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主 論 文 の 要 旨

論文題目　**Nanomaterials Fabrication by using Pulsed Laser Ablation with Sonochemistry in an Aqueous Environment for Composite Materials**
(液相レーザーアブレーションとソノケミストリーを用いた複合材料用ナノ材料の作製)

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論 文 内 容 の 要 旨

1. Nanomaterials

Nanomaterials have gotten a lot of attention as an interesting and novel class of materials with a wide variety of practical applications. The length of one nanometer could be known by lining up three calcium atoms or five sulfur atoms, which equals one nanometer. If the size of materials is in the range of 1 – 100 nm, there are classified as nanomaterials [1]. The physicochemical characteristics of nanomaterials differ from those of bulk materials, which are essentially dependent on their size and form. It is difficult to clarify the exact time of the first utilization of nanosized materials by humans. However, even in the fourteenth and thirteenth centuries BCE, the starting of glassmaking in Mesopotamia and Egypt appears to have begun. Actually, as revealed by many chemical investigations done on these historical treasures, the red color in some glasses is explained by the presence either of cuprous oxide nanoparticles or metal copper nanoparticles [2]. The application of metal nanoparticles was also found in a piece of Roman glass art, the Lycurgus Cup, which is produced in the fourth century CE and exhibited in the British Museum in London [3]. With the development of science and technology, nanomaterials have been applicated in a variety of areas, such as electronics, energy, biomedicine, environment and food. Lee et al. [4] have reported that nano-carbon materials such as graphene and carbon nanotubes (CNTs) have a huge potential to replace silicon as a material for producing faster, smaller and more efficient microchips and electron devices because of excellent elastic properties as well as the outstanding combination of electronic and thermal property compared to conventional silicon material. Besides, in the food industry, Mustafa et al. [5] have found that nanomaterial-based sensors provide the opportunity to detect contamination in the food rapidly. Several types of nanomaterial have been utilized in the food packaging area to extend the shelf-life of foods and inhibit the growth of the bacterial [6].

Among the nanomaterials, nanoparticles (NPs) have attracted a lot of interest in recent years. The particles that range in size from 1 to 100 nanometers can be called NPs, which are almost made up of metal, carbon, metal oxides or organic substances [7]. Compared with their bulk particles at a larger size, NPs exhibit novel physical, chemical and biological properties as a result of a comparatively larger surface area to the volume, enhanced mechanical property and improved stability and reactivity in a process [8]. The unique properties of NPs have led to their application in various areas, such as medicine, affordable and clean energy, catalysis and electronics. Huo et al. [9] have investigated that gold NPs can be utilized to construct biosensors, such as immunosensors, enzyme sensors and DNA sensors, due to the excellent ability to immobilize biomolecules. In addition, as a result of the antibacterial property of silver NPs, they have been utilized to control the growth of bacterial in various areas, such as dental work, biomedical devices and tissue engineering [10]. With the continuous research on nanomaterials, nanotechnology will gain a great future because of its huge potential to change the environment and even the lifestyle of people.

2. Laser Ablation

There are plenty of manufacturing methods and tools utilized for the fabrication of nanomaterials. Each manufacturing method has benefits and drawbacks. Among these methods, laser-assisted fabrication of functional nanomaterials is unquestionably one of the most important methods. Laser, which means a very narrow beam of light, has been widely applicated in a lot of technologies and instruments since it was first invented by Theodore H. Maiman at Hughes Research Laboratories [11]. The letters in the word laser represent Light Amplification by Stimulated Emission of Radiation. Actually, laser ablation is a technique for ablating solid target materials by utilizing a laser as the energy source. In the ablation process, incredibly high energy is concentrated at a particular point on the surface of the solid to evaporate the light-absorbing material. Not only a single photon process (breaking the chemical bonds) but also multiphoton excitation (thermal evaporation) can occur in the process of removing the atoms of the absorbing material, which generates high-purity nanoparticles [12]. Generally, the purity of the target material and surrounding environment (vacuum, gas or liquid) can determine the purity of the fabricated nanoparticles. And the size distribution, crystal structure and agglomeration of the produced nanoparticles are difficult to control due to the complex process of laser ablation [13]. In the laser ablation process. The temperature of the irradiated spot rapidly rises when the laser is focused on the surface of a solid target to vaporize the target material. Collisions between evaporating species (atoms and clusters) and surrounding molecules cause light emission, electron state excitation and the production of electrons and ions, resulting in the generation of a laser-induced plasma plume [14]. The parameters in the process, such as laser parameters, the target material, ambient environment (vacuum, gas or liquid), ambient temperature and pressure, all have an impact on the property of the generated plasma plume. Garrelie et al. [15] have researched the influence of the ambient gas nature and pressure on the laser-induced plasma plume by Monte Carlo simulation and found a huge difference when utilizing different gas as the ambient media (argon and krypton atmosphere). The generated clusters aggregate into nanoparticles, which was then formed nanoparticles chains. The reason may be that the primary nanoparticles adhere to each other during the plume expansion, resulting in the generation of different structures of materials ranging from spherical particles to line nanostructure [16].

The ambient environment can have a huge impact on the fabricated nanomaterials. Generally, since 1965, Smith et al. [17] have studied pulsed laser deposition (PLD) in the vacuum chambers to fabricate the thin film. In the process of PLD, the materials are vaporized from the target solid under the atmosphere of ultrahigh vacuum or in the presence of the background gas to generate the plasma plume, which is subsequently deposited on a substrate and changes to a thin film. This method has been successfully utilized to generate a variety of thin films with an excellent crystalline quality, such as metallic multilayers, ceramic oxides, polycrystalline as well as nitrides [18]. As for the fabrication of the thin films, compared to other methods (metal-organic chemical vapor deposition or molecular beam epitaxy), PLD has a relatively lower cost and the crystalline quality of the fabricated product is higher [19].

With the rise of nanotechnology, laser ablation (LA) has been widely utilized for the fabrication of nanoparticles. Firstly, LA is usually combined with the vacuum chamber. Amoruso et al. [20] have reported the successful generation of silicon nanoparticles with the size of 5-25 nm by LA of silicon targets in the vacuum. Nevertheless, apart from that the LA in the vacuum is an adaptable method to prepare for the nanomaterials, advantages of this method are mainly the broad size and concentration distribution of the fabricated nanoparticles [21]. LA in different ambient gases such as argon, helium and nitrogen has been utilized to improve the production rate and decrease the size of the fabricated silver nanoparticles [22]. It was found that silver nanoparticles can be fabricated and controlled in the range of 4-20 nm by choosing the appropriate type and pressure of the gas. The mean size of silver nanoparticles increased with the increasing molecular weight of the ambient gas and decreased with increasing gas pressure. After various research on the LA in the vacuum and ambient gas, the researchers started trying to change the ambient media to the liquid. Patil et al. [23] firstly reported utilizing LA in liquid to fabricate a metastable product of iron oxide by ablating a pure iron target material in 1987. LA in liquid has been utilized to fabricate nanoparticles as a fungible chemical method since the LA in liquid is regarded as a cleaner and more simple process. The nature of the liquid media has a huge impact on the fabrication of the nanoparticles. For example, Mohammad et al. [24] have found that compared to acetone and distilled water, utilizing ethanol as the ambient media in the LA process can right in the generation of smaller nanoparticles as well as narrow size distribution. A variety of researchers have studied the fabrication of several types of nanoparticles by using LA in the distilled water [25, 26], acetone [27, 28], sodium dodecyl sulfate (SDS) [29, 30], polyvinylpyrrolidone (PVP) [31, 32], liquid nitrogen solutions (LN) [33], ethanol and ethylene chloride [34-36]. Although, the ambient media of LA process can be vacuum and gas, which has been widely developed, the advancement of the methods performed in the liquid media has been of the greatest interest to researchers. Deionized water is also the best medium for generating nanoparticles.

3. Sonochemistry

Sonochemistry, which means molecules undergo chemical reactions as a result of the utilization of powerful ultrasonic irradiation at the frequency of 20 kHz to 10 MHz, has been widely applicated to fabricate nanomaterials [37]. The phenomenon of acoustic cavitation is responsible for the sonochemical effects in liquids. When applicating ultrasonic waves in the liquid media, it can generate a pattern of compressions and rarefactions that exert positive and negative pressure to the liquid phase. This can push or pull molecules together or away from one another in the liquid and generate plenty of bubbles. Within a few microseconds, the growth and immediate collapse of the bubbles in the liquid can generate local special hot spots with high temperatures (up to 5000 ℃) and pressures (exceeding 500 atm) [38]. In addition, the formation of shock waves and micro-jets exceeding 400 km/h also occurs [39]. The sonochemistry method has been one of the earliest techniques to fabricate nanomaterials due to its simplicity of utilization, fastness, and environmental benefits [40]. There are various nanomaterials fabricated by sonochemical synthesize, such as gold nanoparticles [41], iron nanoparticles [42], ZnO nanosized oxides [43] and so on. In addition, sonochemistry is an outstanding method for coating the surface by forming a smooth layer of the coated materials. Gnanaraj et al. [44] have successfully coated $LiMn_2O_4$ with MgO sonochemically.

4. Motivation and Purpose of the Present Work

This work focused on the fabrication of metal nanoparticles by utilizing pulsed laser ablation and sonochemistry. Various parameters which affect the fabricated nanoparticles have been researched to find the optimal conditions. In addition, the fabricated nanoparticles also are further applicated as the source of composite nanomaterials.

The content is as follows. A brief introduction of nanomaterials, laser ablation and sonochemistry is given in previous paragraphs. In Chapters 2 and 3, a detailed discussion about this work is given, about the fabrication of metal nanoparticles by laser ablation and sonochemical synthesize and the further application of fabricated composite nanomaterials by combining metal nanoparticles with polymers.

5. Chapter 2

Laser ablation in liquid (LAL) is known to be a promising method for synthesizing metal nanoparticles. In this study, gold and silver nanoparticles were fabricated by ultrasonic-assisted LAL. Gold and silver plates were ablated using a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser, with a wavelength of 532 nm and energy of 26.4 J cm^{-2}, in distilled water in the presence and absence of an ultrasonic field. The fabricated nanoparticle colloidal solution was analyzed with an ultraviolet–visible (UV–vis) spectrometer, a transmission electron microscope (TEM) with energy-dispersive X-ray spectroscopy (EDS), and zeta potential measurement. The craters on the silver plates were analyzed by a scanning electron microscope (SEM), a laser microscope, and

MATLAB to observe their morphology and calculate the volume to obtain the concentration of fabricated nanoparticle solution. Optical emissions were observed to study the characteristics of the laser. The results showed that ultrasonic-assisted LAL has considerable potential for fabricating superior metal nanoparticles.

6. Chapter 3

Polyvinylpyrrolidone (PVP) is used in a wide variety of applications because of its unique chemical and physical features, including its biocompatibility, and low toxicity. In this study, hollow PVP/silver nanoparticle (PVP/Ag NP) composite fibers were synthesized. Stable, spherical Ag NPs, with an average size of 14.4 nm, were produced through a facile sonochemical reduction method. A small amount of starch as a potent reducing and stabilizing agent was used during the reduction of Ag ions to Ag NPs. The fabricated Ag NPs were then added to a 10 wt% PVP-dichloromethane (DCM) solution, which was utilized as an electrospinning feed solution under a dense carbon dioxide (CO2) environment at 313 K and 5 MPa and an applied voltage of 15 kV. The dense CO2 enabled rapid extraction of DCM from the PVP-Ag NPs-DCM solution, which was then dissolved into PVP/Ag NPs, resulting in a hollow structure. Scanning electron microscopy, Fourier-transform infrared (FT-iR) spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses, and thermogravimetric analysis (TGA) were used to characterize the electrospinning products.

7. Reference

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