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A convenient way to prepare magnetic colloids by direct Nd:YAG laser ablation

G.X. Chen[a,b], M.H. Hong[a,*], B. Lan[a,b], Z.B. Wang[a,b], Y.F. Lu[a,b], T.C. Chong[a]

[a]*Data Storage Institute, DSI Building, 5 Engineering Drive 1, Singapore 117608, Republic of Singapore*
[b]*Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117576, Singapore*

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Abstract

Magnetic colloids with nanoparticles inside have been successfully fabricated by laser ablation of a cobalt target immersed in solutions, using an Nd:YAG laser at wavelengths of 532 and 1064 nm. The liquid environment allows formation of the colloids with nanoparticles in uniform particle diameters. Influences of the laser wavelengths and different solutions on efficiency of particle formation were studied. The magnetic properties of the cobalt nanoparticles inside the colloids generated were also investigated. Using proper parameters, this method provides a convenient way for fabricating magnetic fluid as well as metal nanoparticles.

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Keywords: Nanofabrication; Colloids; Nanoparticles; UV-Vis absorption spectra

1. Introduction

Magnetic colloids have attracted much attention due to their promising applications in various areas such as catalytic chemistry, magnetic fluid and mesoscopic physics. For example, synthesizing carbon nanotubes [1], slurry phase Fischer–Tropsch synthesis [2], preparing nanometric oxide particles [3], frictionless rotary and exclusion seals, damping of vibrations, heat transfer for loudspeakers [4], and carrying drugs to predicted position [5] were studied by using magnetic colloids. With a magnetic field applied to the system, magnetic nanoparticles were proposed to be building blocks for nanoelectromechanical system (NEMS) devices, which can act as nanomotors, nanogenerators or other nanoscale devices [6]. The sizes and properties of the magnetic nanoparticles are crucial factors, which influence their performances in these applications. Therefore, it is an important topic for fabricating magnetic colloid with uniform and stable magnetic nanoparticles inside.

A broad range of techniques from chemistry and physics has been combined to synthesize magnetic nanoparticles. The conventional methods for producing magnetic nanoparticles include solution phase metal reduction [7], organometallic precursors decomposition [8] and mechanical milling [9]. Among

* Corresponding author. Tel.: +65-68748707; fax: +65-67771349.
E-mail addresses: chen_guoxin@dsi.a-star.edu.sg (G.X. Chen), hong_minghui@dsi.a-star.edu.sg (M.H. Hong).

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them the most commonly used method is probably the chemical reduction of metal ions, where magnetic nanoparticles are produced in the reversed micelles by chemical reduction. These methods have shortcomings associated with the material contamination, excessive particle agglomeration, hazardous chemical wastes and complex reaction conditions required. Recently, a relatively simple laser ablation based method for the production of nanoparticles in solution that overcomes many of the shortcomings of the conventional methods has been developed [10,11]. With a pulsed laser beam irradiation, chemically pure nanoparticles are formed by continuously ablating a metal target immersed in a solution. The fabrication rate and morphology of the nanoparticles are dependent upon laser wavelength, pulse energy, absorption of laser energy by the liquid environment and ablation time. Nanoparticles of noble metals and their alloys in solutions have been obtained by manipulating these variables [10–13]. This method can control nanoparticle size down to several nanometers and preserve high purity of nanoparticles with environmentally compliant properties. Thus it provides a relatively convenient way to fabricate magnetic colloids as well as magnetic nanoparticles. As versatile materials, cobalt colloids have been widely studied and used [7,8,14]. In this paper, it is carried out to investigate the preparation of cobalt colloids with stable and size-controlled nanoparticles. Morphology, particle size, absorption spectroscopy and magnetic properties of the obtained colloids and nanoparticles were analyzed by optical microscope, field emission scanning electron microscope (SEM), ultraviolet to visible (UV-Vis) spectrophotometer and vibrating sample magnetometer (VSM). Oxidations of the nanoparticles, influences of laser wavelengths on nanoparticle formation and magnetic properties are discussed. Formation efficiency of nanoparticles during laser ablation also depends on the liquid media.

2. Experimental

The target used in this study is a metal disk of cobalt (6 mm in diameter). Initially, the target was first washed with ethanol and then with deionized water to remove organic contaminations. After that, the oxidized layer was removed with 10% diluted hydrochloric acid for 10 min. Ultrasonic cleaner was used to help clean the surface. A glass dish (60 mm in diameter) was applied as the container, and a p-type (1 0 0) silicon wafer was used as substrate. They were cleaned and rinsed with acetone, ethanol and DI water in sequence assisted by ultrasonic cleaner for 10 min at each step. Fig. 1 shows the experimental setup for fabricating cobalt nanoparticles. The cleaned target was immersed into 20 ml solution, which was used as carrier media for nanoparticles. In this study, DI water and ethanol were used as carrier media, respectively. The depth of the target immersed into the solutions was kept at about 5 mm. During laser ablation the dish was rotated constantly to uniformly ablate the target and ensure that the formed nanoparticles would disperse separately into the solution. An Nd:YAG laser (B.M. Industries, SERIE 5000) with wavelengths of 1064 and 532 nm was applied to ablate the target. The pulse duration of the laser is 7 ns and the repetition rate is 10 Hz. A Scientech Vector H310 laser energy meter was applied to monitor pulse energy. After 10 min of the laser ablation, the obtained colloidal solution was placed on substrates and dried by evaporation in vacuum chamber for optical microscope observation and SEM imaging. An Olympus BH2-UMA optical microscope was applied to check the morphology of the prepared samples. A JEOL JSM-6340F SEM and a Hitachi S-4100 SEM operating at 15 kV were used to determine the particle size and shape. Size distribution was obtained by randomly measuring particle diameters over 300 nanoparticles in sight on the obtained images. The UV absorption

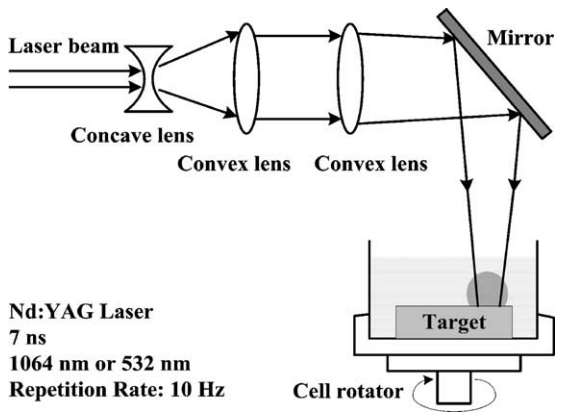

Fig. 1. Schematic diagram of experimental setup for fabrication of nanoparticles in solution by laser ablation.

spectra were obtained by a Shimadzu UV-160A scanning spectrophotometer by placing the colloid into a quartz cell (3.0 ml). A Philips z'pert PRO X-ray diffraction (XRD) was used to measure the components and a Digital Measurement Systems 990 torque VSM was applied to characterize the magnetic properties at room temperature.

3. Results and discussion

3.1. Laser ablation in water

During the laser ablation of cobalt target, it was observed that the water remained transparent and colorless at the beginning. After laser ablation began, the color of solution changed to light gray, then yellow-brown and finally blackish-brown. The deeper the color is, the higher concentration of cobalt nanoparticles, which is demonstrated by absorption spectra and discussed in the later part. An interesting phenomenon is observed that the color of water changed faster for the laser wavelength of 532 nm than 1064 nm at the same laser fluence of 0.9 J/cm^2. But at the high laser fluence of 30 J/cm^2, the color of water changes faster for 1064 nm laser ablation. It may be induced by absorption properties of light by target and colloids formed. At laser fluence of 0.9 J/cm^2 the concentration of the nanoparticles is low. The yield of nanoparticles is dominated by the absorption properties of light by target, which increases while wavelengths decrease. But at high laser fluence the concentration of colloids generated is very high and makes a difference. The theoretical study shows that absorbance of cobalt colloids increases while the wavelength of incident light decreases [15]. Thus at high laser fluence the stronger absorption of laser pulse energy at 532 nm makes the color of water change slower than that at 1064 nm.

During laser ablation, the laser was operated at a repetition rate of 10 Hz (0.1 s per pulse). The formed cobalt nanoparticles may not disperse away quickly in the dense surroundings within such a short time, though the target is rotated constantly. It is possible that the floating particles absorb subsequent laser pulses. The coupling of laser irradiation with suspended nanoparticles may reduce the particle size and narrow the distribution [16]. Thus, this fabrication

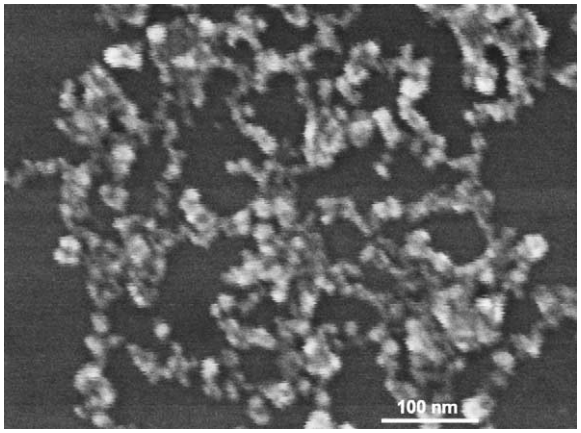

Fig. 2. SEM image of Co nanoparticles obtained by laser ablation of cobalt target in water. The laser fluence is 30 J/cm^2.

can be considered as a "multi-pulse" process. This effect can be used to control the size distribution of cobalt colloids using proper selected pulse energy and repetition rate.

In order to characterize the size of nanoparticles, SEM images were obtained by placing colloidal solution on a clean silicon substrate as shown in Fig. 2. It is found that the nanoparticles are spherical with uniform diameter except the aggregated large ones. Typical histogram of nanoparticle size distribution is shown in Fig. 3. It reveals that the diameters of

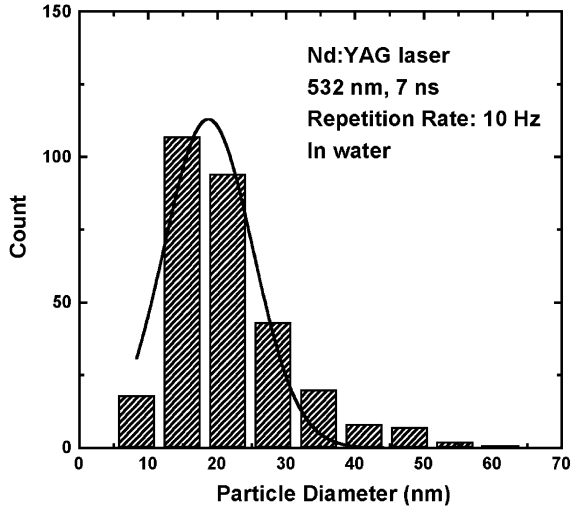

Fig. 3. Size distribution of Co nanoparticles produced in water. The line is Gaussian fitting of size distribution with center at 18.7 nm and standard deviation of 6.4 nm.

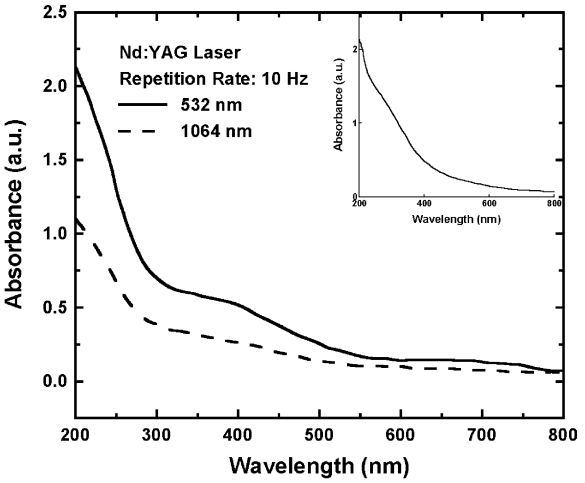

Fig. 4. UV-Vis absorption spectra of nanoparticles colloid fabricated at laser wavelengths of 532 and 1064 nm in water. Inset is theoretical spectrum for pure Co nanoparticles.

nanoparticles are in a range from 6 to 60 nm. During the measurement, no individual particle larger than 60 nm in size is found. A Gaussian fitting is applied to the size distribution (the solid line in Fig. 3). From the Gaussian distribution, it is found that the mean nanoparticle size is 18.7 nm with the standard deviation of 6.4 nm.

The absorption spectra of nanoparticle colloids in water are obtained by UV-Vis spectrophotometer. Fig. 4 presents the absorption spectra of nanoparticle colloids after laser ablation for 10 min in water at laser wavelengths of 532 and 1064 nm, respectively. The absorption spectra increase continuously in the optical density from 800 to 200 nm, which is similar to that predicted for pure metallic cobalt [15]. A small shoulder around 350 nm can also be observed in the given figure. It may be induced by the oxidation of cobalt [16–18]. After keeping in sealed syringes for 1 week, another small shoulder around 650 nm appeared, which did not appear in the spectra of as-prepared cobalt colloid [17–19] and may also be caused by oxidation of cobalt. Furthermore, X-ray diffraction measurement of the nanoparticles fabricated in water also indicates the presence of cubic CoO. At nanometer-scale the thermalization within an individual particle is much fast. The plasma temperature induced by laser ablation can be estimated as high as 10^4 K. It indicates that the oxidation of nanoparticles might be possible, which is proposed as the reaction: $2Co^0 + O_2 \rightarrow 2CoO$ [19]. Thus it suggests that water is an optimal media for fabricating partially oxidized cobalt colloid by laser ablation technique.

In order to compare the spectra of the nanoparticles fabricated at the above two laser wavelengths, laser fluences were set at a same volume of 0.9 J/cm^2. The produced colloids at both laser wavelengths were sampled in equal volume by scaled syringes. It was found that absorbance intensity of samples produced at 1064 nm laser wavelength are lower than that produced at 532 nm as shown in Fig. 4. Therefore, it suggests that the particle densities of samples prepared at 532 nm laser wavelength are higher than that prepared at 1064 nm. It may be concluded that laser wavelength of 1064 nm is less efficient in fabricating nanoparticles than 532 nm in water at low laser fluence. Tsuji et al also found similar phenomena during fabrication of silver in water [20]. It is obvious that the efficiency of nanoparticle production decreases when the wavelength increases due to light absorption properties of the target materials. The absorption coefficient of bulk cobalt under water is estimated to be slightly larger at 532 nm laser light than that at 1064 nm [21]. The 532 nm laser light has two times photon energy as that of 1064 nm, so it gives higher probabilities for the atoms and clusters to be ablated from the target surface because of stronger laser interaction with metal target. Thus, the colloids prepared with 532 nm laser pulses abound with cobalt nanoparticles, which is indicated in the UV-Vis absorption spectra.

Magnetic measurements of the nanoparticles were performed using VSM at room temperature in the field range from −15 to 15 kOe. The typical M-H loop is resented in Fig. 5. As shown in the inset picture, the coercivity is about 100 Oe and is much smaller than that of bulk. There is no obvious tendency of saturation on the curve even at a field of 15 kOe. It is well known that cobalt nanoparticles are predicted to be superparamagnetism at size below 7 nm [22]. The low value of coercivity may be partially induced by small cobalt nanoparticles under the critical size of superparamagnetism. The oxidation of the particles may also contribute to the decrease of coercivity.

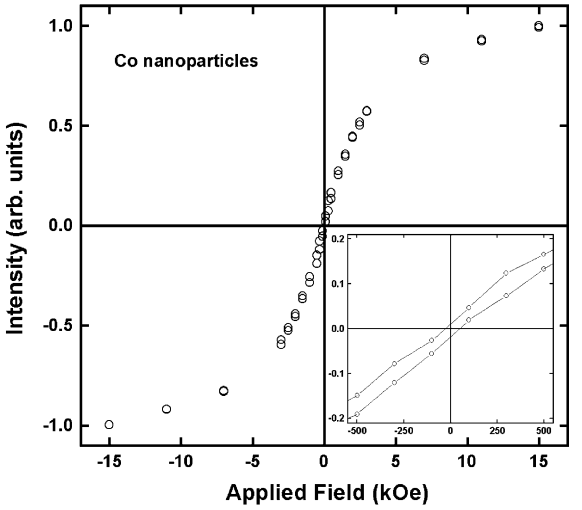

Fig. 5. Magnetization vs. field plot of Co nanoparticles at room temperature.

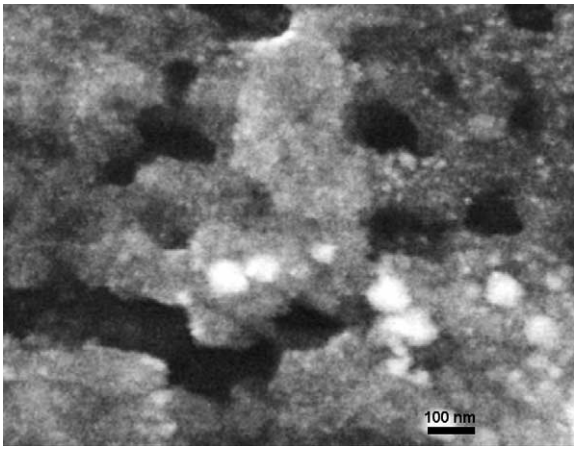

Fig. 6. SEM image of Co nanoparticles obtained by laser ablation in ethanol. The laser fluence is 900 mJ/cm^2.

3.2. Laser ablation in ethanol

Ethanol was applied as solvent in comparison with water. During laser ablation in ethanol, a strong sound can be heard and small bubbles can be observed in the solution, while in water the sound is faint and no bubbles were observed. The color of the ethanol solution changed slowly from transparent to light gray after 10 min ablation, suggesting the formation of cobalt particles.

SEM image of the cobalt nanoparticles produced in ethanol is shown in Fig. 6. The samples for SEM imaging were prepared by drying the colloids on a clean silicon substrate in a vacuum chamber. It is found that many of the nanoparticles aggregated to large particles during preparation of samples due to the magnetic attribute. The individual nanoparticles are spherical with uniform diameter. Typical histogram of nanoparticle size distribution is shown in Fig. 7, revealing a narrower size distribution of nanoparticle diameters from 6 to 35 nm than that of prepared in water. A Gaussian fitting is applied to the size distribution (the solid line in Fig. 7). The center of the Gaussian distribution is at 11.8 nm with the standard deviation of 2.7 nm. The mean size of 11.8 nm is basically satisfied the request of magnetic fluid [4].

The efficiency of particles formation is affected by the properties of solutions. Fig. 8 indicates the UV-Vis absorption spectra from nanoparticle colloids of cobalt in ethanol and water. Both spectra were measured with pure solutions as references avoiding the signals from solutions themselves. The colloids were obtained by laser ablation for 10 min with 532 nm pulses at identical fabricating parameters. It is found that absorbance of samples produced in ethanol is lower than that produced in water. The lower absorbance indicates lower abundance of particles in solution. Thus, it implies that the ablation efficiency in ethanol is lower

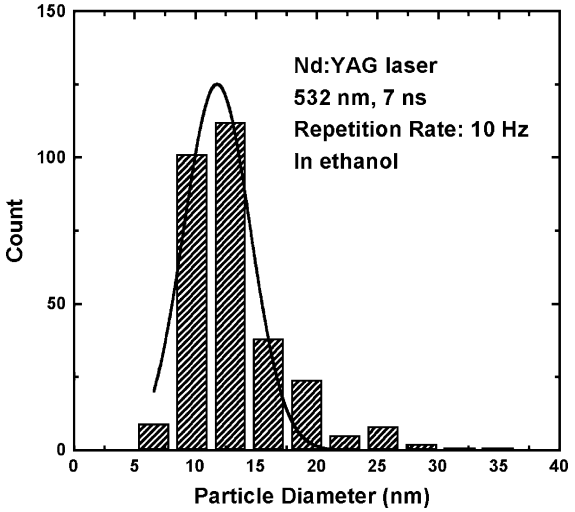

Fig. 7. Size distribution of Co nanoparticles produced in ethanol. The line is Gaussian fitting of size distribution with center at 11.8 nm and standard deviation about 2.7 nm.

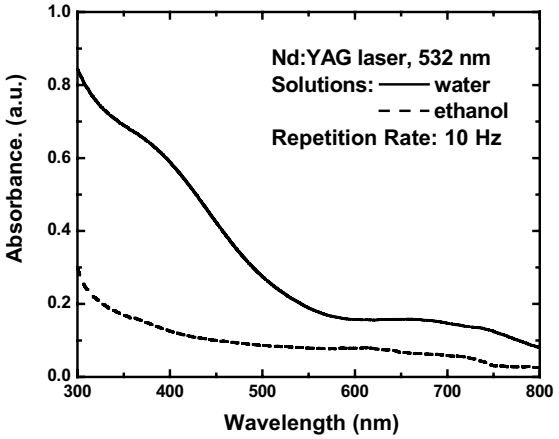

Fig. 8. Comparison of UV-Vis absorption spectra between nanoparticle colloids fabricated in ethanol and water. Laser fluence is 0.9 J/cm^2 at laser wavelength of 532 nm.

than that in water. Mafuné et al. reported a similar result that the yield of silver nanoparticles by laser ablation in organic solution is very low [12].

There are two affecting factors generally taken to explain the growth of nanoparticles in solutions. The first factor is plasma-shielding of laser light. After laser pulse energy is combined with the target, plasma will form and expand to surrounding space. Like the plasma formed by laser ablation in vacuum, the plasma generated in the earlier part of a laser pulse can absorb the latter part of the pulse energy. The second factor is particle-shielding of laser light. Colloids of nanoparticles generated by the earlier laser pulses can absorb, scatter and shield the light of later laser pulses [20]. Especially when the laser fluence is high enough, nanoparticles act as initiation sites for optical breakdown in the solution [23]. The absorption of laser light quickly heats nanoparticles to a very high temperature to form microsized plasmas. The growth and rapid expansion of these micro-plasmas in turn give rise to increases in the absorption and scattering of subsequent laser pulses [24]. But either factor cannot give plausible explanation on low ablation efficiency in ethanol, because the ethanol solution has nearly the same initial transparence as water towards 532 nm light. By comparing the thermal dynamic properties between water and ethanol, we propose that the property of the solution itself is a significant factor. After coupling of pulse energy to the surface of target, plasma species with very high temperature are generated. A thin layer of solution at the interface of ablated area is vaporized to high temperature that far beyond its boiling point and to a high pressure at orders of tens atmospheres [25]. For the thermal conductivity of ethanol (0.17 W/mK at 25 °C) is much smaller than that of water (0.60 W/mK at 25 °C), ethanol solution can be easily vaporized to such an enhanced condition. At high pressure and high temperature, ethanol can decompose to form permanent gases [26]. In water though laser pulses can induce photolysis to form radicals, the radicals recombinate quickly before the end of nanosecond laser pulse at a time order of femtoseconds [27]. The formed permanent gases in ethanol solution aggregate to bubbles that can be seen during laser ablation. The gases bubbles in the path of laser beam in combination with ablated plasma and formed nanoparticles in earlier pulses weaken the laser light that couples to the target. The nanoparticle generation reduces into a lower nanoparticle concentration. As a result it leads to the low absorbance in UV-Vis spectra of samples prepared in ethanol in comparison with that in water.

There are no shoulders at 350 and 650 nm even after keeping for 6 days. It suggests that no oxidation occurs under the protection of ethanol solution. Therefore, ethanol is proposed to be an optimal substitute of water for fabricating pure cobalt colloids. But after 30 days' standstill, flocculent precipitation is formed and the color of the water turns shallow. To prevent the nanoparticle from coagulation, proper dose of surfactant need to be added.

4. Conclusions

In summary, magnetic colloids of cobalt with nanoparticles size down to 6 nm have been produced by simply laser ablation of target in water and ethanol. Through the absorption spectroscopy, it is found that the laser wavelength of 532 nm is more powerful than 1064 nm to produce cobalt nanoparticles in water. It was also found that slight oxidation of nanoparticles formed in water due to the existence of the oxygen in water. The obtained nanoparticles are spherical in SEM images. Magnetic measurement shows that the prepared nanoparticles have low coercivity. Laser ablation for fabricating cobalt nanoparticles in ethanol is less efficient than that in water at wavelength of

532 nm, but with a narrower size distribution. The low efficiency is caused by laser induced bubble formation. It is promising to optimize the fabrication parameters for producing more uniform and stable nanoparticles in colloids.

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