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γ-Fe_2O_3 nanoparticles prepared by laser ablation of a tiny wire

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ABSTRACT A new method of preparing nanoparticles by pulsed laser ablation of a tiny wire is reported. A Nd : YAG pulsed laser with a wavelength of 1064 nm was used to ablate a 0.5-mm-diameter iron wire in a sealed chamber in a flowing mixed gas of N_2, O_2, and air to generate γ-Fe_2O_3 nanoparticles. In the meantime, a bulk Fe sample was ablated in the same chamber with the same laser processing parameters in order to compare the effect of the bulk sizes on the production rates and the sizes of the nanoparticles. The experimental results demonstrated that the production rate of nanoparticles prepared by laser ablation of tiny wires was about eight times that of laser ablation of bulk targets with the same composition, while the sizes of the nanoparticles were basically the same. With a higher power density and/or smaller diameters of the metal wires, it is possible to obtain smaller sizes of the nanoparticles with higher production rates.

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1 Introduction

Pulsed laser ablation has attracted great attention for preparing high-purity, ultra-fine nanoparticles with narrow size distributions and of different materials in the past ten years [1–4]. The targets used for nanoparticle preparation by laser ablation are usually bulk sizes, and the lasers are excimer lasers and pulsed YAG lasers [5, 6]. Although the quality and sizes of the nanoparticles prepared by such systems are widely accepted, the process is still far away from industrialization as the high energy loss conducted by the bulk materials limits the vaporization rates as well as the production rates of the nanoparticles greatly.

There are two routes to enhance the production rates of nanoparticles by laser ablation. One is reducing the volume of the targets in order to utilize the laser energy more effectively. Keto et al., for example, prepared glass and metal nanoparticles by laser ablation of microspheres (LAM) using a KrF excimer laser, and they found that the ablation thresholds of the microspheres are much lower than those of bulk materials because the smaller bulk sizes resulted in smaller energy loss by heat conduction. They also found that the microspheres needed a much smaller threshold energy than bulk materials, which means a greater potential to enhance the production rates of the nanoparticles [6–10]. However, the low hitting rate of the laser beam with the microspheres and the poor collecting method of the nanoparticles are the main restricting factors to enhance the production rates further [6, 7]. Another route to enhance the production rates of nanoparticles is using a higher-power laser system. Because high-power laser systems with UV wavelength are highly costly up to now, it is worthwhile studying the possibility of enhancing the production rates by high-power pulsed YAG lasers with the normal wavelength (1064 nm) in place of the excimer lasers, while the quality of the nanoparticles is not changed significantly. Although there are several reports about nanoparticle preparation by high-power pulsed YAG laser ablation in recent years, the targets used are basically bulk substances and the production rates are not enhanced significantly [11–13].

Hence, one challenging question is what will happen if we try to prepare the nanoparticles by laser ablation of solid targets with small sizes and with a high-power pulsed YAG laser?

2 Experimental

In this paper, tiny wires with diameters of several hundred microns are used as the starting materials. The experimental configuration is depicted in Fig. 1. A metal wire is sent through the pipe furnace to the reaction area by an automatic wire-feeding system, and a pulsed Nd : YAG laser beam (wavelength = 1064 nm) is focused by a plano-convex lens to the tip of the wire at normal incidence with a diameter of 0.5 mm. Other parameters are as follows: laser pulse width 0.3–20 ms, repetition rate 5–150 Hz, and average laser power 400 W. If necessary, the pipe resistance furnace of 1 kW can preheat the wire to any designed temperature with a maximum temperature of 800 °C by an automatic temperature-control system. The wire passes through a specially designed fixture and is irradiated accurately on the wire tip by the laser beam all the time. Prior to laser irradiation, the wire is sent through the pipe furnace to the reaction area. Then, the laser beam irradiates the tip of the metal wire directly and generate plumes composed of the atoms, molecules, and clusters of the target, which collide and condense in the flowing carrier gas and

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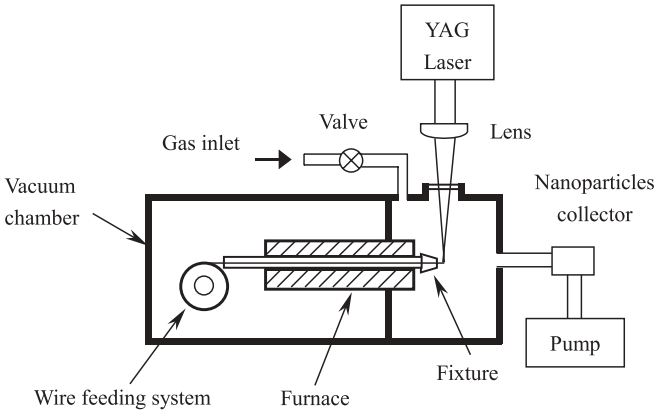

FIGURE 1 Experimental configuration for nanoparticles preparation by laser ablation of tiny wires

form nanoparticles. The generated nanoparticles are continuously transferred into the collector by the pump. Monotype or compound nanoparticles can be generated and collected with inert or reactive carrier gas.

In this report, a mixture of N_2 (99.99%) and O_2 was used as the continuous reactive carrier gas during nanoparticle preparation. We chose an iron wire as the test material for two reasons: (i) ferric oxide nanoparticles have many important applications as magnetic storage media, in the electronics industry, and as catalysts; (ii) iron wire is easy to obtain and prepare to the designed sizes.

The nanoparticles at different processing conditions were characterized by a transmission electron microscope (TEM, Philips CM12). Specimens were prepared by first dispersing nanoparticles in ethanol; a drop is then placed on a carbon film carried on a 3-mm-diameter Cu grid and dried in air. The TEM photographs were analyzed by image-processing software to determine the sizes of the nanoparticles. In our experiments, the effects of both laser power density and carrier-gas pressure on the sizes and size distributions were studied systematically.

3 Results and discussion

Figure 2 shows a TEM photograph of nanoparticles prepared by laser ablation of a 0.5-mm-diameter Fe wire. The concrete experimental conditions are as follows: the Fe wire was preheated to 200 °C by the pipe furnace before laser ablation. The laser power density is 4.5×10^6 W/cm^2. A mixed gas of 0.15 MPa N_2 and 0.05 MPa O_2 is used to cover the laser-irradiated areas during laser ablation. X-ray diffraction apparatus demonstrated that the produced powder is γ-Fe_2O_3; the X-ray diffraction pattern is shown in Fig. 3.

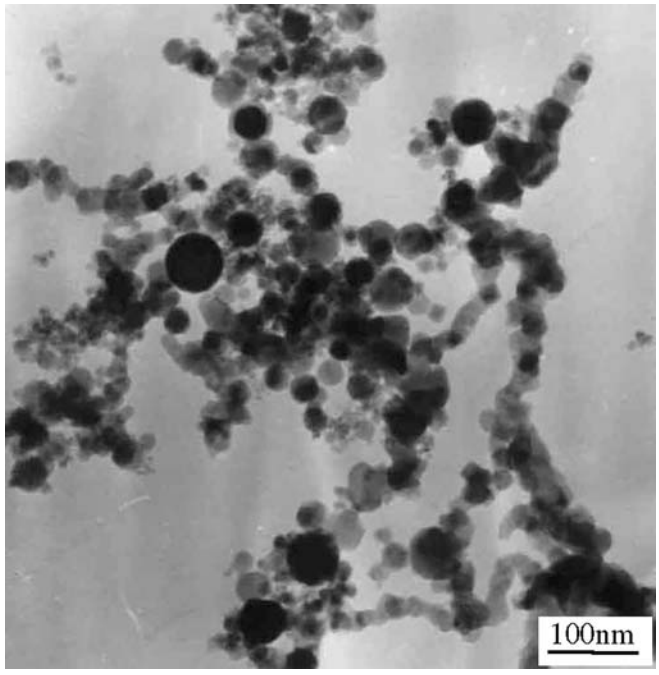

FIGURE 2 TEM micrograph of γ-Fe_2O_3 nanoparticles

From Fig. 2, it can be seen that the prepared nanoparticles are basically spherical in shape and form chain-like structures because of their magnetism. The experimental results demonstrated that there are no big differences among the morphologies of the nanoparticles prepared at different processing conditions.

Table 1 shows the statistics of nanoparticles prepared at different laser power densities with the mixed gas of 0.18 MPa N_2 and 0.02 MPa O_2, from which it can be seen that the mean particle diameters decreased when the laser power density increased from 4.5×10^6 W/cm^2 to 10×10^6 W/cm^2. This result is very interesting, and is opposite to the reports by other researchers that the sizes of the nanoparticles increased with the power densities of the lasers [14–16]. Another interesting result is that, compared with other methods of nanoparticle preparation by laser ablation of bulk materials and/or laser evaporation, the sizes of the nanoparticles are rather homogeneous, and only a very small number of nanoparticles were found with the diameters of 50–90 nm in our statistics. No particles larger than 90 nm were found in any TEM photograph. The histograms of the size distributions at different laser power densities are shown in Fig. 4, which shows a good normal-distribution fit in all the cases. Moreover, the data are also fitted to a log-normal distribution, and the result is listed in Table 2.

Laser power density ($\times 10^6$) W/cm^2	Number	Diameter			σ	$\alpha = \sigma$
		Mean (nm)	Min (nm)	Max (nm)	(nm)	/diameter
4.5	950	29.4	9	90	12.4	0.42
6.8	970	26.1	5	85	12.6	0.48
10	870	24.7	5	80	12.2	0.49

TABLE 1 Normal statistics of nanoparticles prepared at different laser power densities preparation by laser ablation of tiny wires

Laser power density ($\times 10^6$)W/cm^2	Number	Geometric mean diameter (nm)	Min (nm)	Max (nm)	$\ln \sigma_g \approx \alpha$
4.5	950	27.7	9	90	0.42
6.8	970	22.7	5	85	0.45
10	870	21.6	5	80	0.47

TABLE 2 Log-normal statistics of nanoparticle distributions at different laser power densities

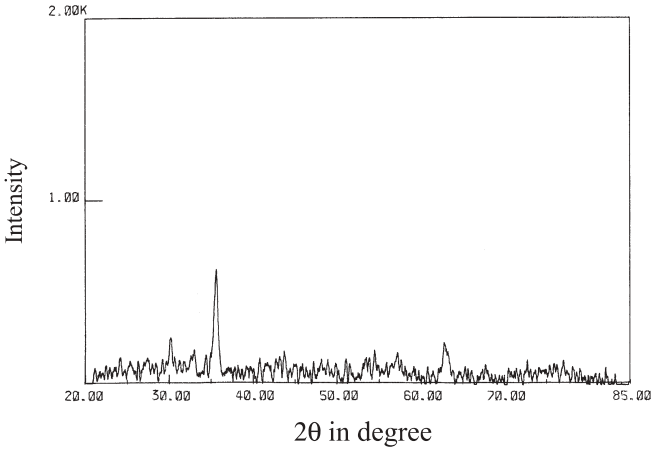

FIGURE 3 X-ray diffraction pattern for γ-Fe_2O_3 nanoparticles prepared by laser ablation of wire

The effect of the mixed ambient-gas pressure on the mean particle diameters is shown in Fig. 5, which demonstrates that the diameters of the nanoparticles decreased with the increase of the carrier-gas pressure. This result is the same as that we reported for the excimer lasers [14, 15]. We chose this pressure range due to the fact that the nanoparticles were easily collected in these conditions. The above results also demonstrates that it is more convenient to control the sizes of the nanoparticles accurately by changing the carrier-gas pressure than by changing the laser power density.

It is very significant to compare the differences between laser ablation of metal wires and of bulk targets. We conducted an experiment by laser ablation of a bulk Fe target with the size of $60 \times 50 \times 6\,mm^3$ in the same chamber. The results demonstrated that the threshold value of the power density for laser ablation of metal wires (with the diameter of 0.5 mm) is $0.88 \times 10^6\,W/cm^2$, while that for laser ablation of bulk targets is about $1.9 \times 10^6\,W/cm^2$. That is to say, it is much easier to get the nanoparticles with the smaller target sizes. Besides, the experimental results showed that the production rate of γ-Fe_2O_3 nanoparticles by laser ablation of metal wires is about 2 g/h at 400-W output, almost eight times as much as that by laser ablation of bulk targets (about 0.25 g/h at 400-W output). It is significant to point out that the production rates of nanoparticles by laser ablation of metal wires are much higher than those by laser ablation of microspheres reported by Keto et al. [6–10].

Table 3 shows the statistical data comparison of the nanoparticles prepared by laser ablation of a Fe wire and a Fe bulk sample. In all the conditions, the ambient was the mixed gas of 0.18 MPa N_2 and 0.02 MPa O_2, and hence we can get γ-Fe_2O_3 nanoparticles. The results demonstrated that the target sizes have no big effect on the sizes of the γ-Fe_2O_3 nanoparticles, although the production rate has been enhanced greatly.

It is significant to discuss the mechanism of nanoparticle formation during laser ablation of metal wires. When irradiated by a laser beam, the tip of an iron wire is heated to a high temperature in a very short time, and intense explosive evaporation occurs to generate atoms, ions, and clusters of iron, which react with oxygen of the flowing carrier gas and form many nuclei particles. The nuclei particles collide with each other and form nanoparticles. With the high pressure of the carrier-gas flow, the collision time (or the average free distance) of the nuclei particles is reduced, and hence smaller nanoparticles are generated.

It is very important to explain the reason why the sizes of the nanoparticles decreased with the increase of the laser power density by laser ablation of metal wires, and why the sizes of the nanoparticles increased with the increase of the laser power density by laser ablation of bulk Fe material. As far as laser ablation of bulk Fe is concerned, the plume can only be evaporated along the normal direction of the bulk target surface. The bigger the power densities, the more Fe atoms evaporated from the surface of the target, and therefore the more intense the plume's density, which increased the colliding chance of the cluster and resulted in the growth of the nanoparticles. As far as laser ablation of Fe wires is concerned, however, the volume of the wire tip is limited, that

Target shape	Power density ($\times 10^6$) W/cm^2	Number	Diameter Mean (nm)	Min (nm)	Max (nm)	σ (nm)	$\alpha = \sigma$ /diameter
Ø 0.5 mm Fe wire	10	870	24.7	5	80	12.2	0.49
Fe bulk sample	25	740	24.6	5	80	11.3	0.46

TABLE 3 Comparison of statistics of nanoparticles prepared by laser ablation of Fe wire and Fe bulk sample

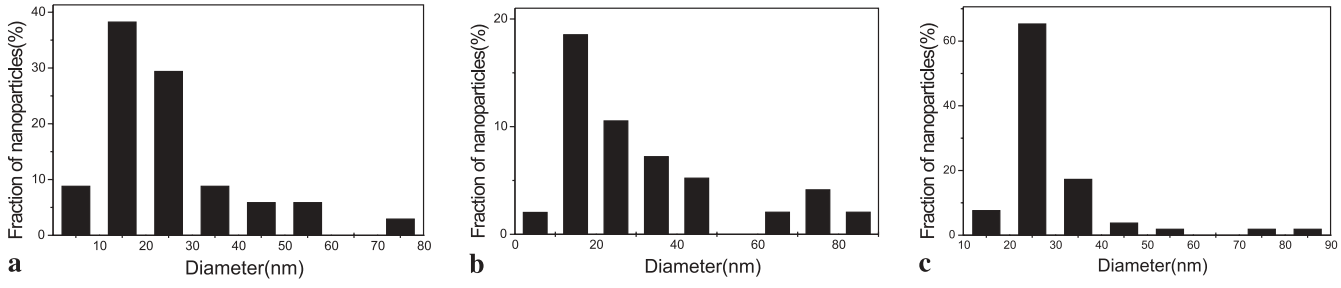

FIGURE 4 Size distributions of γ-Fe_2O_3 nanoparticles prepared at different laser power densities. **a** $4.5 \times 10^6\,W/cm^2$, **b** $6.8 \times 10^6\,W/cm^2$, and **c** $10 \times 10^6\,W/cm^2$

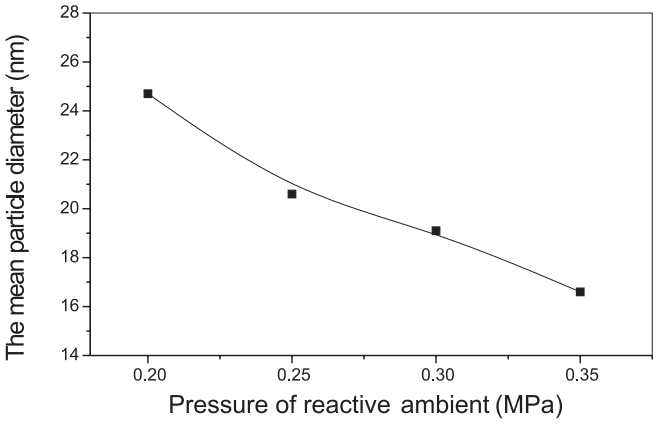

FIGURE 5 The relationship of total pressure of reactive ambient with the mean particle diameter at a laser power density of 10×10^6 W/cm^2 and a fixed oxygen pressure of 0.02 MPa

is, only the tip was irradiated by the laser beam and evaporated each time. The bigger the laser power density, the more rapidly the wire tip evaporated, and the lower the plume density, which increased the average free distance of the cluster and finally resulted in the smaller size of the nanoparticles. According to this principle, the bigger the power density and/or the smaller the diameters of the metal wires, the smaller the nanoparticles generated. This conclusion is very useful for determining how to get smaller nanoparticles.

Finally, it should be pointed out that the wire-feeding rate is not an important parameter to affect the quality and sizes of the nanoparticles; the wire-feeding rate only needs to match the laser power and repetition rate.

4 Conclusions

In summary, we have developed a new method for generating γ-Fe_2O_3 nanoparticles by pulsed laser ablation of a tiny iron wire. The threshold value of laser ablation of tiny wires is much lower than that of laser ablation of bulk materials, and the production rate of laser ablation of tiny wires is eight times that of laser ablation of bulk targets. The sizes of the nanoparticles were in the range of 5 to 90 nm, basically the same as those prepared by laser ablation of bulk materials. This technique is expected to be able to prepare nanoparticles of any material that can be drawn into wires.

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