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Efficient Extraction of Iron Metallic Nanopowders from Thin Films Prepared by Physical Vapor Deposition Technique

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Abstract
In this work, the effects of different extraction parameters on the particle size of the nanopowders extracted from metallic iron thin film samples were studied. These films were deposited by the dc magnetron sputtering, which is one of the physical vapor deposition (PVD) techniques. These nanopowders were obtained by the conjunctional freezing-assisted ultrasonic extraction method. Results showed that extraction parameters such as freezing temperature, ultrasonic frequency and application time are very effective in determining the nanoparticle size, which is very important for many applications and uses of highly-pure nanomaterials and nanostructures.

Keywords: Nanopowders; Nanoparticles; Physical vapor deposition; Iron
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1. Introduction

Typical breakthroughs in spectroscopic and photonic applications are continuously satisfied when highly pure nanomaterials are employed. For example, titanium dioxide nanoparticles can be perfect nanophotocatalysts (NPCs) when no other material exists in the fabricated device as this quantum activity is individually attributed to the titanium dioxide [1,2]. Similarly, quantum dot photonic devices (QDPDs) are critically sensitive to the presence of any material with the active nanomaterial [2,3]. Hence, the small contribution may result in a big effect on the device operation. Accordingly, measurements and characterization tests should be carried out with as much as possible guarantee that the prepared nanomaterial is highly pure [4]. Minimizing the probability of existing substrate's material in the extracted material makes any method or technique with such advantage most preferred in nanomaterials and nanotechnology. Unfortunately, mechanical methods cannot overcome this problem for accurate structural and spectroscopic applications [5]. Thermal methods are obviously avoided because the consequent increase in nanoparticle size is not desired at all [6]. Chemical methods are also avoided because they definitely include some reactions with tiny particles forming very large area (nanosurfaces) [7].

A recently invented method – known as conjunctional freezing-assisted ultrasonic extraction method – submits a highly efficient tool to get nanopowders from thin film samples without any probability to detect residual from substrate's material in the final product. However, the operation parameters of this method can reasonably affect the nanoparticle size. Therefore, further more typical jumps can be made in nanomaterials and nanotechnology as the nanoparticle size is sufficiently controlled [8].

In this work, the effects of some operation parameters of conjunctional freezing-assisted ultrasonic extraction method, such as freezing temperature, ultrasonic frequency and application time, on the particle size of extracted nanopowders are studied.

2. Experimental Part

A homemade dc sputtering system employing a closed-field unbalanced dual magnetrons (CFUBDM) assembly was used to deposit nanostructured thin films on nonmetallic substrates. This system was used to prepare thin films from several elemental and compound materials, such as iron (Fe), silver (Ag), copper (Cu), nickel (Ni), iron oxides, copper oxides, nickel oxide (NiO), silicon nitride (Si_3N_4), silicon dioxide (SiO_2), and titanium dioxide (TiO_2) [9-13]. The operation parameters and preparation conditions of these samples were separately optimized. More details on the specifications and operation of this system can be found elsewhere [14,15].

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Highly-pure (99.99%) iron sheet was used as a sputter target to be maintained on the cathode of the discharge system. Argon gas is used to generate discharge plasma. The discharge electrodes could be cooled using a cooling system employing water as a coolant. The crystalline phase of iron nanostructures could be determined by controlling the operation parameters of magnetron sputtering system, especially gas pressure and anode temperature. Iron nanostructures were prepared using 0.5 mbar Ar gas and a heat sink under the substrate on which the thin film is deposited. Without cooling, the anode temperature might reach 150-180°C. Using electrical heater on the anode can raise its temperature to 400 °C, which sufficiently induces the anatase structures to convert into rutile completely.

As the deposition time is varied, the thickness of the prepared film is proportionally varied. Film thickness was measured by laser-fringes method. The nanopowder was extracted from thin film samples by the conjunctional freezing-assisted ultrasonic extraction method. Full description and specifications of this method can be introduced in reference [8] and schematically shown in Fig. (1). The structural properties of the extracted nanopowders were determined by x-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, field-emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM).

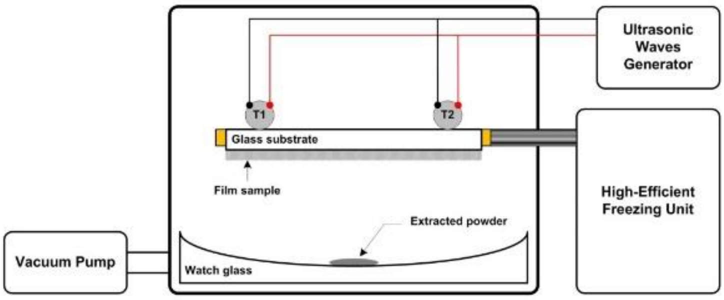

Fig. (1) Schematic diagram of the experimental setup of the conjunctional freezing-assisted ultrasonic extraction method used in this work [8]

Table (1) Experimental results of the elemental iron powders extracted from their films deposited by different physical vapor deposition techniques

Sample	Deposition method	Film particle size (nm)	Powder particle size (nm)	Ultrasonic Frequency (MHz)
Fe	Magnetron Sputtering	20	20	11.0
Fe	Pulsed-Laser Deposition	15	15	10.8
Fe	Thermal Evaporation	25	30	12.0

3. Results and Discussion

Figure (2) shows the variation of nanoparticle size of the three different samples prepared in this work with the deposition time, which determines film thickness. As the deposition time is increased, the film thickness is increased and hence the layers of the thin film are further grown. This growth results the grains to get larger as observed in this figure.

As the nanopowders were extracted from the thin film samples using the conjunctional freezing-assisted ultrasonic extraction method, the effect of freezing temperature on the value of ultrasonic frequency at which the nanopowder was completely extracted is shown in Fig. (3). As the freezing temperature is decreased, lower frequency is required to extract the nanopowder because lower freezing temperature lead to further shrinkage of the nonmetallic substrate and hence the adhesion of the film to the substrate gets lower.

It is clear that the values of ultrasonic frequencies required for the extraction of nanopowders are relatively convergent regardless the grown phase of iron oxide.

The variation of nanoparticle size with the ultrasonic frequency at which the nanopowder was extracted for the iron nanostructures prepared in this work is shown in Fig. (4). As the thin film is typically composed of at least several layers of iron oxide particles, higher ultrasonic frequency can vibrate atoms in different layers and hence extract larger particles.

The time taken to apply the ultrasonic waves to the thin films sample before the extraction of nanopowder was completed is an effective parameter. Accordingly, the variation of nanoparticle size with application time at frequency of 10.8-12 MHz is shown in Fig. (5) for the iron thin films. It is clearly observed that the particle size of the extracted nanopowder does not show large differences for application times from 30 to 210 minutes. This is attributed to the fact that particles of certain size are extracted by ultrasonic waves of given frequency regardless the application time. Extraction of particles containing molecules from different layers within the thin film is carried out at certain range of sizes as a function of ultrasonic frequency. Larger particles are extracted due to their further growth within the deposited film.

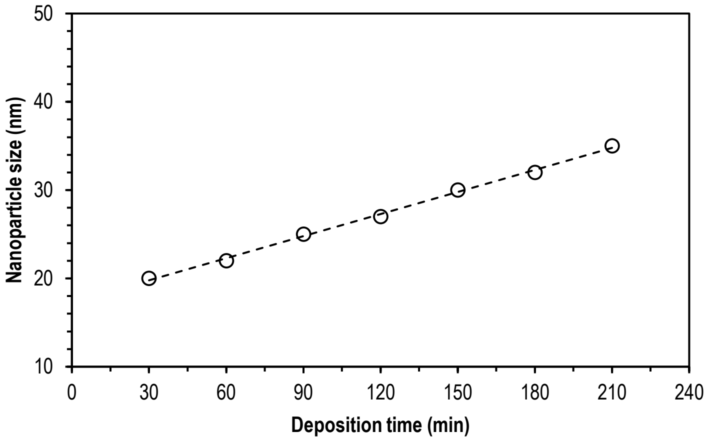

Fig. (2) Variation of nanoparticle size with deposition time for the iron oxide nanostructures prepared in this work

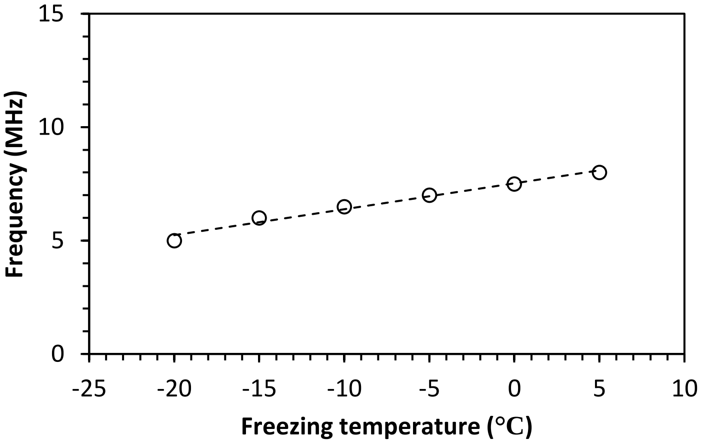

Fig. (3) Variation of ultrasonic frequency with freezing temperature for the iron oxide nanostructures prepared in this work

As the extraction method mainly depends on the freezing stage, the freezing temperature may be very effective in determining the particle size of the extracted nanopowder. Figure (6) shows the variation of nanoparticle size with freezing temperature for the iron samples prepared in this work.

It was mentioned before that the lower freezing temperature leads to larger shrinkage in the substrate on which the thin film is deposited and hence the adhesion between the film and the substrate gets lower and the film surface breaks earlier at the same value of ultrasonic frequency. Accordingly, larger particles can be extracted from the thin film before partitioning into smaller ones. In contrast, freezing to relatively higher temperatures leads to smaller shrinkage in the substrate and the adhesion between the film and the substrate gets higher. Therefore, the application of ultrasonic waves can extract iron particles from the upper surface layer of the thin film, which means smaller particles. Layer-by-layer extraction at higher freezing temperatures produces smaller nanoparticles when compared to the case of lower temperatures.

According to the results obtained from this work, the principle of the conjunctional freezing-assisted ultrasonic extraction method can be shown in Fig. (7). The thin film layers are typically deposited on the substrate as shown in Fig. (7a) as each single layer may contain nanoparticles or molecules of the thin film material. Freezing of the prepared sample causes the nonmetallic substrate to shrink faster than the thin film and as soon as the temperature of the sample rises, the substrate again expands faster than the thin film. Therefore, their dimensions get different and the film surface is broken to form islands over the surface of the substrate. These islands keep adhered to the substrate surface at some points with loosen terminals, as shown in Fig. (7b). Strong vibration of these islands may soon extract large parts, as shown in Fig. (7c), while the weak vibration may extract smaller parts over relatively long time of application ultrasonic waves, as shown in Fig. (7d).

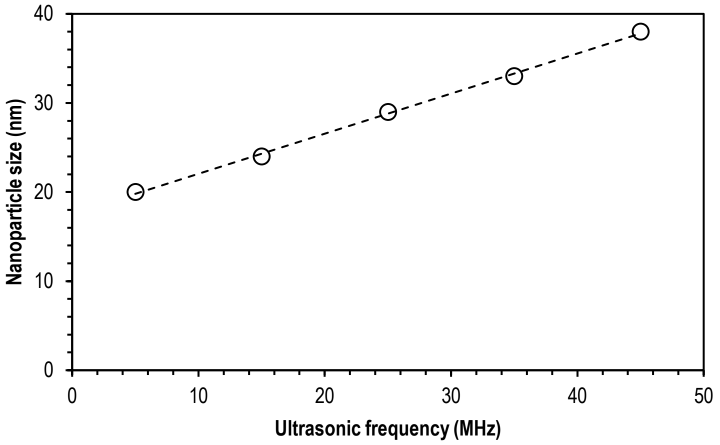

Fig. (4) Variation of nanoparticle size with the ultrasonic frequency for the Fe nanopowders prepared in this work

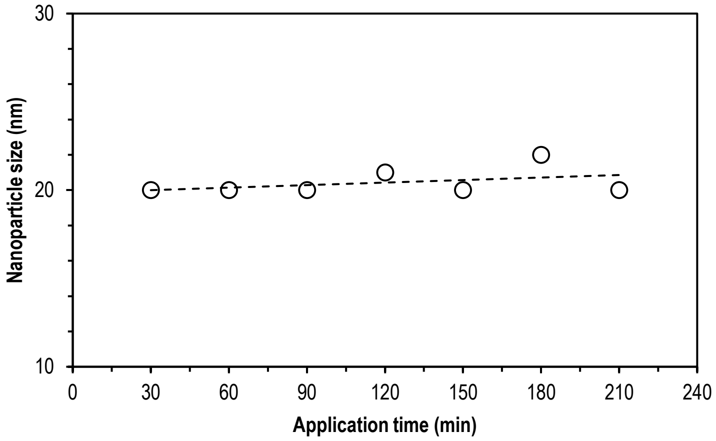

Fig. (5) Variation of nanoparticle size with application time of ultrasonic waves for Fe nanopowders prepared in this work

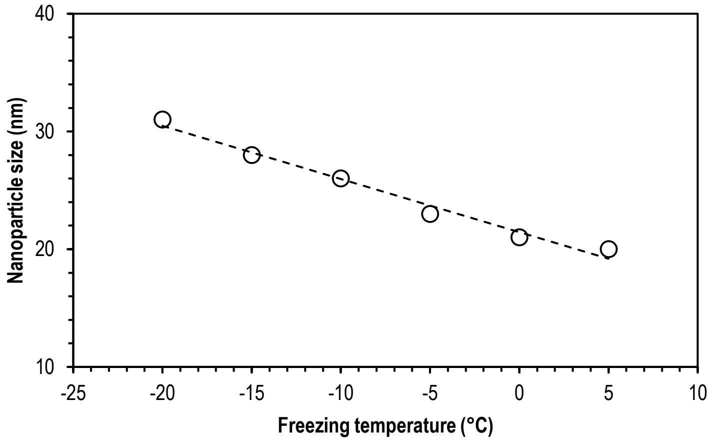

Fig. (6) Variation of nanoparticle size with the freezing temperature for the Fe nanopowders prepared in this work

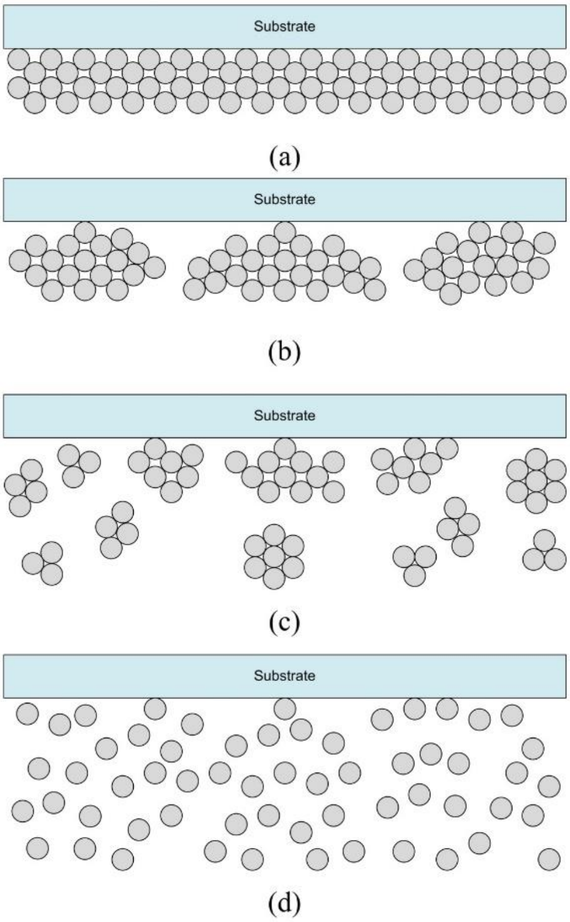

Fig. (7) Schematic representation of the conjunctional freezing-assisted ultrasonic extraction method

From the results graphically shown in Fig. (8), we can observe that the metallic iron powders can be extracted from their deposited films prepared by magnetron sputtering (MS) or pulsed-laser deposition (PLD) without increasing the particle size compared to the particle size of the film deposited by thermal evaporation (TE), which exhibited an increase in the particle size. Some PVD techniques, such as PLD and magnetron sputtering, do not cause an increase in the nanoparticle size, which may be attributed to the fact that no clustering or aggregation occur. Samples prepared by magnetron sputtering (MS) were the best to keep the nanoparticle size of the extracted powder comparable to that of the film from which the powder is extracted. This feature may be attributed to the high uniform adhesion of deposited films on the substrates. As well, the particle density for the films prepared by magnetron sputtering is extremely homogeneous when compared to other physical vapor deposition methods [28-32]. Pulsed-laser deposition (PLD) exhibited rather lower quality than magnetron sputtering but reasonably better than other methods and techniques.

4. Conclusion

As conclusions, freezing temperature, ultrasonic frequency and the time taken to apply ultrasonic waves on nanostructured thin films deposited on nonmetallic substrates are very effective to determine the nanoparticle size of nanopowders extracted from these thin film samples. The conjunctional freezing-assisted ultrasonic extraction method can be successfully used to extract highly-pure nanoparticles with approximately the same size of nanoparticles in the thin films deposited by physical vapor deposition methods and techniques. This technique is reliable, efficient and low cost to produce highly-pure nanomaterials with as low as possible particle sizes.

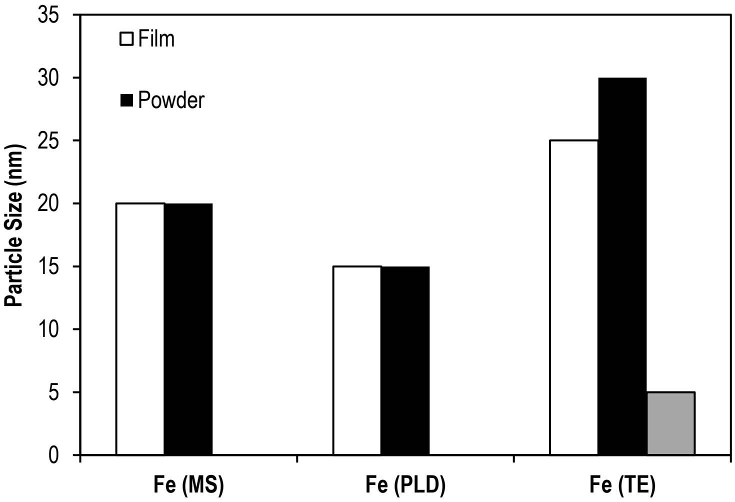

Fig. (8) Nanoparticle sizes of iron film and powder samples prepared by different deposition methods

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