Microwave-assisted synthesis of oleic acid-capped silver nanoparticles as lubricant additives

Ha Quoc Bang*

Institute of Chemistry and Materials, Academy of Military Science and Technology, Cau Giay, Hanoi, Vietnam.

*Corresponding author: haquocbang@gmail.com

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ABSTRACT

Recently, metal nanoparticles have been studied extensively as lubricant additives. Owning to their nanometer size, the nanoparticles can fill micro defects on contacting surfaces, acting as repairing agents. In this work, we describe a simple and fast method to fabricate monodisperse silver nanoparticles using oleic acid as a capping agent. In particular, silver nitrate was reduced by oleylamine in the oleic acid medium using acetonitrile as a co-solvent, and the reaction was heated by a microwave source. Results showed that the particle size was greatly affected by varying the reductant concentration. The average diameter of synthesized nanoparticles ranges from 3.0 nm to 4.0 nm at optimum conditions. The dispersibility in the oil of the product is attributed to the long-chain alkyl from fatty acid grafted on the surface layer, which constitutes about 21% of the weight of the nanoparticles as determined by thermogravimetric analysis.

Keywords: Silver nanoparticles; Lubricant additive; Capping agent; Oleic acid; Oleylamine.

1. INTRODUCTION

Metallic silver nanoparticles (AgNPs), which display physicochemical properties different from their bulk counterparts, have been intensively studied for applications in multiple areas. Besides the most common use as anti-bacterial agents in the health industry, food storage [1], and other environmental purposes [2], AgNPs have been applied in different fields for their excellent electrochemical, catalytic, optical, and tribological characteristics [3]. In the lubricant industry, metal NPs have advantages over conventional additives because these organic substances need time to react with the contact surface to make an anti-friction layer. Another benefit of metal NPs is their ability to fill up the microdefect on friction surfaces, acting as a repairing agent [4]. Also, the higher thermal conductivity of metal NPs contributes to the dissipation of heat generated by friction.

The properties of the AgNPs strongly depend on the size, homogeneity, and morphology of the crystal, which can be controlled by synthesis methods. Among several chemical approaches for the fabrication of Ag nanoparticles, reduction is the most frequently applied method. Commonly used reductants are citrate [5], ascorbate [6], and borohydride [7]. It is well-known that reaction rate has a crucial effect on particle size: the faster the reaction, the smaller the NPs. So, elevated temperature and strong reductants are often associated with the synthesis of monodisperse AgNPs. But even strong reductants such as borohydride can’t completely prohibit the formation of larger particles. So, to further control the NP's size, a surfactant, called a capping agents, is added to limit the crystal growth. These agents bind to the particle's surface, avoiding aggregation and making the NPs dispersable in desired solvents.

In this paper, we report a simple and fast method to produce uniform nano-sized Ag particles that can be dispersed in the oil phase by using oleic acid as solvent and capping agent. Oleylamine, a long-chain amine that can act as an electron donor at elevated temperatures and is miscible with oleic acid, was selected as a reductant. With the microwave-assisted, the reaction rate was drastically improved, narrowing down the particle size distribution. The effect of reductant proportion and reaction time on the size of Ag nanoparticles was carefully investigated. As the long-chain hydrophobic ankyl group

grafted on the AgNPs surface, the product showed excellent dispersibility in oil.

2. EXPERIMENTAL

Materials and method

Silver nitrate ($AgNO_3$) 99%, sodium hydroxide (NaOH) 96%, ethanol (C_2H_5OH) 99.7%, and acetonitrile (CH_3CN) 99% were purchased from Xilong, oleic acid ($C_{17}H_{33}COOH$), oleylamine ($C_{18}H_{35}NH_2$) were purchased from Macklin, China.

The synthesized AgNPs were characterized using X-ray diffraction (XRD) with CuKα radiation (λ = 1.5406 Å), 40 KV, and 40 mA in the range of 2θ from 5 to 90^o on Ccrystal impact, Bonn. Then, lattice parameter and crystal size were calculated using the Debye Sherrer formula, Fourier transform infrared (FT-IR) using Nicolet iS10 with a scan range of 400-4000 cm^{-1} to identify the functional groups. Morphology of the materials was observed using Scanning electron microscopy (SEM) on Hitachi-S-4600. Thermogravimetric analysis was measured by NETZSCH STA 409PC/PG up to 800 °C at heating rate of 10 °C/minute.

Synthesis of Ag nanoparticles

The silver nanoparticles were produced by reducing silver precursor with oleylamine in an oleic acid medium. In this process, oleic acid served the dual purpose of acting as a solvent and a capping agent. Because of its miscibility with oleic acid and containing an electron donor group, oleylamine was chosen as a reducing agent. Silver nitrate is not soluble in fatty acid, so acetonitrile was used as a co-solvent. In a typical procedure, 0.01 mol silver nitrate was dissolved in 5 mL acetonitrile, then 20 mL oleic acid was added, and the mixture was stirred for 30 minutes. After that, oleylamine at different proportions was added and stirred for another 30 minutes. The mixture was then transferred to a conventional microwave oven and heated for three minutes at the power level of 800 W. A similar process was performed to make a sample without using the co-solvent acetonitrile.

After the microwave heating process, ethanol was added to attenuate the solution. The thinning effect of ethanol made the AgNPs easier to separate from oleic acid. The product was retrieved by centrifugation, washed with ethanol several times, and finally vacuum dried at 60 ^{o}C for 12 hours.

Tribological properties of synthesized AgNPs

To evaluate the lubricating effect of the AgNPs, the obtained nanoparticles were dispersed in SN500 base oil to examine their compatibility and tribological characteristics. The concentration of added AgNPs was set from 0,01 to 0,04 g/L, and the lubricant oil's extreme-pressure properties were tested using the four-ball method at rotating speed 1760 rpm(ASTM D2783-03). Anti-wear improvement of the AgNPs was calculated by percentage between improved weld point value over weld point of sample without the additive.

3. RESULTS AND DISCUSSION

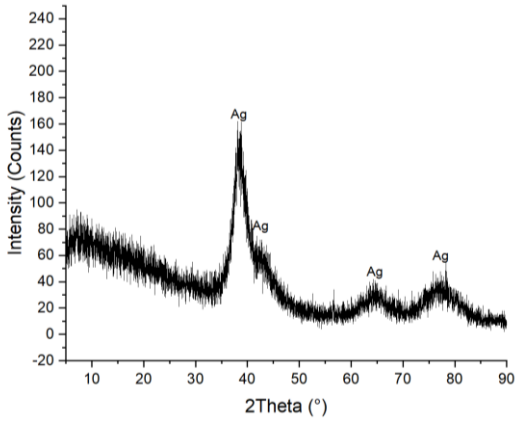

Figure 1. *XRD pattern of synthesized AgNPs at oleylamin/$AgNO_3$ at 2/1.*

To identify the phase composition of the product, the sample at oleylamine/Ag nitrate molar ratio 2/1 and reaction time of 3 minutes was characterized by PXRD (figure 1). In the pattern, it can be seen that The lattice parameter of synthesized silver nanoparticles at various hydrothermal times and different pH was determined by the PXRD (figure 1). In the figure, it can be seen the diffraction peaks at 2θ angles of 38.1°, 44.3°, 64.4°, and 77.4°, which correspond to silver metal characteristic peaks of (111), (200), (220), (311) crystal faces. Because no other peaks were detected, it can be concluded that the phase is pure, and no other silver substance was created.

It can be seen that the peaks are broad relative to their intensity, to the point where peaks at 38.1° and 44.3° are overlapping, indicating that the crystal size is in the nanoscale. Using the Debye Scherrer formula for the highest intensity peak at 31.8° of AgNPs, the calculated average crystal sizes are in the range of 3 nm. The results proved that at elevated temperatures, oleylamine can reduce silver precursor to silver metal.

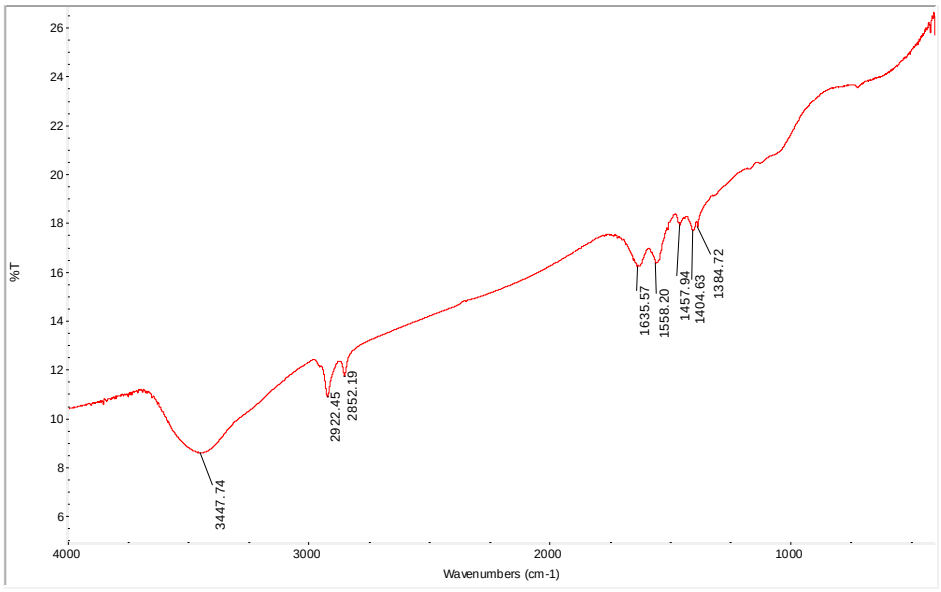

Figure 2. *The FTIR spectrum of AgNPs at an oleylamine/silver nitrate ratio of 2:1.*

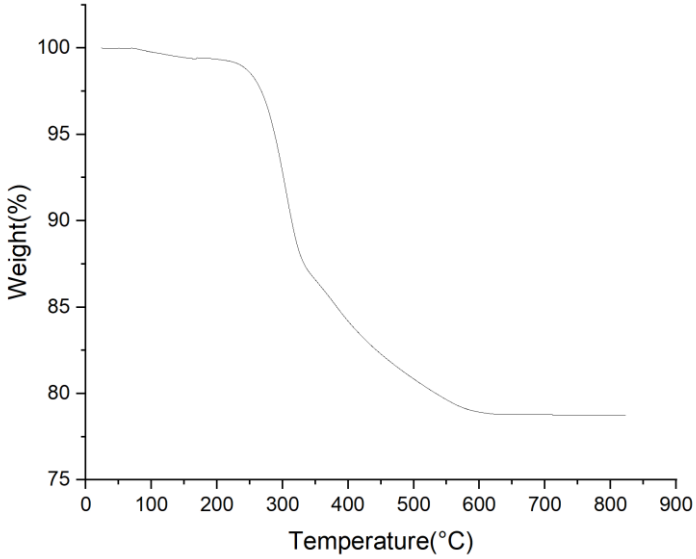

Figure 3. *Thermogravimetric analysis of as-prepared oleic acid-capped Ag nanoparticles.*

In the FT-IR spectra of AgNPs at oleylamine/$AgNO_3$ ratio 2:1 (figure 2), the characteristic vibration of -OH stretching can be found at ~ 3450 cm^{-1}. The peaks 2922 cm^{-1} and 2852 cm^{-1} could be assigned to methylene (-CH_2-) asymmetric and symmetric stretching, respectively. The absence of the same stretching vibration of methyl group (-CH_3) can be explained that the number of methyl groups in oleic acid is quite small compared to methylene groups (1:14). The peaks 1635 cm^{-1} could be assigned to the double bond (-C=C-) stretching. The band at 1558 cm^{-1} corresponds to asymmetric carboxylate stretching, while the lower region is attributed to symmetric carboxylate vibration.

The thermogravimetric analysis of optimal AgNPs samples was carried out, and the results are shown in figure 3. Meanwhile, there is an insignificant change in the weight at low temperatures, the mass of oleic acid-capped AgNPs drastically reduced at elevated temperatures. The weight loss is attributed to the thermal decomposition of oleate groups grafted on the Ag nanoparticle surface. It can be seen that at 300 °C, the pyrolysis of the alkyl chain started to happen. The absence of weight loss at about 100 °C, which is caused by the evaporation of water, showed that there is no water in any of the samples, indicating their hydrophobicity. At 600 °C, the weight stops decreasing, meaning the alkyl groups are completely calcined. The final weight of the sample is equal to 78.7% of the original, so the amount of oleic acid grafted on the AgNPs surface constitutes about 21% of the whole sample.

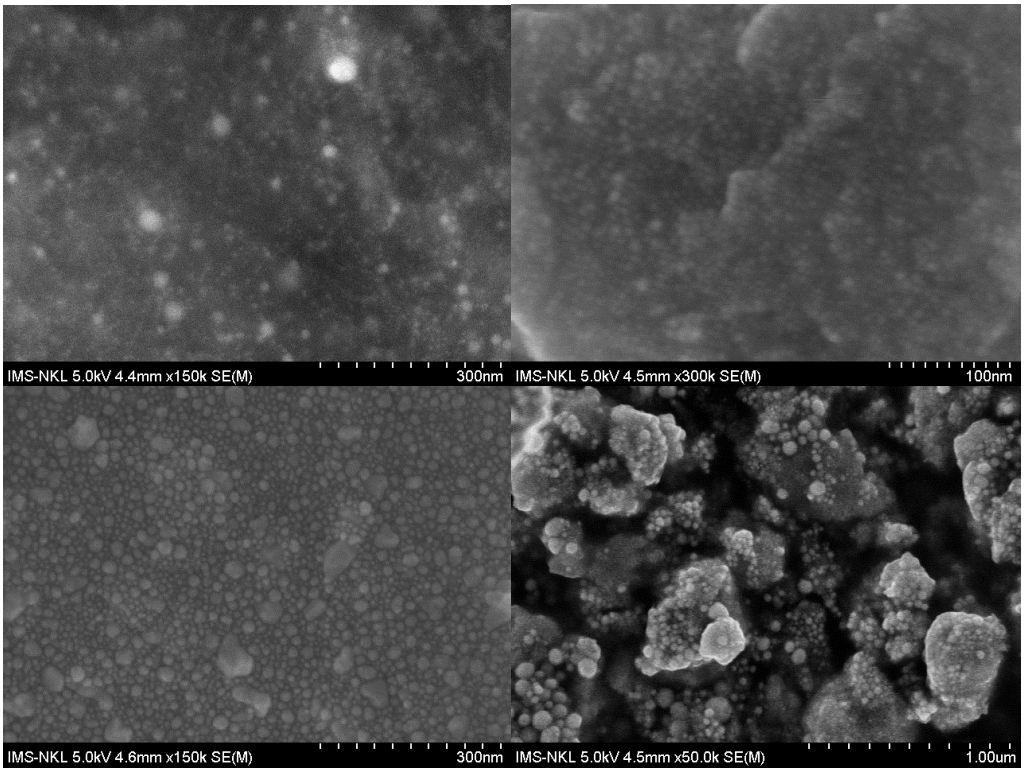

Figure 4. *The SEM images of AgNPs at different synthesis conditions: (a) Oleylamine/$AgNO_3$ ratio 1:1, (b) Oleylamine/$AgNO_3$ ratio 2:1, (c) Oleylamine/$AgNO_3$ 3:1, (d) Without using CH_3CN as co-solvent.*

Because the homogeneity of particles can significantly affect its application, especially in the lubricant field, the morphology and size distribution of synthesized AgNPs were carefully studied. By varying reductant ratios, the silver nanoparticles using various oleylamine concentrations were imaged by SEM and shown in figure 4. Using an equivalent molar of silver source and oleylamine, silver nitrate was reduced but not completely, as can be seen in figure 4a. In the image, there are bigger particles with different shades than the rest. The size of particles also varied greatly,

indicating that silver precursor is not fully reacted. A sample in which the oleylamine amount was twice that of silver nitrate showed the best results (figure 4b). The AgNPs is uniform in shape and size, with a very narrow distribution of 3-4 nm, which agrees with the average size calculated from XRD data. Particles formed at higher reductant proportions are inhomogenous (figure 4c). The heterogeneity of AgNPs morphology is clearer as more oleylamine was used. As the amount of oleylamine increases, the particle size becomes bigger and shows greater diversity in dimension. It can be seen that the co-solvent acetonitrile plays an essential role in the morphology of the product. Without CH_3CN, silver nitrate was not dissolved in oleic acid. As a result, the product was aggregated and had particles formed that were micrometer-sized (figure 4d).

The anti-wear properties of the lubricant oil using synthesized AgNPs as additives were tested by the four-ball method (table 1). The extreme pressure results showed that adding a very small amount of silver nanoparticles into the base oil can significantly improve its anti-wear properties. The more AgNPs content in the oil, the higher the weld point, which means better lubricating ability. The wear-reducing effect of AgNPs was attributed to the converting of sliding friction into rolling friction as these particles slide in between contacting surfaces. The anti-wear improvement effect was almost linear with the added AgNPS content at first. However, as the nanoparticle content increases, their effectiveness lessens. Doubling the amount of AgNPs from 0.02 g/L to 0.04 g/L only improves the anti-wear effect from 12.5 to 15%. Considering the cost of AgNPs production, the content of 0.02 g/L satisfies the usage requirements. The weld point is still low, however in practice, AgNPs is often used in combination with other lubricant additives.

Table 1. *Four-ball test results of lubricant oil using different AgNPs concentration.*

No.	AgNPs content, g/L	Weld point, kg	Anti-wear improvement, %
1	0.00	120	-
2	0.01	128	6.67%
3	0.02	135	12.5%
4	0.03	137	14.17%
5	0.04	138	15%

4. CONCLUSIONS

Oleic acid-capped silver metal nanoparticles were successfully fabricated using oleylamine as a reductant with microwave-assisted heating. The product has a nanoscale crystal size of 3-4 nm and a very narrow size distribution. The homogeneity is attributed to the careful control of the reductant amount and the rapid temperature increase due to microwaves. Analytical results showed that the long alkyl chains were grafted onto the AgNPs and constituted 21% of the weight of the product. Such functional groups are responsible for the hydrophobicity and oil dispersibility of the product. Lubricating oil using synthesized AgNPs as an additive at a contentof 0.02 g/L showed a significant improvement in anti-wear properties.

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TÓM TẮT

Tổng hợp nano bạc gắn axit oleic bằng phương pháp vi sóng ứng dụng làm phụ gia bôi trơn

Trong công trình này, nhóm nghiên cứu công bố một phương pháp nhanh và đơn giản để chế tạo các hạt nano bạc có kích thước đồng đều sử dụng axit oleic làm chất kiểm soát kích thước. Cụ thể, tiền chất chứa bạc được khử bằng oleylamin trong môi trường axit oleic sử dụng chất trợ dung môi acetonitrile và phản ứng được gia nhiệt bằng vi sóng. Kết quả chỉ ra rằng, kích thước hạt thu được bị ảnh hưởng rất nhiều khi sử dụng chất trợ dung môi cũng như khi thay đổi nồng độ chất khử. Kích thước trung bình của hạt nano chế tạo được nằm trong khoảng từ 3,0 nm đến 4,0 nm ở điều kiện tối ưu. Khả năng phân tán tốt trong dầu của sản phẩm là do trên bề mặt có gắn các nhóm ankyl mạch dài của axit béo, chiếm 21% khối lượng của các hạt nano, được xác định bằng phân tích nhiệt. Dầu bôi trơn sử dụng nano bạc chế tạo được làm phụ gia ở hàm lượng 0.02 g/L cho thấy có sự cải thiện rõ rệt về hiệu quả giảm mài mòn.

Từ khóa: Nano bạc; Phụ gia bôi trơn; Axit oleic; Oleylamin.