



POLY (AMIDOAMINE) POLYMER-PROTECTED SILVER NANOPARTICLES THROUGH A RAPID, SINGLE-STEP PREPARATION MICROWAVE-BASED THERMAL PROCESS

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ABSTRACT

The microwave-based thermal process was applied to the preparation of Poly (amidoamine) polymer-protected silver nanoparticles. The formation of silver nanoparticles occurs rapidly in a single step, carried out by directly heating a fourth generation poly(amidoamine) polymer–AgNO₃ aqueous solution in a microwave oven without the introduction of additional reducing reagents and protective reagents. The nanoparticles thus formed were characterized by UV–vis spectra and transmission electron microscopy (TEM). The influence of the molar ratio of poly(amidoamine) polymer to silver on the formation of silver particles was also examined.

Keywords: Poly(amidoamine)polymer; Silver nanoparticles; Microwave irradiation.

INTRODUCTION

Noble metal nanoparticles hold promise for use as advanced materials with novel electronic, optical and thermal properties as well as catalytic properties due to their potential applications in the fields of physics, chemistry, biology, medicine, material science and their different interdisciplinary fields^[1] and thus the synthesis and characterization of such nanoparticles have attracted considerable attention from a fundamental and practical point of view^[2]. Up to now, a variety of preparative methods have been well-established^[3]. Among them, chemical reduction of metal salts in liquid is still the most widely used and convenient route. However, since nanoparticles tend to be fairly unstable in solution, special precautions have to be taken to avoid their aggregation or precipitation. The most common strategy for the formation of stable nanoparticles in liquid is the use of a protective agent, which not only prevents their aggregation, but also results in functionalized particles^[4]. Poly(amidoamine) polymer are a new class of monodisperse macromolecules with regular and highly branched three-dimensional architecture and surface functionality and widely used in the fields of medicinal chemistry, host–guest chemistry, and catalysis^[5]. They were widely used as templates for inorganic nanoparticles and on the other hand, also served as protective reagents to control the growth of nanoparticles by adsorbing at particle surfaces^[6,7]. However, in the above mentioned methods, Poly(amidoamine) polymer were only used as template or protective reagents for nanoparticles and additional reducing reagents were introduced into these reaction systems to reduce metal salts and therefore, two steps were involved in the preparation: firstly, mixing a metal salts solution and Poly(amidoamine) polymer solution; secondly, adding other reducing reagents to such mix solution to reduce metal salts resulting in the formation of Poly(amidoamine)polymer-hosted or protected nanoparticles. More recently, Sun et al. have demonstrated a single-step method for preparing Poly(amidoamine)polymer -protected silver nanoparticles by routine heat treatment of a fourth-generation Poly(amidoamine) polymer-G4–AgNO₃ aqueous solution at 100 °C for 70 min without the additional step of introducing other reducing agents and protective agents^[8]. Compared with routine heat treatment, microwave irradiation is a more efficient heating method and many microwave-based fast, simple, and energy efficient synthetic routes have been developed^[9]. To the best of our knowledge, no work deals with microwave based preparation of Poly(amidoamine)polymer-protected silver nanoparticles. In this letter,

we reported a rapid method for the single-step preparation of stable, Poly(amidoamine)polymer -protected silver nanoparticles by microwave-based heat treatment of a Poly(amidoamine)polymer –G4–AgNO₃ aqueous solution in a microwave oven for several minutes. As formed nanoparticles were characterized by UV–vis spectra and transmission electron microscopy (TEM). The influence of molar ratio of Poly(amidoamine)polymer to silver on the formation of silver particles was also investigated and it was interestingly found that moderate ratio could produce silver nanorods.

EXPERIMENTAL

Poly(amidoamine)polymer G-4 and AgNO₃ were purchased from Aldrich. All reagents were used as received without further purification. The water used was purified through a Millipore system. The silver nanoparticles (sample 1) were prepared as follows: 40 μL of 0.040M Poly(amidoamine)polymer –G4 aqueous solution was introduced into 40 mL of 0.80 mM of AgNO₃ aqueous solution with molar ratio 1:20 of Poly(amidoamine)polymer –G4 to silver, followed by heating the as-formed mix solution in a microwave oven operated at 100% power of 600W for 8 min (based on the experimental fact that the preparation is carried out in an aqueous solution in an unsealed container, the estimated reaction temperature of the sample during the microwave irradiation is ca. 100 °C). UV–vis spectrum was collected on a SHIMAZU2100 Scan UV–vis–near infrared spectrophotometer. Samples for TEM characterization were prepared by placing a drop of silver sample on a carbon coated copper grid and dried at room temperature. TEM measurements were made on a JEOL 2010 transmission electron microscopy operated at an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

Figure 1 shows the UV–vis spectrum of the as-prepared silver nanoparticles in water. The colloidal silver solution thus formed exhibits a strong absorption at 419 nm. Metallic silver is known to have an intense plasmon absorption band in the visible region, and it was confirmed that the Ag 4d to 5sp interband transition generally occurs around an energy corresponding to 320 nm^[10]. The characteristic red shift of the Plasmon absorption band confirms the formation of Poly(amidoamine)polymer-protected silver nanoparticles^[11]. The yellow color of the colloidal silver sample (inset) provides clear evidence for the formation of silver nanoparticles^[12].

TEM image was further used to characterize as-formed silver particles. Figure 2 shows a typical TEM image (A) and the corresponding particle size distribution histogram (B) of silver nanoparticles produced. The photograph shows that most of the particles are nearly spherical. The size distribution histogram reveals that such silver particles range from 20 to 40 nm in size and mainly consist of nanoparticles with 25 nm diameter. Note that all these particles are well separated from each other.

It was reported that lower generation Poly(amidoamine)polymer, due to their small size, stabilize nanoparticles by attaching multiple Poly(amidoamine)polymer to one particle, leading to the formation of Poly(amidoamine)polymer -protected nanoparticles^[13]. From the size of Poly(amidoamine)polymer –G4 Poly(amidoamine)polymer (2.4 nm)^[14] it is expected that the silver nanoparticles cannot be formed inside the Poly(amidoamine)polymer because the size of the formed silver particles is larger than the Poly(amidoamine)polymer itself. Therefore, It can be suggested that the Poly(amidoamine)polymer molecules stabilize silver nanoparticles by attaching multiple Poly(amidoamine)polymer to one particle. Note that silver nanoparticles thus formed were free from flocculation or aggregation for several months, suggesting that the Poly(amidoamine)polymer serves as a very effective protective agent for silver nanoparticles. Sun et al. have previously found that the surface of silver nanoparticles is oxidized into Ag₂O when routine heat treatment is used to prepare Poly(amidoamine)polymer G4 –protected silver nanoparticles^[8]. Therefore, the surface of silver nanoparticles formed in this present study may also be oxidative. As expected, both the XPS spectrum and XRD data (data not shown) obtained are quite similar to Sun's observations, indicating that the as-formed particles are also silver nanoparticles coated with Ag₂O. To examine the influence of the molar ratio of Poly(amidoamine)polymer –G4 to silver on as formed silver nanoparticles, we prepared another two silver samples with molar ratio 3:20 and 9:20 of Poly(amidoamine)polymer –G4 to silver, respectively, under otherwise identical conditions used for preparing sample 1. Fig. 3 shows typical TEM images of the as-formed silver nanoparticles. When the molar ratio is increased up to 3:20, we obtain silver nanorods as well as nanoparticles (Fig. 3A).

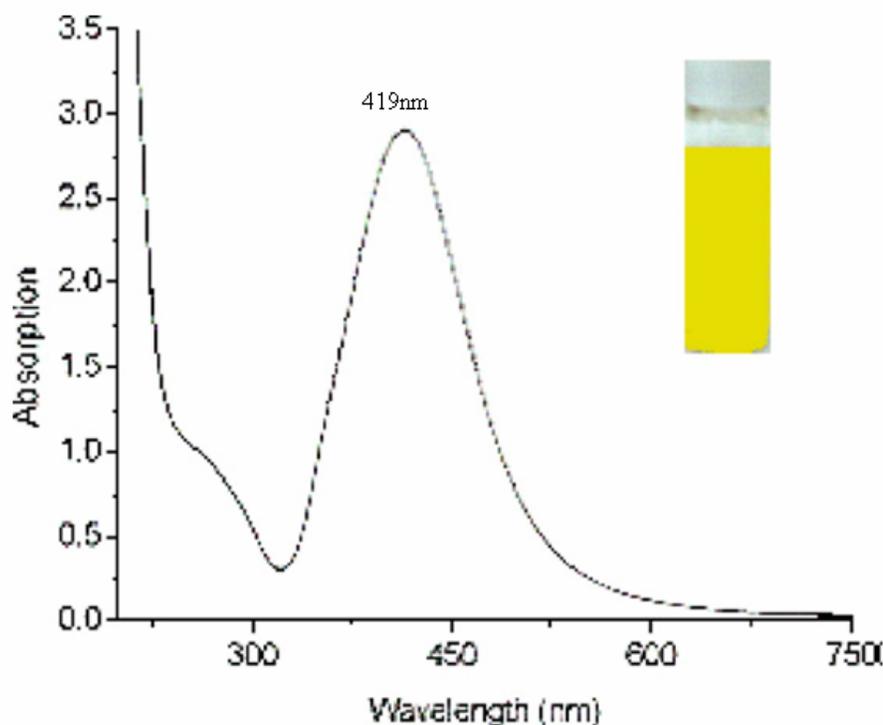


Fig.-1: UV-vis spectrum of the colloidal silver solution thus formed

However, when the molar ratio is further increased up to 9:20, only silver nanoparticles are observed, and further analysis indicates that such nanoparticles range from 5 to 20 nm in size and mainly consist of nanoparticles with 10 nm diameter (Fig. 3B). These observations indicate that molar ratio of reactants heavily influences the formation of silver nanoparticles during the microwave heat treatment of the Poly(amidoamine) polymer-AgNO₃ solution. When the molar ratio of Poly(amidoamine)polymer G4 to silver is changed from 2:20 to 6:20, the number of Poly(amidoamine)polymer molecules available to interact with silver particles increases and therefore, the growth of silver nanoparticles can be more effectively controlled by the Poly(amidoamine)polymer molecules^[6] resulting in the formation of silver nanoparticles with decreased particle size. However, the formation of nanorods at molar ratio 2:20 is quite interesting and the detailed mechanism is not clear at the present time and needs further investigation.

CONCLUSION

We have used microwave heat treatment as an effective method for the single-step preparation of stable, Poly(amidoamine)polymer-protected silver nanoparticles directly from a Poly(amidoamine)polymer-AgNO₃ aqueous solution, without the additional step of introducing other reducing reagents and protective reagents. It provides a simple, rapid, and general methodology for the preparation of amine-functionalized Poly(amidoamine)polymer-protected silver nanoparticles.

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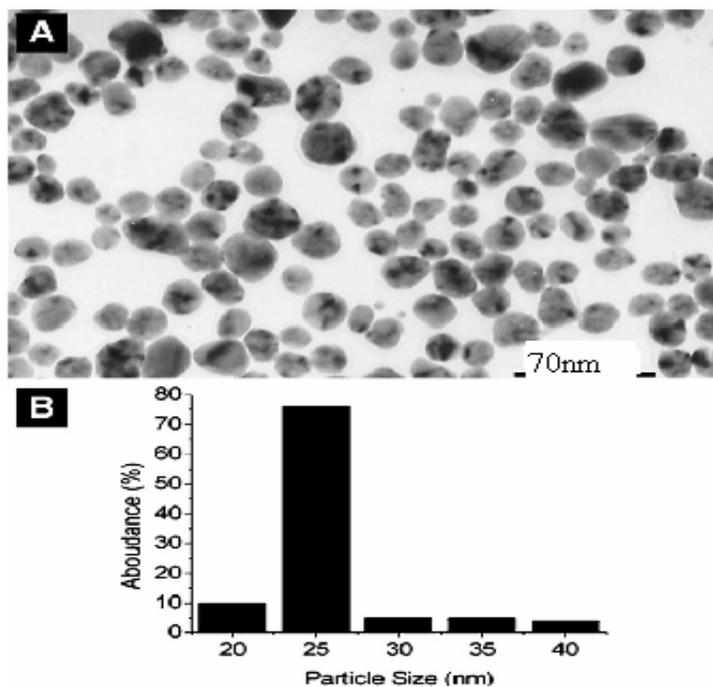


Fig.-2: Typical TEM image (A) and corresponding size distribution histogram (B) of silver nanoparticle thus formed

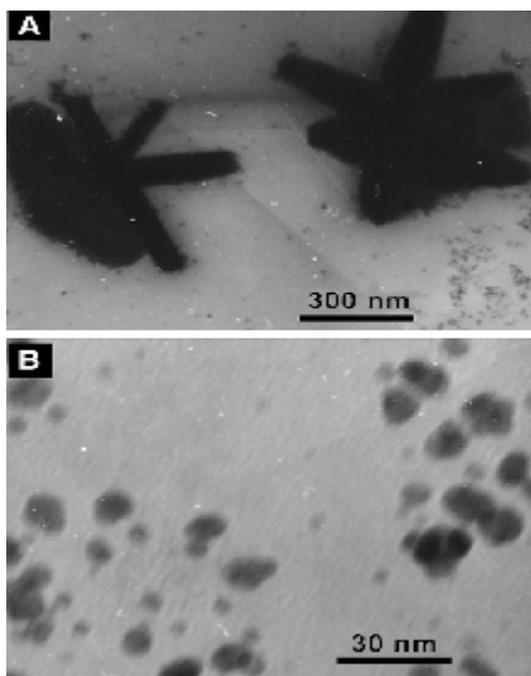


Fig.-3: Typical TEM image of silver nanoparticles obtained with molar ratio of (A) 2:20 and (B) 6:20 of poly (amidoamine)-G4 to silver

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