 100%.

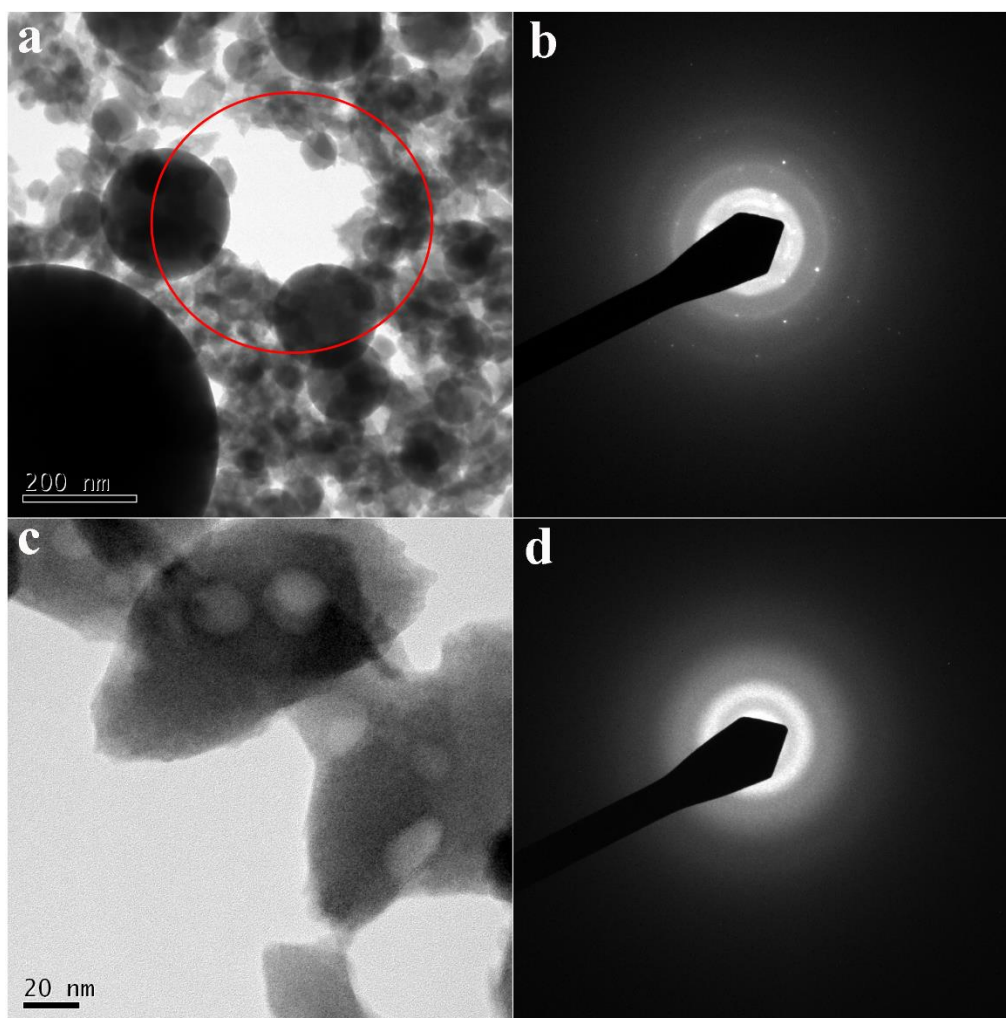


Figure 3-5. TEM analysis of nanoparticles in sample 10%E. a) TEM image, b) SAED pattern of the area marked by red circle in a), c) HR-TEM image and d) SAED pattern of c).

3.3.3 Optical properties of as-obtained nanoparticles

PL spectra were measured for the nanoparticles obtained in water-ethanol mixtures as displayed in Figure 3-6. The excitation wavelength was 280 nm. The results showed that all the spectra presented the typical PL properties of $\text{YVO}_4:\text{Eu}^{3+}$ phosphor. The spectra were clearly dominated by 619 nm emission of Eu^{3+} . Peaks in the emission spectrum ranging from 580 to 720 nm were associated with the transitions from the excited level of 5D_0 to the levels of 7F_J ($J = 1, 2, 3$, and 4) of Eu^{3+} [13]. This results indicated that $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles were successfully obtained by LAL in water-ethanol mixtures. In Figure 3-6, one can see that the PL intensity of sample 0%E was much stronger than that of the other samples. The strongest PL intensity was ascribed to the better crystallinity of ovoid-like nanoparticles obtained in DI water.

Figure 3-7 showed the UV-vis absorption spectra of as-obtained nanoparticles. All the samples exhibited broad an asymmetrical absorption band between 250 and 300 nm. The absorption band between 250 and 300 nm of all samples in UV-vis spectra were due to the charge transfer from oxygen ligands to central vanadium atoms inside the VO_4^{3+} complexes. Clear absorption peak valley in sample 0%E and 100%E were observed compared with other samples. In addition, it is noted that the blue-shift of UV-vis spectra of sample 100%E indicated by the peak value could be caused by the decreased covalence of V-O bonds [14], owing to the existing amorphous phase in 100%E. The weak absorptions of nanoparticles in sample 10%E, 30%E and 50%E indicated the absence of YVO_4 crystals, which was consistent with the TEM results.

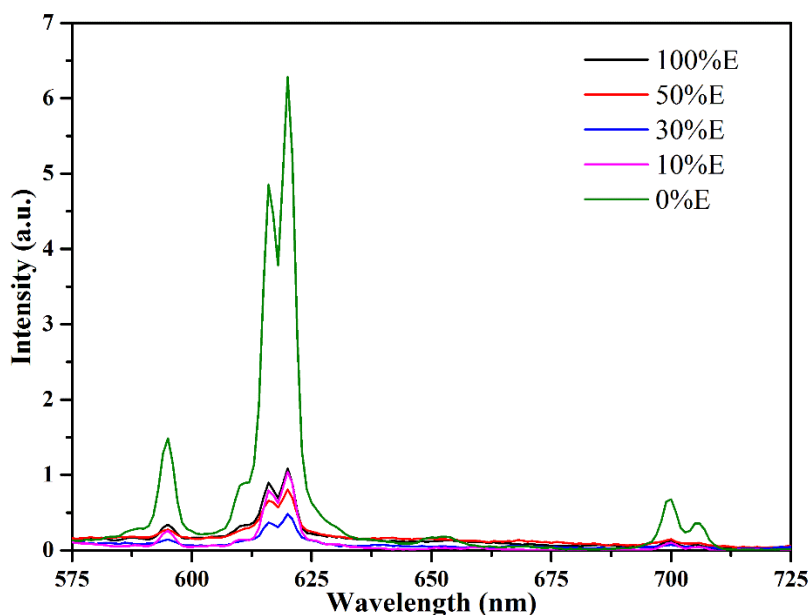


Figure 3-6. PL (Ex = 280nm) of nanoparticles fabricated in water-ethanol mixtures.

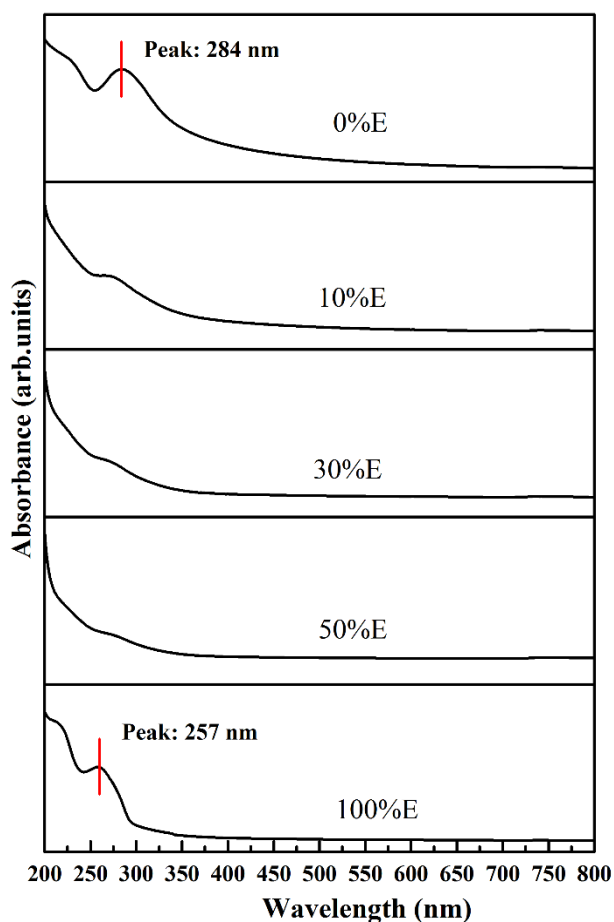


Figure 3-7. Absorption spectra of nanoparticles fabricated in water-ethanol mixtures.

3.4 Conclusions

In this chapter, we demonstrated that the $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles were fabricated by laser ablation in water-ethanol mixtures with ethanol volume contents of 0%, 10%, 30%, 50% and 100%. According to the experimental results, the conclusions were summarized as follows:

- I. The sphere- and ovoid-shaped nanoparticles simultaneously formed in water-ethanol mixtures, and only spherical nanoparticles was obtained in pure ethanol. The size distribution of nanoparticles obtained in pure ethanol was broader than that of the result in DI water.
- II. The liquid medium had effects on the crystallinity rate of the obtained nanoparticles. The crystallinity rate of the nanoparticles obtained in DI water is the highest, and decreased in the nanoparticles obtained in pure ethanol. The nanoparticles obtained in water-ethanol

mixtures (10%, 30%, 50%) had the lowest crystallinities, proved by the HR-TEM and SAED results of counting a number of nanoparticles.

- III. The blue-shift of UV-vis spectra of sample 100%E indicated by the peak value could be caused by the decreased covalence of V-O bonds.
- IV. The differences in crystallinity and morphology of as-obtained nanoparticles might relate to the passivation of the ethanol molecules and the properties of the liquid. More mechanism need deeper studies.

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Chapter 4. Effect of Sequential Laser Irradiation on $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles Formation by Laser Ablation in Liquid

4.1 Introduction

In chapter 2 and 3, the conventional set-up for laser ablation was presented: a slice of moulding target or metal material was put at the bottom of a beaker. The beaker was covered with some liquid media. Then target surface was ablated by the focused laser beam, as shown in Figure 2-2. The nanoparticles ablated from the target surface could be collected in liquid.

P. Wagener [1] et al. put forward an approach, which described that the suspension with micron-particles inside flow downside to the collecting bottle from a free liquid reactor, and the liquid filament was irradiated by the laser beam during the flowing. The liquid filament used was very narrow. LAL and PLML processes occurred depending on the used laser fluence. In comparison to the PLML, the fluence gradients along the laser beam would be effectively decreased due to the short laser path length in narrow liquid filament. The detailed experiment setup was depicted in Figure 4-1. M. Lau [2, 3] et al. developed this technique to fabricate the zinc oxide. The result showed that the particle size decreased with an irregular morphology after the laser irradiation.

Chapter 2 showed that the ovoid-like $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles were successfully synthesized by LAL. However, the collected nanoparticles were dispersed in the surrounding liquid, and most of the nanoparticles could not be captured for irradiation. In order to investigate the effect of the laser irradiation on the nanoparticles, a free liquid reactor was used, in which a liquid filament could be formed, and flowed from upper side. Therefore, all the nanoparticles could be irradiated again, owing to the narrow liquid filament and high repetition rate of the applied laser. N. Koshizaki [4-6] et al. proposed pulsed laser melting in liquid (PLML) to fabricate sub-micron particles from nanoparticles by laser irradiation at low fluence. As detailed described in chapter 1. However, this experiment was different from the PLML, since the high laser fluence was applied, and laser ablation occurred. The result was found that as-obtained nanoparticles had spindle shape from growth of smaller ovoid-like nanoparticles when increasing the irradiation cycles. Furthermore, well-defined, $\text{YVO}_4\text{:Eu}^{3+}$ single-crystalline was fabricated here in DI water without any ligands by this special and novel technique, and a proposed mechanism of the particle formation will be discussed.

4.2 Experimental

4.2.1 Laser setup

Commercial $\text{YVO}_4\text{:Eu}^{3+}$ particles with micron-scale were dispersed in water with a concentration of 0.1 wt%. Then, the suspension was moved into a free liquid reactor with a 1.3-mm capillary. A liquid filament was formed during the flowing. The suspension flowed downside into the collection beaker from the reactor. At the same time, the liquid filament was irradiated during the flowing. The same procedure was repeated for twelve times. After that, the suspension was collected after one, three, five, eight, and twelve irradiation cycles, which were labeled as 1-cycle, 3-cycles, 5-cycles, 8-cycles and 12-cycles, respectively. To determine the laser power, a power meter was put at same horizontal space level with the laser beam behind the liquid filament. Figure 4-1 shows the experimental setup. A Nd:YAG laser was utilized as the laser source, providing a 40-ns pulse at 355 nm wavelength and a 85 kHz repetition rate. The laser fluence was changed by tuning the distance between the liquid filament and the lens. Laser fluence of $60 \text{ mJ/cm}^2\cdot\text{pulse}$ was used after the optimization. Suspensions obtained after irradiation at 60 mJ/cm^2 for various cycles were collected for various characterization. Effect of the laser fluence was not emphasized because the particle properties were very similar when the laser fluence increased to 140 mJ/cm^2 . However, nanoparticles were not obtained when the fluence is below $30 \text{ mJ/cm}^2\cdot\text{pulse}$, which might be too low to produce $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles (below threshold).

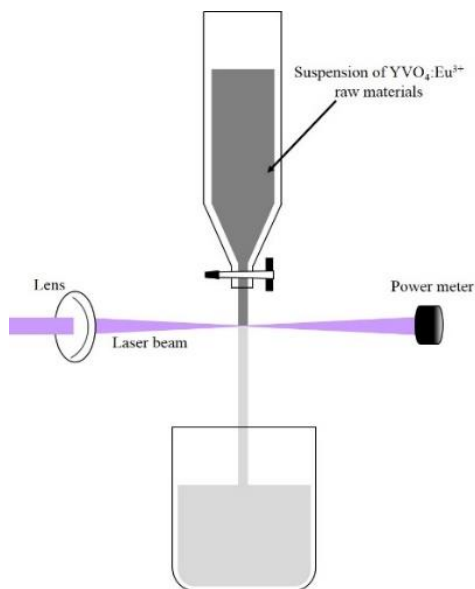


Figure 4-1. Reactor for the production of $\text{YVO}_4\text{:Eu}^{3+}$ nanostructures by laser irradiation of a sequential flowing aqueous suspension. A 1.3 mm capillary is provided at the bottom of the reservoir to form a liquid filament and the suspension flowed downstream into the container after pulsed laser irradiation.

4.2.2 Characterization

In addition to the characterization used in chapter 2, this chapter utilized the cathodoluminescence (CL) combined with TEM (JEM-2100F) to characterize the luminescent properties of one single nanoparticles.

4.3 Results and discussion

4.3.1 Morphology of as-obtained nanoparticles

Figure 4-2 shows the SEM results and the corresponding size distributions of the target particles and nanoparticles. The target particles had irregular shape with micron-size and smooth surfaces. After laser irradiation for one cycle, the particle size decreased to less than 100 nm as shown in SEM result (1-cycle). In sample 1-cycle, only target particles and the nanoparticles less than 100 nm were observed. In sample 3-cycles, the larger nanoparticles were observed. In sample 12-cycles, the spindle-shaped particles longer than 600 nm appeared. In addition, ablation craters could clearly be observed after laser irradiation (Figure 4-3). One can see that particles grew up along the long-axis of ovoid-like nanoparticles regularly, and finally form into a spindle-shaped particle. Size distributions of as-obtained nanoparticles were described by counting the numbers of particles in SEM images for better understanding the growth behaviors of YVO_4 based nanoparticles. Log-normal functions were used to fit the size histograms of different samples, and obtained corresponding fitting results were shown in Figure 4-2. Sample 1-cycle showed a narrow size distribution, and the median diameter was around 42.4 nm. This result was quite similar with in sample 3-cycles. Moreover, the larger ovoid-like nanoparticles (≥ 200 nm) were obtained in sample 3-cycles in contrast with that in sample 1-cycle. The particle size increased when increasing the irradiation cycle number, and also the size distribution became broader. Start from sample 5-cycles, log-normal function fitting with mode of bimodal peaks matched better than the single peak. Note that we found that spindle-like nanoparticles with sizes bigger than 600 nm and smaller than 100 nm simultaneously existed in 12-cycles product. This indicated that small nanoparticles were still fabricated after more cycles of laser irradiation, as indicated in Figure 4-2 (the left tails of the log-normal fitting).

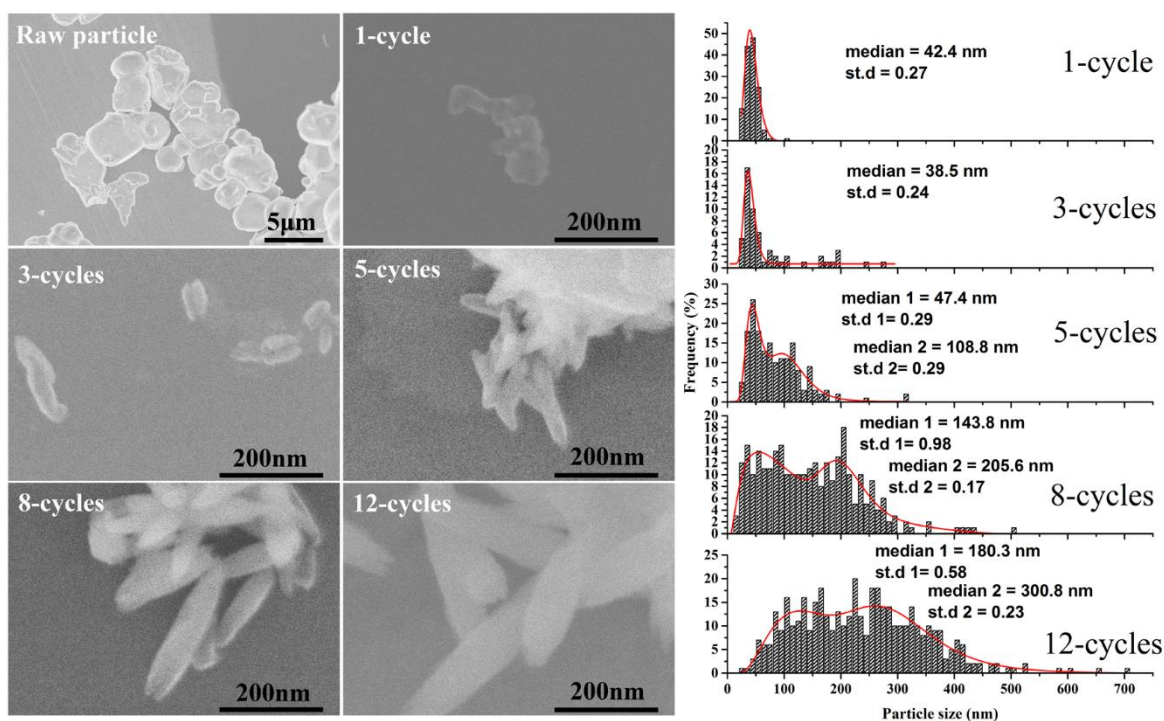


Figure 4-2. SEM images of YVO₄:Eu³⁺ raw particles and nanoparticles obtained in different cycles of laser irradiation and the corresponding size distribution. [7]

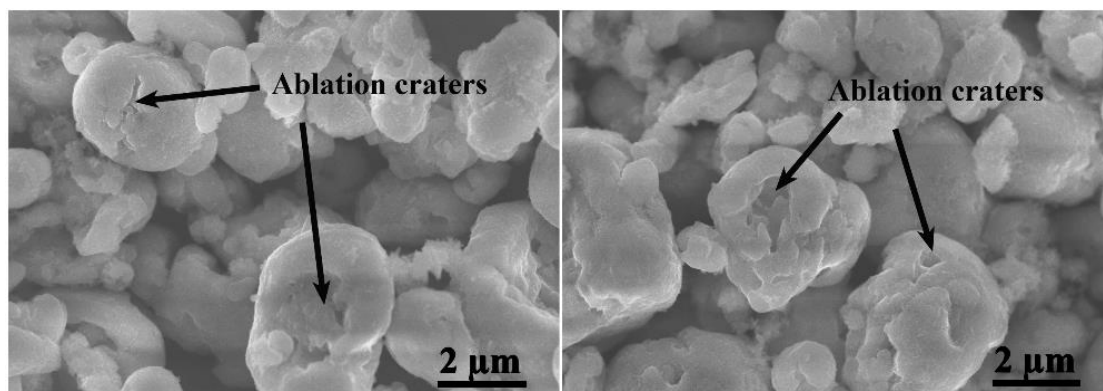


Figure 4-3. The ablation craters after laser irradiation captured in sample 12-cycles. [7]

4.3.2 Crystallinity of as-obtained nanoparticles

The color of the colloid changed from milky white to gray as the laser irradiation progressed for several cycles in sequential flowing reactor, indicating that the particle size was changed after laser irradiation. The phases of the raw particles and the products after 1, 5 and 12 cycles of laser irradiation were characterized by XRD (Figure 4-4). It could be seen that the

diffraction peaks of sample 1-, 5- and 12-cycles agreed with the tetragonal structure of YVO_4 having cell parameters $a = b = 0.7119 \text{ nm}$, and $c = 0.6289 \text{ nm}$. The result also indicated that no impure peaks were detected in the products after laser irradiation. Moreover, the phase information of one single nanoparticle was characterized by HR-TEM techniques because the XRD only detect the whole powders.

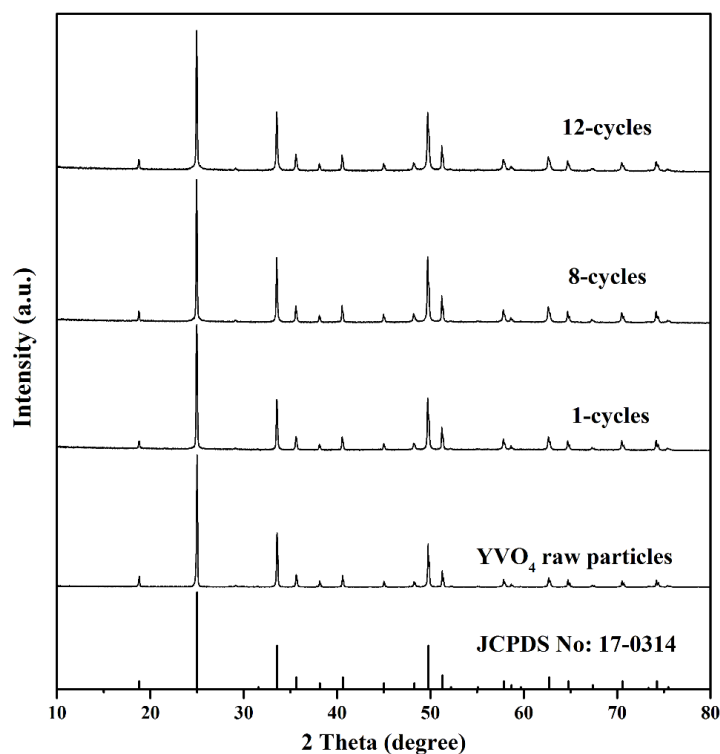


Figure 4-4. XRD patterns of $\text{YVO}_4:\text{Eu}^{3+}$ powders obtained after 1, 5, and 12 cycles of laser irradiation. [7]

Figure 4-5 presents the typical TEM results after laser irradiation for 8 cycles. The selected area electron diffraction pattern (SAED) in rectangular box part in Figure 4-5 indicated that the spindle-shaped nanoparticles were well-defined single-crystals with quite high crystallinity. This was quite important for luminescent materials because good crystallinity usually had strong luminescence. The nanoparticle grew up into longer one when increasing irradiation cycle number, as mentioned above. Interestingly, the spindle-like nanoparticles form into a flower-like structure (Figure 4-6) when the suspension was irradiated for 5-cycles or more. However, the particle formation mechanism was different from the “oriented attachment” described in chapter 2. When the $\text{YVO}_4:\text{Eu}^{3+}$ suspension was irradiated for several cycles, all the particles were irradiated for several times. Therefore, the obtained nanoparticles in the initial irradiation cycle would be

irradiated and heated again by the laser. The flower-like and bigger nanoparticles were obtained after merging with their neighboring particles. The broad size distribution would be caused by this process, as shown in Figure 4-2 (right side of the distribution tail). As a result, the growth process was expected to occur through atoms diffusion and coalescence. While the nanoparticles were irradiated by the laser, the kinetic energy of the atoms also increased, providing more energy to nanoparticles for colliding, merging, and growing [8]. As a result, the ovoid-like nanoparticles merged and grew into spindle- and flower-like nanoparticles. The generation of flower-shaped particles confirmed the growth mechanism which occurred through the atom diffusion and coalescence: because the spindle-like particles acted as the petals of the flower-like particles. Furthermore, the effect of colloid aging time was also considered, because the particles could also grow when increasing the aging time reported by some groups [9]. In our experiment, the aging time increased as the increase of irradiation cycle number, which might influence the particle growth. However, the particle size was very stable for two weeks, as we observed. This would be caused by the electric bilayer at the nanoparticle surface, resulting in the high stability of colloid. The electrostatic repulsive force between nanoparticles must be lower than the kinetic energy of the atoms provided by the laser for merging during diffusion and coalescence [8, 10]. Therefore, the aging time was not an influence factor for $\text{YVO}_4\text{:Eu}^{3+}$ growth in water. Finally, we concluded that the right-hand tail of the log-normal curves were due to the growth caused by diffusion and coalescence, whereas the left-hand side was due to the particle growth via “oriented attachment”, as depicted in Figure 4-2.

Figure 4-5c-d) display the HR-TEM and fast Fourier transformation (FFT) of the rectangle area marked in Figure 4-5a). The crystallinity properties of spindle-like nanoparticles were confirmed by the clear lattice fringes in HR-TEM image. FFT results showed that the lattice spacing was in good agreement with planes (112) and $(11\bar{2})$ of YVO_4 tetragonal structure, indicating the zone axis of electron incidence was $[\bar{1}10]$. The detailed indices of the crystal plane were displayed in FFT pattern. The measured angle (116°) between planes $(11\bar{2})$ and (112) was consistent with the theoretical value. As a result, we deduced that the long axis of the spindle-like nanoparticles was aligned along [001] direction. Figure 4-5 e-f) shows the structure of another particle. The lattice spacing corresponds to (200) and (101) planes (Figure 4-5e) respectively, and the 49° angle between (200) and (101) planes was also consistent with the FFT result (Figure 4-

5f), confirming the well-defined single-crystalline and tetragonal phase properties of the spindle-like nanoparticle, the preferential growth direction along the long axis was [001]. This result is consistent with other groups, who reported that the tetragonal YVO_4 had preferred orientation along [001] [11, 12].

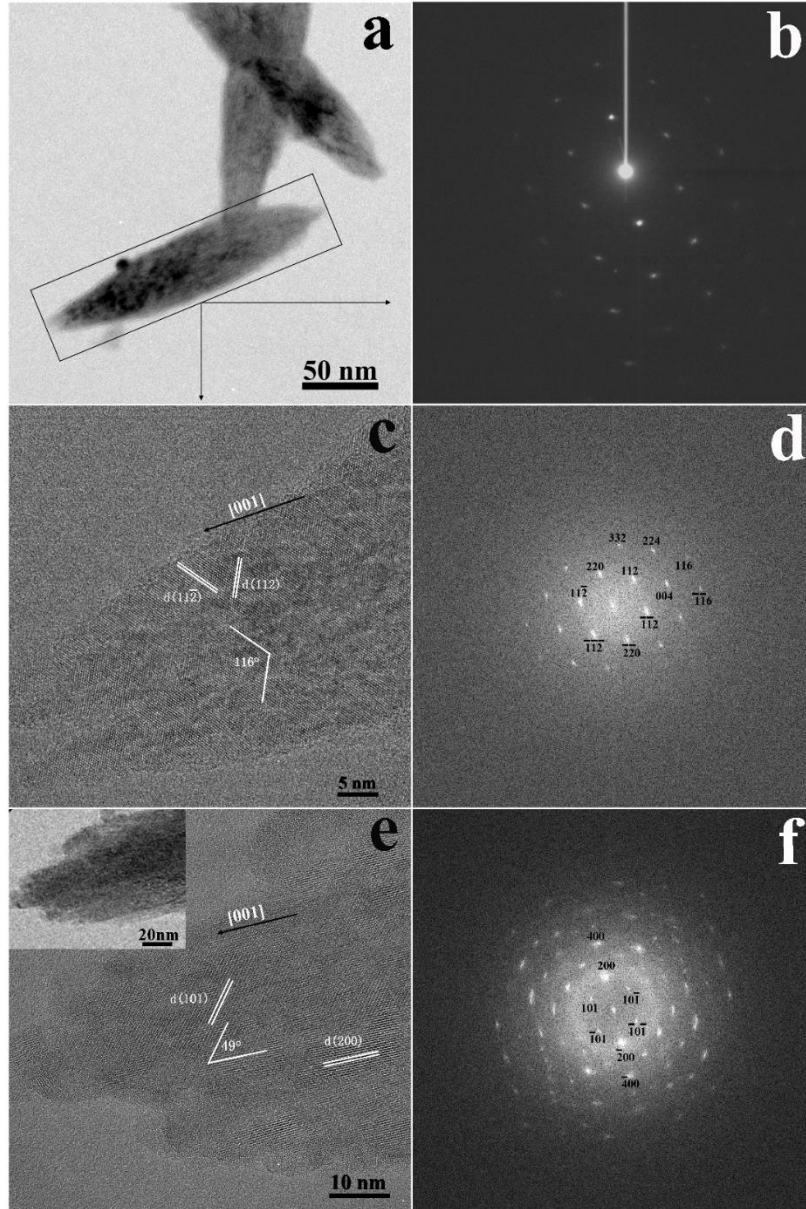


Figure 4-5. (a) TEM image and b) SAED of spindle-like $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles. (c) HR-TEM and d) FFT images of the part of the spindle-like particle indicated in rectangle box. (e) HR-TEM and f) FFT images of a different spindle-like $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticle. The inset of (e) is the corresponding TEM image with low resolution. [7]

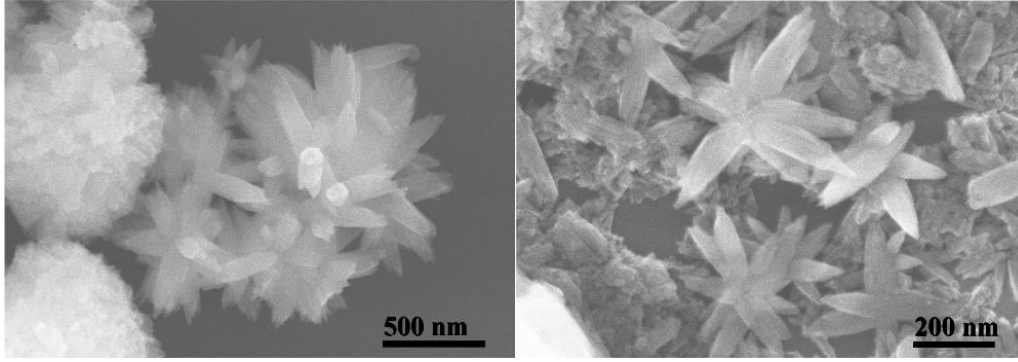


Figure 4-6. Flower-like nanoparticles after laser irradiation in sample L12. [7]

The elemental distribution was characterized by the elemental mapping as indicated in Figure 4-7. The result showed the uniform distribution of elements Y, V, O, and Eu. This result was confirmed that the formed nanostructures were enriched in the target elements, indicating that LAL was a feasible technique to synthesize dopant oxide nanoparticles.

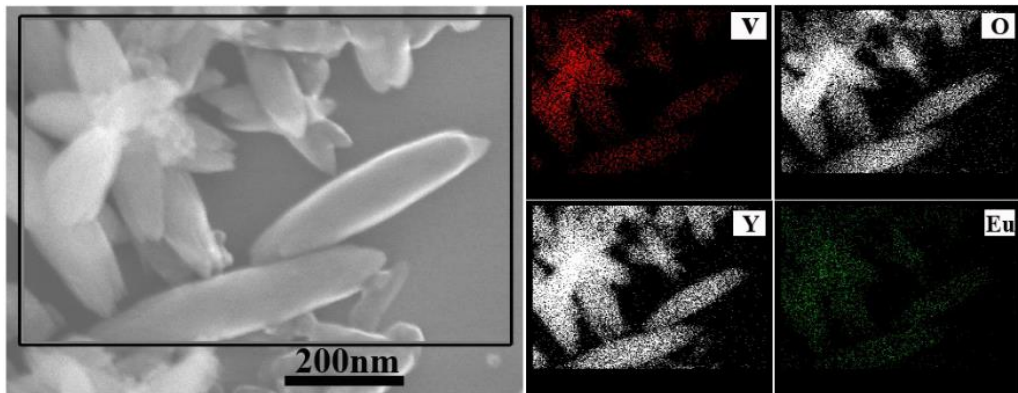


Figure 4-7. EDS elemental mapping of the area of sample L8 marked by the rectangle box of SEM image (left side). [7]

4.3.3 Optical properties of as-obtained nanoparticles

Figure 4-8 shows the optical properties of raw particles and the products after laser irradiation for eight cycles (excitation wavelength: 280 nm). The absorption in UV range was attributed to the charge transfer from oxygen to vanadium ions inside the VO_4^{3-} groups. The emission peaks marked in the figure corresponded to $^5\text{D}_0\text{-}^7\text{F}_J$ ($J = 1, 2, 3, 4$) transitions of the Eu^{3+} ions, respectively [13]. $^5\text{D}_0\text{-}^7\text{F}_2$ transition dominated the emission spectra owing to the absence of inversion center of YVO_4 structure (D_{2d} symmetry) [13]. The $^5\text{D}_0\text{-}^7\text{F}_2$ transition split into mainly

two components at 615 and 619 nm owing to the lowering of local site symmetry of Eu^{3+} ion [14]. The CL properties of the obtained particles were characterized to confirm the luminescent properties of one single nanoparticles as shown in Figure 4-8b. Identical CL curves were exhibited between the raw particles and obtained nanoparticles after laser irradiation, confirming the phase purity of $\text{YVO}_4:\text{Eu}^{3+}$ spindle-like nanoparticles. To get the uniformity of the luminescent signal, the emission mapping was also conducted for single nanoparticle. The various colors in nanoparticles illustrated different emission intensities. Overlapping area between the two nanoparticles exhibited the strongest emission portion (white color). The blue portion at the particle edge indicated the weakest emission. The emission differences were due to the different emission volumes in nanoparticles. The weakest emission portions were due to the dangling bonds surrounding Eu^{3+} ions at particle surface. From the mapping image, one can see the symmetrical emission color in one spindle-like nanoparticle, indicating the uniform distribution of the Eu^{3+} ions. This result was in good agreement with the elemental mapping results.

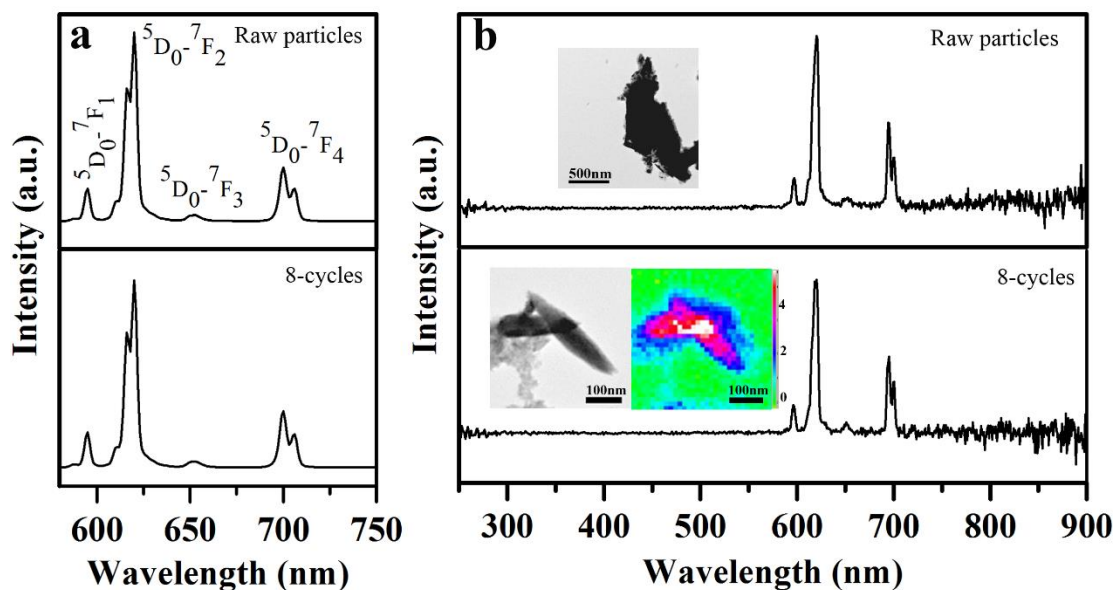


Figure 4-8. (a) PL (excitation at 280 nm) and b) CL emission spectra of $\text{YVO}_4:\text{Eu}^{3+}$ raw particles and particles after eight cycles of laser irradiation (L8). The insets of panel (b) are the TEM images of corresponding particles and emission mapping for CL measurement; acquisition wavelength: 620 nm; acceleration voltage of electron beam: 8 kV, current: 4 nA. [7]

4.3.4 Mechanism of nanoparticle formation

The nanoparticle formation and growth mechanism were explained as follows. A plasma plume was created at the solid surface when $\text{YVO}_4\text{:Eu}^{3+}$ raw particles were irradiated by first pulsed laser beam. The plasma plume was rapidly quenched by the surrounding liquid media. Then, the primary nanocrystals could be obtained after the quenching of the plasma plume. Subsequently, the cavitation bubble was formed and the primary nanocrystals were released into the cavitation bubble and grow up inside. “Oriented attachment” growth occurred inside the cavitation bubble which was well explained in chapter 2 [15]. In this experiment, “oriented attachment” mechanism was most likely to occur because the ovoid-like nanoparticles were composed of many primary nanocrystals and the existence of defects in nanoparticles, as described in chapter 2.

Moreover, the ovoid-like nanoparticles clearly grew up as the suspension was irradiated for several cycles by the pulsed laser. And the growth here was assigned to the overlapped cavitation bubble, which will be explained at the end of this chapter. The HR-TEM and SAED results confirmed the growth direction of [001].

The final morphology of as-obtained nanoparticles depends on the competitive growth of different crystallographic planes. YVO_4 has a tetragonal crystal structure with space group of $I4_1/amd$ [13], and it has the anisotropic growth characters since $a = b \neq c$ in tetragonal system. The plane (100) is more closely packed, thus, the growth of plane (100) is slower than the growth of plane (001) perpendicular to the growth direction. And surface energy of plane (001) is higher than plane (100) [12]. “Oriented attachment” mainly occurs on high surface energy planes in order to keep the final particles the low energy [15]. Therefore, the obtained primary crystals grow up through the combination of plane (001) and finally grow up along with the [001] direction. Finally, this process leads to more rapid growth along [001] direction, thereby forming nanorods [11]. The sharp tips on the side of nanorods lead to the spindle shape, and this might be resulted from the insufficient supplies of reactants due to the short growth periods. Furthermore, the TEM results confirmed the growth direction.

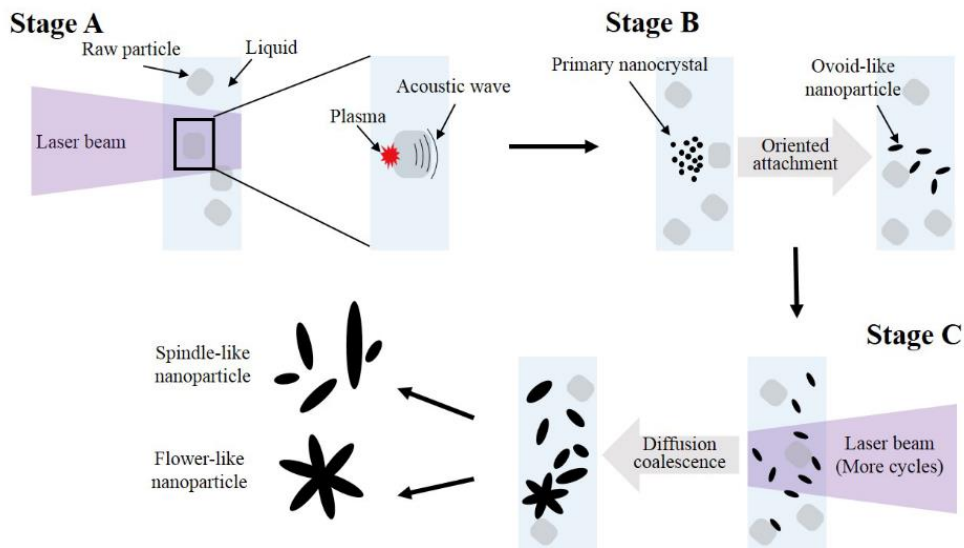


Figure 4-9. Schematic illustration of laser-induced formation and growth of $\text{YVO}_4:\text{Eu}^{3+}$ nanostructures.

Figure 4-9 illuminates the process of laser-induced particle formation and growth. Stage A describe that the primary nanocrystals were fabricated from plasma plume with high pressure, high temperature and high density when the surfaces of $\text{YVO}_4:\text{Eu}^{3+}$ raw particles were irradiated by the laser. Then, the primary nanocrystals grew into an ovoid-shaped nanoparticle through “oriented attachment”. In stage C, the ovoid-like nanoparticles grew into spindle-like single-crystalline and flower-like nanoparticles while the suspension was exposed to more cycles of laser irradiation. The particles grew up along [001] direction.

Figure 4-10 shows the ablation and growth process when the laser beam irradiated the nanoparticles. When the nanoparticles were irradiated by the laser, the nanoparticles could be ablated to the plasma. After the rapid cooling of the plasma and the energy exchange with the surrounding liquid, the cavitation bubbles were created surrounding the plasma. The primary nanocrystals were released into the cavitation bubble when the plasma totally disappeared. Importantly, every nanoparticle was captured and irradiated again in this case owing to the high repetition rate of applied lasers. Therefore, this would lead to many cavitation bubbles. When the neighboring nanoparticles were irradiated, their cavitation bubbles could overlap with each other. The primary nanocrystals would grow up through “oriented attachment” inside the overlapped cavitation bubble. Therefore, the longer spindle-like nanoparticles were expected grown from the overlapped cavitation bubble. When one side of spindle-like nanoparticle attached on one side of

the other nanoparticles, after the laser irradiation, these two nanoparticles would grow up into a flower-like particle.

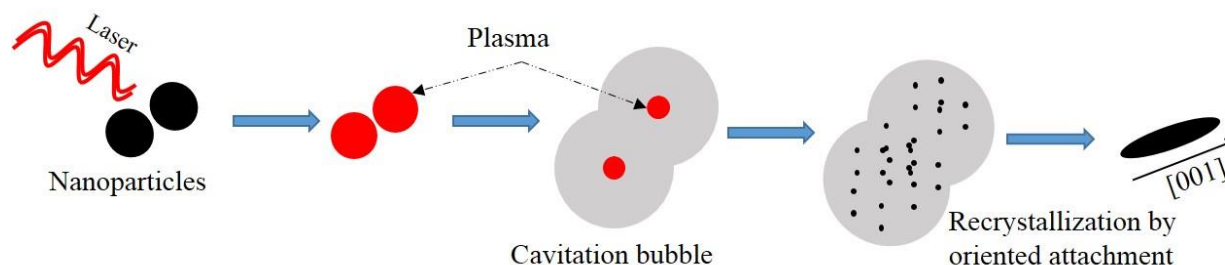


Figure 4-10. Schematic illustration nanoparticles' growth when the nanoparticles were irradiated by the laser beam.

4.4 Conclusions

In this chapter, a unique method to fabricate $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles by laser irradiation from a sequential flowing aqueous suspension in a free liquid reactor was put forward. Through this method, the obtained nanoparticles could be irradiated for several times by the pulsed laser beam, which was very different from, and also compensate for chapter 2.

- I. The spindle-like nanoparticles were formed from the ovoid-like nanoparticles after laser irradiation for several cycles. The size distribution became more wider when increasing laser irradiation cycle number.
- II. The spindle-like nanoparticles were single-crystalline confirmed by the XRD and HR-TEM results, which was very important for luminescence properties of the crystals. No impurities were detected and the CL results state the high luminescence intensity of one single nanoparticles.
- III. The particle formation mechanism were proposed: ovoid-like nanoparticles were formed from the primary nanocrystals via "oriented attachment". The ovoid-like nanoparticle grew up along the [001] direction to form spindle-like single-crystalline when the suspension was exposed to the laser beam for more cycles. Spindle- and flower-like nanoparticles were formed after laser irradiation to the neighboring nanoparticles owing to the overlapped cavitation bubble.

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Chapter 5. Dynamics of Cavitation Bubble in Nanoparticles Formation Induced by Laser Ablation in Liquid

The cavitation bubble generated during laser ablation in liquid is considered to be an important factor for nanoparticles fabrication. It is therefore quite necessary to observe the bubble dynamics throughout the entire process to better understand the role in nanoparticles growth. In this chapter, the imaging approach was utilized to conduct the real-space, time-resolved observation of YVO₄ nanoparticles generation by laser ablation in liquid. The pressure inside the cavitation bubble was estimated more than 100 bar using Rayleigh-Plesset equation, and the temperature could reach up to 1000 K using isentropic relation.

Chapter 6. General Conclusions and Perspectives

6.1 General conclusions

In this dissertation, $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles were fabricated by a facile and green physical method: laser ablation in liquid (LAL). $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles have potential applications in biological field such as toxins tracking by imaging and as sensors to detect redox molecules, which have been reported. The morphology, crystallinity, and optical properties of as-obtained nanoparticles were investigated. And the mechanism of the LAL was studied: the imaging system was used to capture the oscillation process of cavitation bubble. These results are summarized in this chapter as follows.

In chapter 2, the water based solvents were used as the working liquid media. First, the $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles were obtained in DI water at various fluences. The nanoparticles obtained at low fluences such as 1.7 J/cm^2 were uniformly dispersed in DI water. However, aggregations of nanoparticles occurred at high fluence of 8.9 J/cm^2 . SEM results confirmed that the nanoparticles had an ovoid shape. EDS studies showed that the content of Eu^{3+} ions was well kept after LAL. The emission ratio of $I_{615\text{nm}} / I_{619\text{nm}}$ and $I_{700\text{nm}} / I_{706\text{nm}}$ for nanoparticles were obviously changed, indicating the symmetry variations around europium ions. The formation of ovoid-shaped nanoparticles followed the “oriented attachment” growth mechanism. Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) solutions were used as the working liquid media to quench the particle size. The nanoparticles with mean size of 50 nm was obtained when using SDS solution, and also the morphology was changed from the ovoid-shape to nearly spherical shape. The effect of cationic CTAB was negative owing to the amorphous phase of the obtained nanoparticles.

In chapter 3, the water-ethanol mixtures were used as the working liquid media. The sphere- and ovoid-shaped nanoparticles simultaneously formed in water-ethanol mixtures, and only spherical nanoparticles were obtained in pure ethanol. The size distribution of nanoparticles obtained in pure ethanol was broader than that of the result in DI water. The crystallization rate of the nanoparticles obtained in DI water was the highest, and decreased in the nanoparticles obtained in pure ethanol. The nanoparticles obtained in water-ethanol mixtures (10%, 30%, 50%) had the lowest crystallization rate, proved by the HR-TEM and SAED results of counting a number of nanoparticles. The blue-shift of UV-vis spectra in nanoparticles obtained in pure ethanol could be caused by the decreased covalence of V-O bonds. The differences in crystallinity and morphology

of as-obtained nanoparticles might be related to the passivation of the ethanol molecules and the properties of the liquid.

In chapter 4, a free liquid reactor was used to fabricate $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles by laser irradiation from flowing suspension containing $\text{YVO}_4:\text{Eu}^{3+}$ micron-particles. Through this method, the obtained nanoparticles could be irradiated for many times by the pulsed laser beam, which was very different from chapter 2. The spindle-like nanoparticles were formed from the ovoid-like nanoparticles after several irradiation cycles. The size distribution became broader when increasing the laser irradiation cycle number. The spindle-like nanoparticles were single-crystalline confirmed by the XRD and HR-TEM results, which was very important for luminescence properties of the crystals. The particle formation mechanism was proposed: an ovoid-like nanoparticle was formed from the primary nanocrystals through “oriented attachment” growth mechanism. The ovoid-like nanoparticle grew up along the [001] direction to form spindle-like single-crystalline when the suspension was exposed to laser beam for several cycles. Spindle-nanoparticles were formed from the recrystallization of the primary nanoparticles formed in overlapped cavitation bubble after several laser irradiation cycles.

In chapter 5, the dynamics of cavitation bubble were studied using a videography through combining the pump laser, probe laser and high-speed camera. The results showed that the bubbles underwent several repeated expansions and shrinkages within a millisecond time range. The pressure and temperature were estimated using the Rayleigh-Plesset theory and isentropic relation, which showed that the pressure could reach up to 100 bar, and the temperature could reach up to 1000 K inside the cavitation bubble. These results also supported that the primary nanocrystals could grow up inside the cavitation bubbles.

Finally, the main results were graphically summarized as displayed in Figure 6-1. In chapter 2, the ovoid-like nanoparticles were fabricated after LAL followed the growth mechanism of “oriented attachment” of primary nanocrystals. When the experiment was performed in surfactant solution and ethanol, the particle morphologies were changed to nearly spheres and clear spheres. This change could be caused by the modification of the surfactant and ethanol molecules on the surface of the nanoparticles, which might hinder the growth of nanoparticles. More detailed studies need to be investigated in the future. In chapter 4, when the nanoparticles were irradiated by the laser, the nanoparticles grew up along [001] direction formed into spindle-like single-

crystalline, which was caused by the growth of primary nanocrystals inside the overlapped cavitation bubble around neighbored nanoparticles.

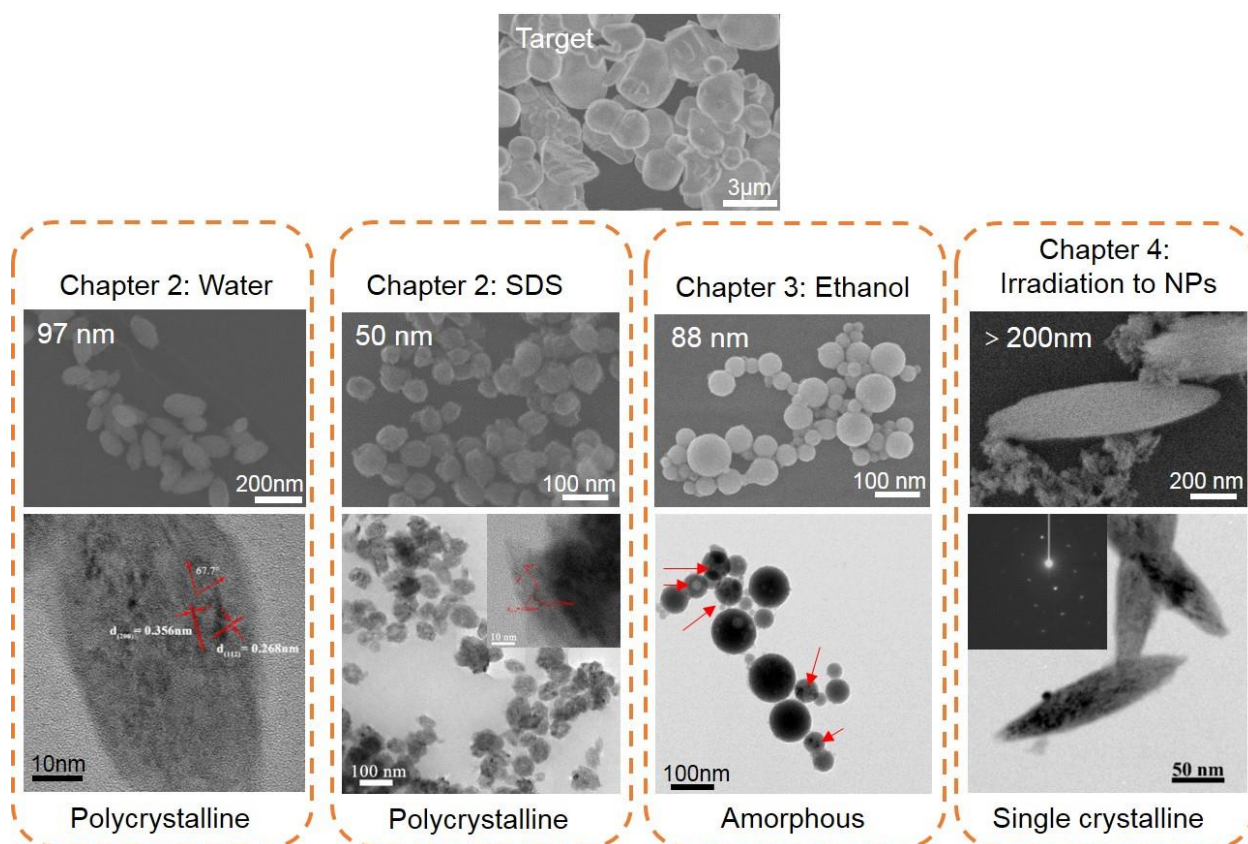


Figure 6-1. Morphologies, particle sizes and crystallinities of target and nanoparticles obtained in chapter 2, 3, and 4.

6.2 Perspectives

First, in this research, the uniform ovoid-like and spherical nanoparticles were created in water and ethanol, respectively. However, there are some amorphous phase existed when using ethanol as liquid medium. In the future, my next objective is to fabricate the nanoparticles with different sizes and morphologies of YVO_4 based nanoparticles with pure phase and clean surface. The nanosecond laser (Nd:YAG) was used in this research. The femtosecond laser will be used because of its ultra-short duration leading to the different laser ablation mechanism. If possible, the $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles will be applied in biological applications.

Appendix data 1

In chapter 2, the Nd:YAG laser with wavelength of 532 nm, repetition rate of 10 Hz, and pulse width of 13 ns was used to ablate a $\text{YVO}_4\text{:Eu}^{3+}$ target in pure DI water. And the ovoid-like nanoparticles were obtained. Besides the experimental data shown in the main body of thesis, here I gave some result obtained at different laser parameters to support the research. Since no changes was observed, these data were not put in the main body of the thesis.

A picosecond laser with wavelength of 532 nm, pulse width of 10 ps, and repetition rate of 100 kHz was used to ablate a $\text{YVO}_4\text{:Eu}^{3+}$ target in pure DI water. In addition, the wavelength was also adjusted to 1064 nm to investigate the effect to the nanoparticles formation. Figure A11 shows the SEM images obtained by the picosecond laser ablation. As can be seen that the morphology of the nanoparticles was an ovoid-like shape obtained by both laser wavelengths. And the particle size was also quite similar with that obtained by the nanosecond laser ablation as described in the main body of the thesis. Therefore, the laser parameters were not the main factor which can influence the morphology and the size of the $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles.

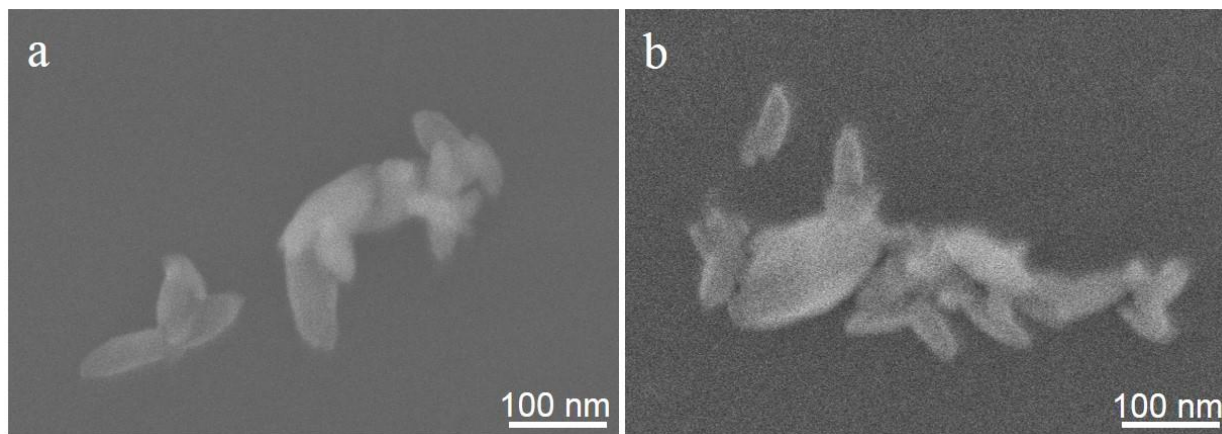


Figure A11. SEM images obtained by a picosecond laser ablation in water with a) 532 and b) 1064 nm wavelengths.

Appendix data 2

Ca- α -SiAlON:Eu²⁺ nanoparticles

Besides the YVO₄:Eu³⁺ nanoparticles, I also explored the Ca- α -SiAlON:Eu²⁺ phosphors which was considered as a candidate to replace oxide phosphors for white LED because of its stable chemical and thermal properties [1]. Ca- α -SiAlON:Eu²⁺ phosphor absorb the light in the range of 280-470 nm and emit the light in the range of 550-600 nm [2]. As far as we know, Ca- α -SiAlON:Eu²⁺ nanoparticles have not been reported up to date. Because the synthesis of Ca- α -SiAlON:Eu²⁺ material needs quite high temperature and pressure. Here, the laser ablation in liquid (LAL) was put forward to try to fabricate the Ca- α -SiAlON:Eu²⁺ nanoparticles. When the laser irradiates the Ca- α -SiAlON:Eu²⁺ target surface, the plasma plume consisting of Ca- α -SiAlON:Eu²⁺ cluster species was formed. The Ca- α -SiAlON:Eu²⁺ primary nanocrystals could be obtained after the quenching of plasma plume. The experimental and results are described as follows.

Firstly, the Ca- α -SiAlON:Eu²⁺ target was prepared by the solid state method. The raw reaction materials stoichiometric CaCO₃, Si₃N₄, AlN, and Eu₂O₃ were mixed and sintered at 1750 °C for 4 h under 0.92 MPa of gas pressure. After that, the obtained powder was pressed into a pellet, which was then transferred to the furnace for the sintering at the same condition with that described above. As for the laser ablation experiment, the same set-up with that in chapter 2 was used here. After the experimental optimization, the laser fluence was set at 1.27 J/pulse cm² after calculating the ratio of the laser power and the burned area in burning paper after one shot laser irradiation.

Figure A21 shows the XRD result of the target materials synthesized by solid state method. As can be seen that all the diffraction peaks could be indexed as trigonal *P31/c* crystal (PDF, No.33-0261). The particles were highly crystallized without any impurities. Figure A22 shows the SEM images of the target material. One can see that the target particles consisted of regularly shaped 0.8-1.2 μ m particles.

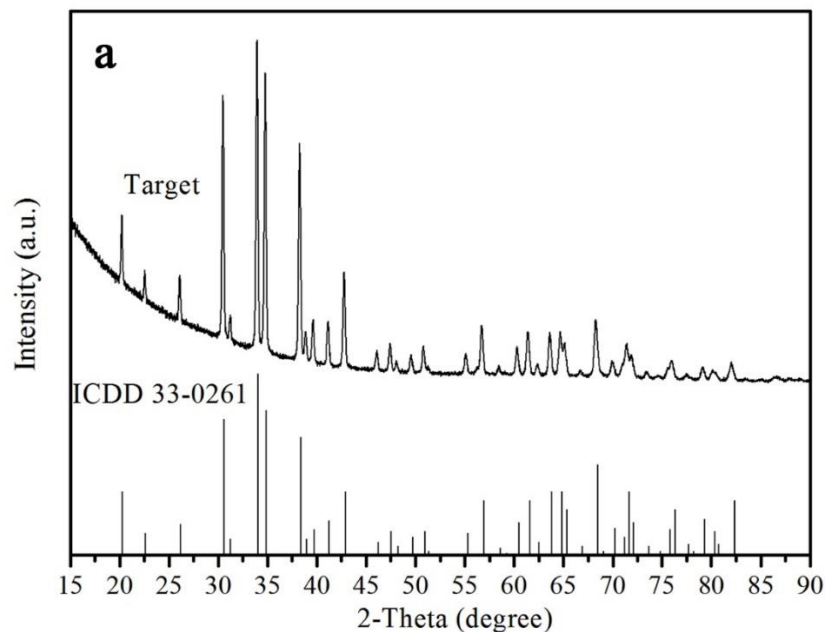


Figure A21. XRD of micrometer-sized Ca- α -SiAlON:Eu²⁺ target synthesized by solid state method.

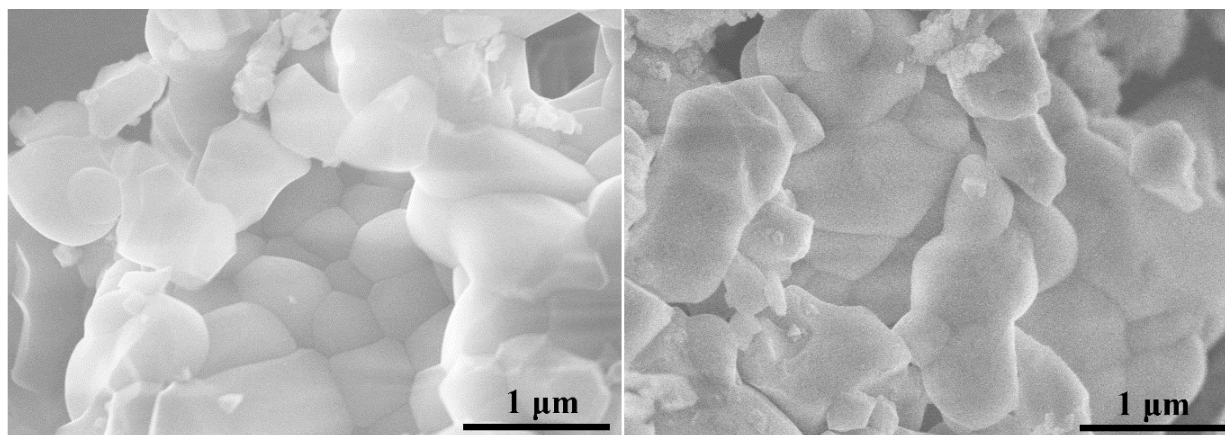


Figure A22. SEM image of micrometer-sized Ca- α -SiAlON:Eu²⁺ target synthesized by solid state method.

After the LAL, the colloid was directly collected and dropped onto the copper grid for SEM/TEM observation. Figure A23 shows the SEM result after laser ablation. One can see that, the nanoparticles were formed and most of the nanoparticles had the sphere shape with the size of less than 200 nm. However, some particles with a round shape and a long tail was attached. This would be caused by the incomplete formation of nanoparticles and the nanoparticles aggregated with each other.

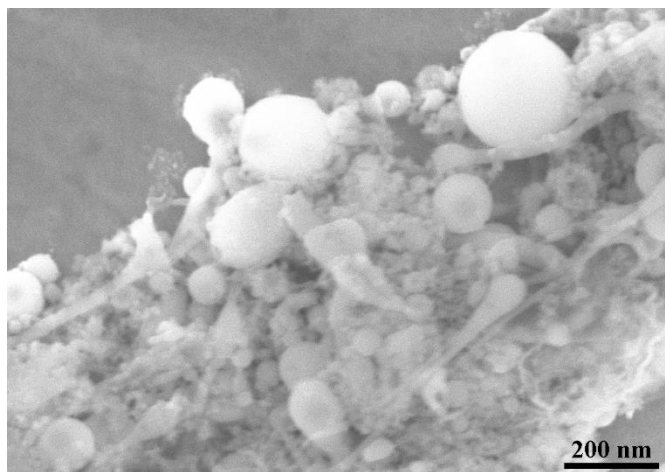


Figure A23. SEM image of the particles after laser ablation.

Figure A22 shows the TEM, EDS, and HR-TEM results of obtained nanoparticles after LAL in DI water. One can see that the secondary aggregated nanoparticles ranges between 90 and 110 nm were composed of small crystalline sized of less than 20 nm. The lattice fringe was clearly visible with a lattice spacing of 3.37 Å, approximately agreed with the lattice spacing of the (200) plane of Ca- α -SiAlON:Eu²⁺. The EDS result indicated the elemental composition of the nanoparticle to be Ca, Si, Al, O, N, and Eu. For a quantitative analysis, the amount of Si seems to evaporate during the process of LAL owing to its decreased content from 40.1 $\pm$ 2.9 at.% to 33.6 $\pm$ 4.3% at.%. The ratio of other elements did not significantly change. However, N and O were not investigated because of the inherent inaccuracy of EDS measurement for light elements.

Figure A24 shows the TEM and HR-TEM results. Figure A24 a) shows the nanoparticles at low magnification. As can be seen that the spherical nanoparticles were presented, which was consistent with the SEM results. Figure A23 b-c) indicated the nanoparticle showed a secondary particle, while it is composed by many primary nanocrystals. The HR-TEM image shows that the measured lattice spacing corresponds to the place (200) of trigonal crystal (PDF, No.33-0261) of Ca- α -SiAlON. The poly-crystalline structure of the nanoparticle was formed from the growth of primary nanocrystals. When the target surface was irradiated by the laser beam with enough laser fluence, the plasma plume was firstly created by the high laser energy. The plasma plume was composed of atoms, electrons of Ca- α -SiAlON:Eu²⁺. After the rapid quenching of the plasma plume, the primary Ca- α -SiAlON:Eu²⁺ nanocrystals were obtained. During the quenching process, the energy exchanged with the surrounding liquid and the vapor layer was formed surrounding the

plasma plume.

After the totally disappear of plasma plume, the cavitation bubble was induced from the vapor layer. The formed primary nanocrystals then transferred to inside the cavitation bubble. The lifetime of cavitation bubble usually last for several hundreds of microseconds. The primary nanocrystals would grow up inside of the cavitation bubble till its collapse. Finally, the formed nanoparticles were released to the liquid.

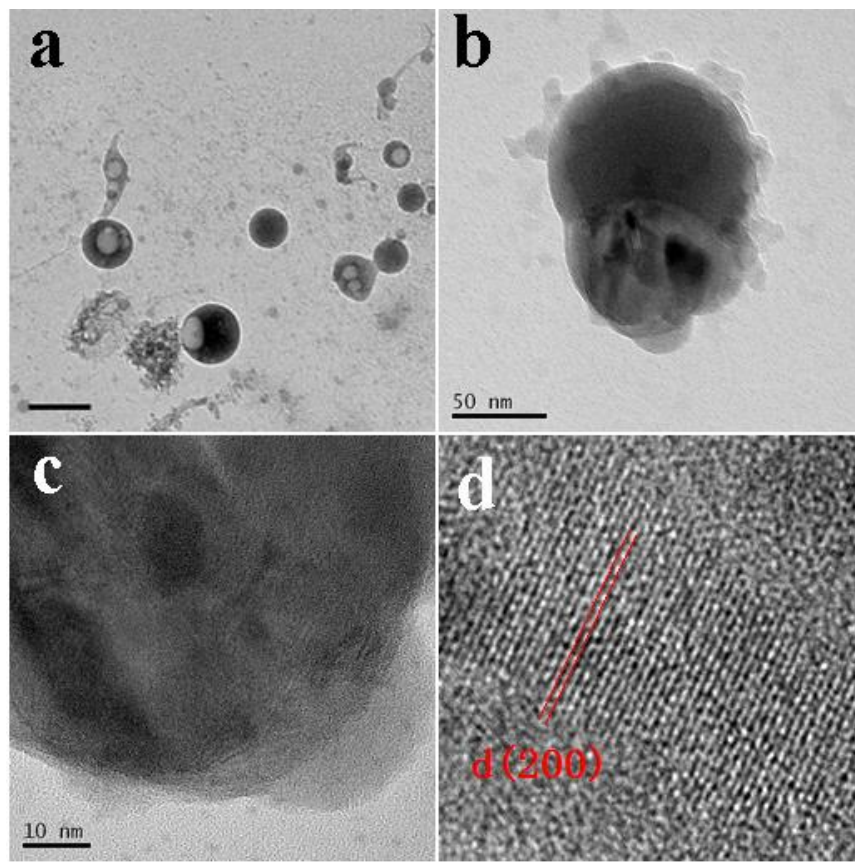


Figure A24. TEM image and HR-TEM images of a nanoparticle after LAL.

However, besides the spherical nanoparticles, there were also some nanoparticles with irregular shape as indicated in Figure A25. According to the selected area electron diffraction result, these particles were single crystals, which was different from the spherical ones. These particles were expected obtained from the fragmentation of the shock wave induced by the laser with high power. As described in chapter 2, the shock wave is firstly created when the laser irradiated the target surface. This result was also consistent with that observed in chapter 2. Moreover, these particles directly from the target are able to be removed by using the filters.

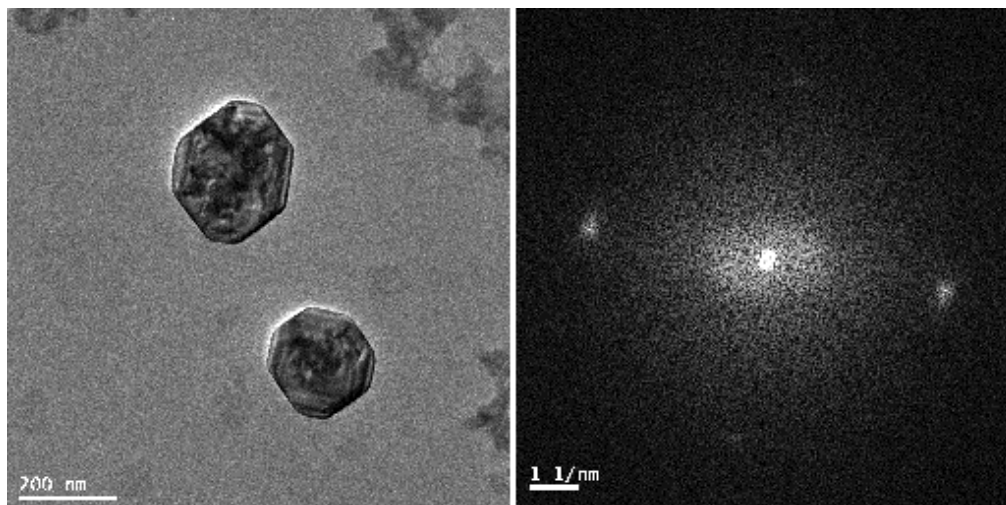


Figure A25. TEM image and SAED result of particles after LAL.

The composition of the nanoparticles was investigated by EDS measurement. Figure A26 shows the EDS result by measuring the particle in Figure A24. As can be seen that the particle contained Si, Al, O, N, Ca, Eu, and Cu elements, and we also investigated the ratio of elements that is shown in Table A21. The atomic ratio of nanoparticles was also consistent with that of the target materials, indicating the nanocrystals were $\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$. The EDS result showed the elemental discrepancy between the target and nanoparticles specially in N element. This discrepancy was mainly caused by the inherent inaccuracy of EDS measurement for light elements.

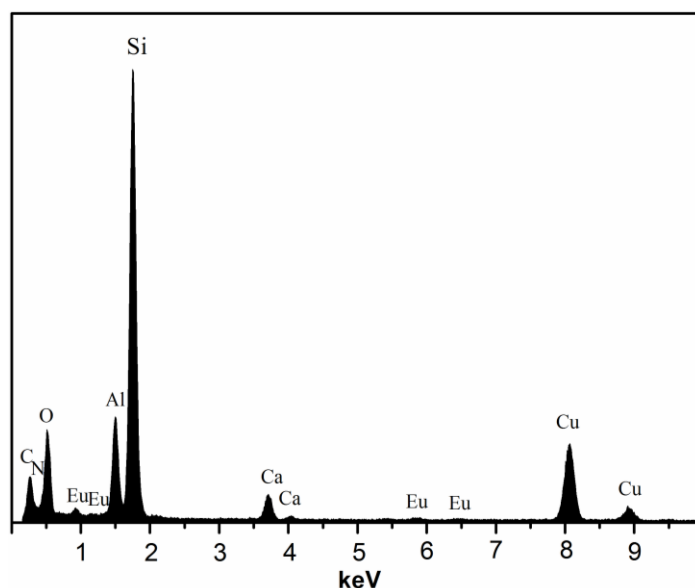
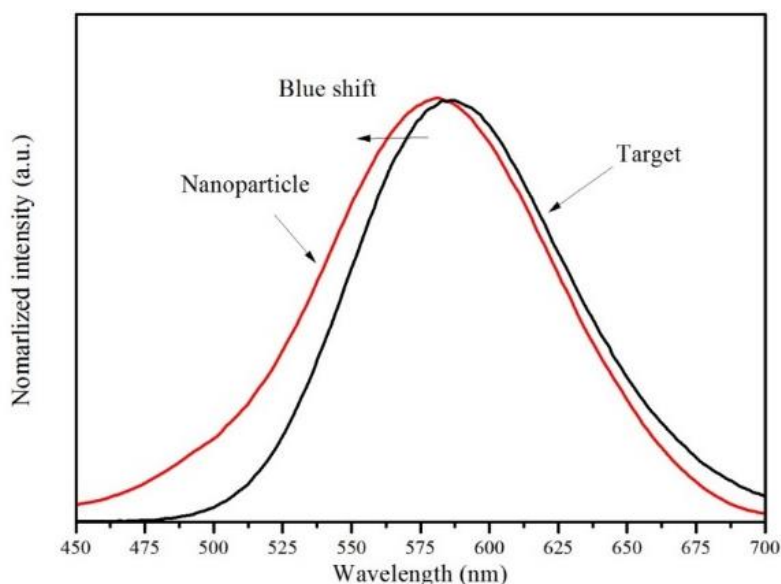


Figure A26. EDS result of the nanoparticles by measuring the point in figure A23 b).

Table A21. Atomic ratio of Ca, Si, Al, and Eu from EDS analysis for Ca- α -SiAlON:Eu²⁺ target and nanoparticles.

	Ca	Si	Al	Eu
Target	4.3 $\pm$ 0.9	40.1 $\pm$ 2.9	11.1 $\pm$ 1.9	0.5 $\pm$ 0.2
Nanoparticles	4.3 $\pm$ 1.0	33.6 $\pm$ 4.3	12.4 $\pm$ 2.9	0.6 $\pm$ 0.2

The PL spectra of the target and corresponding nanoparticles was shown in Figure A27. The both emission spectra (excited at 450 nm) exhibited a single broad band due to the allowed $4f^65d^1 \rightarrow 4f^7$ transition of Eu²⁺ [3]. The blue shift of the spectra from the 585 nm (target) to 580 nm (nanoparticles) suggested the changes of crystal field around Eu²⁺ ions.

**Figure A27.** The PL spectra of Ca- α -SiAlON:Eu²⁺ target and nanoparticles.

Herein, Ca- α -SiAlON:Eu²⁺ nanoparticles were obtained by LAL at 1.27 J/pulse cm². We also performed the experiment at other laser fluence, however, the similar result including SEM, TEM, and PL properties. The obtained nanoparticles showed the spherical shape, which were polycrystalline. The nanoparticles consisted of many primary nanocrystals proved by HRTEM. A clear blue shift was observed in nanoparticles compared with the PL spectrum of target material. This phenomenon could be caused by the change of crystal field surrounding Eu²⁺ ions. However, the XRD could not be measured owing to the limited amount of obtained nanoparticles. More studies are needed in the future.

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Accomplishments

Journal publications

1. **Haohao Wang**, Osamu Odawara and Hiroyuki Wada. "Facile and Chemically Pure Preparation of $\text{YVO}_4\text{:Eu}^{3+}$ Colloid with Novel Nanostructure via Laser Ablation in Water", *Scientific Reports*, 6 (2016), 20507.
2. **Haohao Wang**, Osamu Odawara and Hiroyuki Wada. "One-step Preparation of $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles by Pulsed Laser Ablation", *Journal of Alloys and Compounds*, 683 (2016) 1.
3. **Haohao Wang**, Marcus Lau, Takumi Sannomiya, Bilal Gökce, Stephan Barcikowski, Osamu Odawara, Hiroyuki Wada. "Laser-induced Growth of $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticle from Sequential Flowing Aqueous Suspension", *RSC Advances*, 7 (2017), 9002.
4. **Haohao Wang**, Osamu Odawara and Hiroyuki Wada. "Morphology and optical properties of $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles fabricated by laser ablation in ethanol", *Applied Surface Science*, 425 (2017), 689-695.

Related publications

1. **Haohao Wang**, Touichirou Tomiya, Takashi Takeda, Naoto Hirosaki, Osamu Odawara and Hiroyuki Wada. "Fabrication of Nano-scale $\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$ Phosphor by Laser Ablation in Water", *Applied Physics Express*, 8 (2015) 115001.

Presentations (oral)

International conferences

1. **Haohao Wang**, Osamu Odawara, Hiroyuki Wada. Facile and Chemically Pure Preparation of $\text{YVO}_4\text{:Eu}^{3+}$ Colloidal Nanoparticle via Laser Irradiation in Water, Intl. Symp. Phosphor Mater. (Phosphor safari 2011), Niigata (2015/07/29).
2. **Haohao Wang**, Osamu Odawara, Hiroyuki Wada. Facile Synthesis of $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles via Laser ablation in Liquid. 4th Conf. Adv. Nanoparticle Generation and Excitation by Lasers in Liquids (ANGEL 2016), Essen, Germany (2016/5/11).

Domestic conferences

3. **Haohao Wang**, Osamu Odawara, Hiroyuki Wada. Fabrication of $\text{YVO}_4\text{:Eu}^{3+}$ Nanoparticles by Laser ablation in Liquid, The 77th Japan Society of Applied Physics Autumn Meeting (2016 JSAP), Niigata (2016/9/13).

Related presentations (oral)

International conferences

1. **Haohao Wang**, Touichirou Tomiya, Takashi Takeda, Naoto Hirosaki, Osamu Odawara, Hiroyuki Wada. Preparations of $\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$ nanoparticles by laser ablation in water, 7th Intl Cong. Laser Adv. Materials Processing (LAMP 2015), Kitakyushu (2015/5/28).

Domestic conferences (oral)

1. **Haohao Wang**, Touichiou Tomiya, Takashi Takeda, Naoto Hirosaki, Osamu Odawara, Hiroyuki Wada. Facile Synthesis of Nano-scale Ca-a-SiAlON:Eu²⁺ by Laser Ablation in Water, The 76th Japan Society of Applied Physics Autumn Meeting (2015 JSAP), Nagoya (2015/9/16).

Book

1. **Haohao Wang**, Hiroyuki Wada. Oxynitride and Nitride Nanophosphor, Development of Next-Generation Phosphor Materials, CMC Press (2016/7).

Fellowship

1. Scholarship from China scholarship council (CSC), 2014–present.