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Synthesis of Silver Nanoparticles Using Poly(acrylic acid) as a Capping Agent for Conductive Ink in Inkjet Printing Application

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Abstract: The main purpose of this research is to synthesize stable silver nanoparticles in solution which could be used as inkjet printing conductive ink. For this purpose, poly (acrylic acid) was used as a capping agent to protect and prevent silver nanoparticles from agglomeration. In this study, we prepared silver nanoparticles in an aqueous solution or ethylene glycol by reducing silver nitrate in the presence of a surface capping agent and a reducing agent, ethanolamine (mEA). The obtained silver nanoparticles solution was characterized by using Ultraviolet-visible (UV-Vis) spectrophotometry, X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The surface plasmon resonance peak of the silver colloidal solutions showed absorption peak from 410 to 420 nm. TEM images illustrated that the morphology and size distribution of silver nanoparticles with the average sizes were 22 nm in water and 3 nm in ethylene glycol. The silver colloidal solution was stable up to 10 wt% of silver nitrate and for at least three months. The synthesized silver nanoparticle solution, which had good stability, unclogged and the highest possible concentration of silver nanoparticles could be used for ink-jet conductive ink application.

Key words: Silver nanoparticles, capping agent, electrical conductivity, inkjet printing

1. Introduction

In recent years, metallic nanoparticles have drawn attention due to their wide range of applications in many different branches of science and technology. Among them, silver nanoparticles (AgNPs) are of great

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interest to scientists due to its applications such as catalysts [1,2], lithography and surface-enhanced Raman spectroscopy [3,4], antibacterial activity [5], sensors, electronic devices, components in composite materials [6], conductive inks [7,8], [9] and other applications [10-13]. It is important to develop synthesis processes that give stable, non-agglomerated, uniform nanoparticles solution with spherically-shaped, a well-controlled mean diameter and a narrow size distribution. Typically, the simple fabrication method has been performed by reducing the precursor with reducing agents in the presence of capping agents. Polymers and surfactants have been used as capping agents to prevent the irreversible aggregation of AgNPs. Moreover, different sizes and shapes of AgNPs can also be controlled. The larger molecular weight of polymer is used, the more difficult it is removed. An excess of polymer after centrifugation will directly affect the conductivity of AgNPs-based ink. Therefore, using the suitable polymer to protect AgNPs, and easily be eliminated through centrifugation is very important. Nowadays, among the common polymers, Poly (acrylic acid) (PAA) exhibits some interesting characteristics, including stability, controlled particle size and easy - functionalized ability. In addition, PAA with lower molecular weight can be easily removed or decomposed after centrifuging and sintering.

In this study, we present a process of synthesizing AgNPs using poly (acrylic acid) as a surfactant, ethanolamine as a reducing agent in aqueous solution or ethylene glycol. Some experiments to investigate the influence of PAA concentrations, the volume of reducing agents, the effects of AgNPs synthesis in two different media were performed and discussed. The entire fabrication process used the ultrasonic stirring method, which had more advantages than magnetic stirring method. This is the first approach in synthesis of silver nanoparticles-based conductive ink for printed electronics.

2. Materials and Methods

2.1. Materials

The chemicals were used as follows: Silver nitrate ($AgNO_3$, 99.8%), Poly (acrylic acid) (PAA, Mw 1800 g mol-1), ethanolamine (mEA, 99%) were purchased from from Sigma-Aldrich. Ethylene glycol (EG) was bought from China. All aqueous solutions were prepared using de-ionized (DI) water with a resistivity of 18.2 MΩ.cm.

2.2. Preparation of silver nanoparticles

Silver nitrate (0.1 and 1.12 mol/L) was first dissolved completely in DI water under vigorous stirring. A 5.25 ml of an aqueous solution containing poly (acrylic acid) (0.01 mol/L) and ethanolamine (2.02 g) was

prepared. After that, the $AgNO_3$ solution was added drop by drop into aqueous solution under ultrasonic stirring (250 W, Sonic ruptor 250 Ultrasonic Homogenizer). Immediately, the color of the solution changed from colorless to light yellow, then turned into dark brown and finally in yellowish black after continuously stirring for 2 min. The prepared AgNPs were precipitated out using poor solvent such as ethanol. After decanting the supernatant, the PAA-coated AgNPs were centrifuged at 10,000 rpm for 15 min. to further concentrate the silver powder for storage and analysis. Similar experiments were carried out in ethylene glycol instead of DI water to determine the effect of the solvent on the stability and control of the size of AgNPs.

2.3. Characterization

Synthesized samples were analyzed by UV-Vis absorption spectroscopy with a double-beam spectrophotometer (Cary 100, Varian, Australia) in the wavelength range from 190 to 1100 nm. The morphology and size of AgNPs were characterized by transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan). ImageJ software was used to calculate the average diameter and distribution of the AgNPs. The crystallinity of the AgNPs was carried out using X-ray diffraction (XRD).

3. Results and Discussion

3.1. The formation of silver nanoparticles

The original solution, which included PAA and mEA in water/EG was colorless. When $AgNO_3$ was added drop by drop into the solution, reduction of Ag^+ proceeded slowly. The color of the solution changed gradually from light yellow to dark brown and yellowish black. It indicated the nucleation and development of AgNPs [9]. When the nucleus occurred, some of the Ag^0 species were converted to nucleus, some of the Ag^+ ions were continuously reduced to become Ag^0, and the granulation step continued for a while time. During the growth of AgNPs, the mixture gradually became dark and opaque because the big particles reflected and dispersed more lightly than the small particles [9]. After 2 minutes, the color of the mixture unchanged, indicating the end of granular growth and AgNPs solution were formed.

3.2. The influence of PAA concentration

To investigate the effects of the capping agent, various concentrations of PAA were used in this experiment. Figure 1 shows the UV-Vis spectra of the AgNPs with varying PAA concentrations in aqueous solution. At the lowest amount of PAA (0.002 mol/L), the surface plasmon resonance (SPR) peak was not

observed. When the PAA concentration increased up to 0.01 mol/L, the intensity of the SPR peak rised rapidly (at 414 nm). Afterwards, with the increase in the concentration of the polymer, the intensity of the maximum absorption peak decreased, which indicated that AgNPs were covered by PAA [14]. It could be seen that when the PAA concentration increased, the SPR peak shifted toward the long wavelength region as well as became wider. According to the Mie theory, the broadening of the SPR peak illustrates the existence of a wider range of sizes in the solution [14-15]. Therefore, AgNPs would be unstable in water because of its big size. In the next experiment, ethylene glycol (EG) would be used as solvent to reduce particle size.

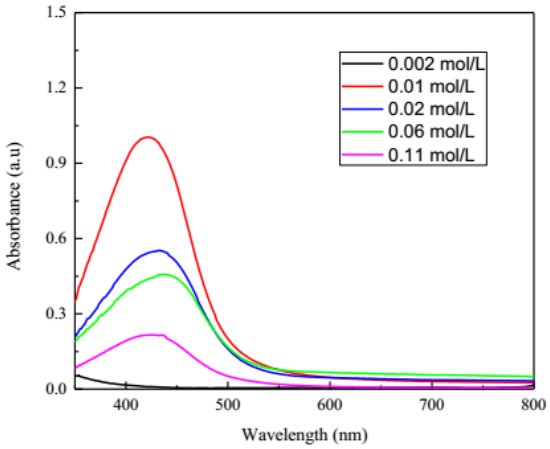

Fig. 1 The UV-Vis spectra of the AgNPs with varying PAA concentrations in aqueous solution

Organic solvents also play a major role in controlling size of AgNPs. EG solvent speeds up the formation of nuclei leading to the formation of smaller particles. Besides, EG is a weak reducing agent because of its hydroxyl groups (OH-). As shown in Figure 2, the intensity of SPR peak was higher than in aqueous solution, which indicated that the particle density in the solution was increased [15]. SPR peak of the samples with the PAA concentrations at 0.08 mol/L and 0.11 mol/L was narrower and sharper, it was significant that the narrow size distribution of the AgNPs which were obtained in EG. In UV-Vis spectra (Figure 2), the shift of the peak toward the shorter wavelength was accompanied by a decrease in the size of the prepared AgNPs inversely proportional with the PAA concentration up to 0.11 mol/L. The narrow SPR peak of the sample with PAA concentration at 0.08 mol/L was at 412 nm, which indicated the formation of smaller particle size and more uniformity.

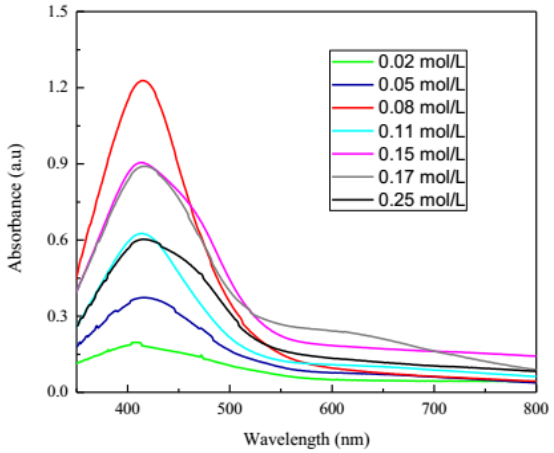

Fig. 2 The UV-Vis spectra of the AgNPs with varying PAA concentrations in ethylene glycol

It is remarkable that the more PAA concentration was added, the larger AgNPs were obtained. This result can be observed through the extensibility of the SPR peak. PAA is a weak anionic polyelectrolyte and degree of ionisation is dependent on pH of solution [16]. At low pH (less than 4.41), the PAA was not deprotonated completely, the interaction between the carboxyl groups and Ag^+ was weak. Hence, the formation of nuclear under ultrasound and heating in EG produced large amounts of nuclei in a short time but it was not encapsulated by PAA molecules, leading to the mean size of AgNPs was large. In addition, with electrostatic repulsion between negative polyacrylate anions in high concentration solution, the small AgNPs would be unstable and then agglomerated to larger particles.

3.3. The influence of reducing agent

The ethanolamine (mEA) contains CH_2OH group, which plays a role as reducing agent. In this part, the effect of reducing agent on the formation of AgNPs was investigated. When ethanolamine was not used, the reduction of AgNps could not occur, even though they were stirred for a long time. With the mEA volume less than 1 ml (pH = 4), the mixture gelatinized and clotted rapidly. When pH of the solution was rised to 10 (VmEA = 2 ml), the reduction of Ag^+ occurred as well as the nucleation and growth rate of AgNPs increased.

Figure 3 shows the maximum absorption peak with varying volume of mEA in two solvents, water and EG. In general, volume of mEA increased to limit, the SPR peak of the samples shifted towards the short wavelength, indicating a reduction of particle size [5]. But increasing until the excess of EA corresponding

with EG (> 5 ml) and water (> 10 ml), the absorption peak of AgNPs tended to shift towards the long wavelength, demonstrating the particle size increased again.

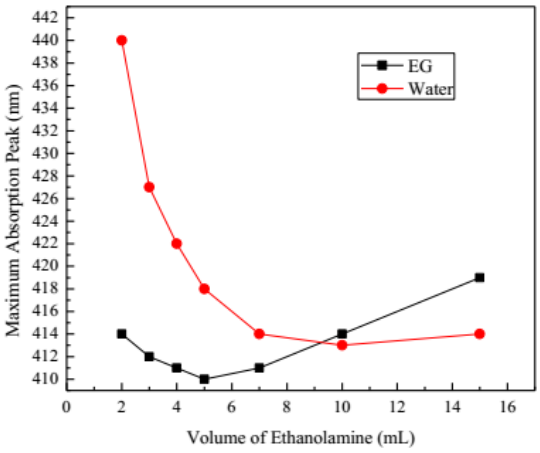

Fig. 3 The maximum absorption peak with varying volume of ethanolamine in two solvents, water and ethylene glycol

Some researchers have attributed a key role of amine in the Ag^+ reduction due to its decrease in the potential of Ag^+/Ag (EAg^+/Ag) which promoted the reaction [16,17]. However, there has not been substantial evidence that confirms this assumption. At higher pH, smaller AgNPs were achieved in comparison to lower pH values. This difference can be attributed to the difference in the rate of reaction [17].

3.4. The results of XRD and TEM analysis

Figure 4 shows X-ray diffraction pattern of the AgNPs prepared in EG and water. For this analysis, silver powders were sintered at 200°C in 2 hours. Four sharp peaks appeared at $2\theta = 38.5^o$, 44.7^o, 64.7^o, and 77.6^o, which could be assigned to the (111), (200), (220), and (311) planes of the face-centred cubic structure of metallic silver, respectively [18]. According to Scherrer's equation $D = k\lambda/\beta \cos\theta$, when the XRD peak of the nanoparticle was much narrower, indicating that the size of the nanoparticle was large. In contrast, the particle diameter was small [19, 20]. Thus, it can be concluded that the size of AgNPs synthesized in water was larger than in EG.

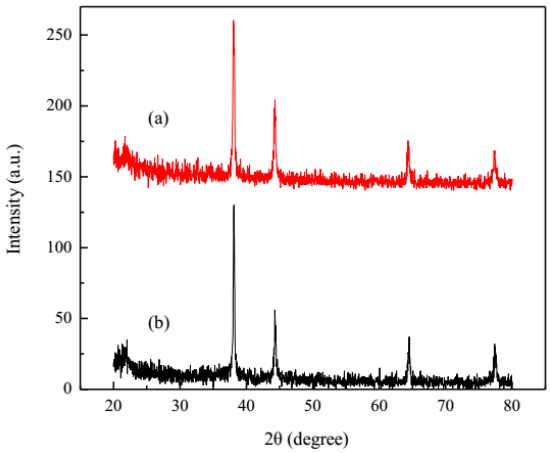

Fig. 4 X-ray diffraction pattern of synthesized silver nanoparticles: (a) in ethylene glycol (b) in water

The morphology and size distribution of AgNPs was investigated by TEM images. Figure 5 shows TEM images of AgNPs solutions with concentration of Ag^{+} up to 10 wt%, [PAA]/[$AgNO_3$] = 0.01 in EG and water.

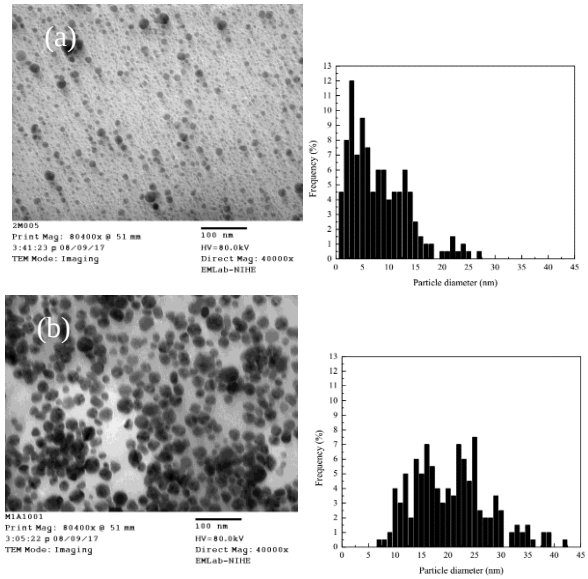

Fig. 5 TEM image and size distribution of synthesized silver nanoparticles solution: (a) in ethylene glycol (b) in water

According to the TEM image and chart of size distribution, the majority of spherical particles and large size distribution with average size was in two ranges of 14 ±2 nm and 22 ±3 nm in aqueous solution and 3 ±

2 nm in EG. It was clear that the AgNPs in EG were much smaller than in water. These results were also reasonable with the above XRD patterns. The synthesized AgNPs in EG were stable for about 3 months.

4. Conclusion

In this report, AgNPs were synthesized by chemical reduction method in EG and water using ultrasonic probe. AgNPs were determined by the appearance of the surface plasmon resonance in the region of 410-420 nm. The general parameters affecting the particle size were the amount of poly(acrylic acid), pH of the solution (volume of ethanolamine) and different solvents. The colloidal silvers were stable for more than 3 months. The XRD results showed characteristic peaks of the silver-structure influenced by drying process at 200 ℃ in ambient atmosphere. The TEM results showed relatively particle size of about 14-22 nm in water and 3 nm in EG. This study played an important role in synthesis of silver nanoparticles-based conductive ink for printed electronics.

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References

[1] Thomas Nesakumar et al, Green synthesis of silver nanoparticles using Terminalia cuneata and its catalytic action in reduction of direct yellow-12 dye, Molecular and Biomolecular Spectroscopy, **161** (2016), 122–129.

[2] F. A. Al-Marhaby, R. Seoudi, Preparation and characterization of silver nanoparticles and their use in catalytic reduction of 4-Nitrophenol, World Journal of Nano Science and Engineering, 6 (2016), 29-37.

[3] Bhui, D., Bar, H., Sarkar, P., Sahoo, G., De, S. and Misra, A., Synthesis and UV-VIS Spectroscopic Study of Silver Nanoparticles in Aqueous SDS Solution, Journal of Molecular Liquids, 145 (2009), 33-37.

[4] Zhengxia Xu and Guoxin Hu, Simple and green synthesis of monodisperse silver nanoparticles and surface-enhanced Raman scattering activity, RSC Advances, 2 (2012), 11404-11409.

[5] Alaa Fahmy et al, Ultra-thin films of Poly(acrylic acid)/Silver nanocomposite coatings for antimicrobial applications, Journal of Spectroscopy, 10 (2016), 11 pages.

[6] Yingsi Wu et al, Fabrication and interfacial characteristics of surface modified Ag nanoparticle based conductive composites, RSC Adv., 7 (2017), 29702-29712.

[7] Fuliang Wang, Peng Mao and Hu He, Dispensing of high concentration Ag nano-particles ink for ultra-low resistivity paper-based writing electronics, Scientific reports, 6 (2016), 21398.

[8] Archana Ghosale et al, Direct-writing of paper based conductive track using silver nano-ink for electroanalytical application, Electrochimica Acta, 209 (2016) 511-520.

[9] Qijin Huang et al, Properties of polyacrylic acid-coated silver nanoparticle ink for inkjet printing conductive tracks on paper with high conductivity, Materials Chemistry and Physics, 147 (2014), 550-556.

[10] W. Desong, A. Jing, L. Qingzhi, L. Xueyan, L. Minna, A convenient approach to synthesize stable silver nanoparticles and silver/polystyrene nanocomposite particles, J. Appl. Polym. Sci., 110 (2008), 3038-3046.

[11] H. Hiroki, E. Frank, A. Osterloh, A simple large-scale synthesis of nearly monodisperse gold and silver nanoparticles with adjustable sizes and with exchangeable surfactants, Chem. Mater., 16(13) (2004), 2509–2511.

[12] L.M. Huang, C.C. Tsai, T.C. Wen, A. Gopalan, Simultaneous synthesis of silver nanoparticles and poly(2,5-dimethoxyaniline) in poly(styrene sulfonic acid), J. Polym. Sci. Part A: Polym. Chem. 44(12) (2006), 3843–3852.

[13] X.K. Wang, L. Shao, W.L. Guo, J.G. Wang, Y.P. Zhu, C. Wang, Synthesis of dendritic silver nanostructures by means of ultrasonic irradiation, Ultrason. Sonochem. 16 (2009), 747–751.

[14] Yaguo Cai et al, Large-scale and facile synthesis of silver nanoparticles via a microwave method for a conductive pen, RSC Adv., 7 (2017), 340041-34048.

[15] Muhammad Akram Raza et al, Size- and shape-dependent antibacterial studies of silver nanoparticles synthesized by wet chemical routes, Nanomaterials, 6 (2016), 74, 15 pages.

[16] Zhiqian Jia, Huijie Sun, Qingyang Gu, Preparation of Ag nanoparticles with triethanolamine as reducing agent and their antibacterial property, Colloids and Surfaces A: Physicochem. Eng. Aspects, 419 (2013), 174–179.

[17] M. Tajdidzadeh et al, Synthesis of silver nanoparticles dispersed in various aqueous media using laser ablation, The scientific world journal, (2014), 324921, 7 pages.

[18] Lin Cao et al, The preparation of Ag nanoparticle and ink used for inkjet printing of paper based conductive patterns, Materials, 10 (2017), 1004, 9 pages.

[19] G. Suriati, M. Mariatti and A. Azizan, Synthesis of silver nanoparticles by chemical reduction method: effect of reducing agent and surfactant concentration, International Journal of Automotive and Mechanical Engineering (IJAME), 10 (2014), 1920-1927.

[20] Danhui Zhang and Youbo Yang, Synthesis of 1-dodecanethiol-capped Ag nanoparticles and their high catalytic activity, Applied Physics A, 10 (2017), 7 pages.