Green synthesis of silver nanoparticles using wolfberry fruits extract and their photocatalytic performance

L Sun¹, P C Lv, Y C Yin, H N Li and F Wang

School of Energy and Power Engineering, University of Shanghai for Science and Technology, Jun Gong Road 516, Shanghai 200093, China

¹ E-mail: marybrother@yeah.net

Abstract. Spherical Ag nanoparticles (NPs) was synthesized using the Chinese wolfberry fruits extract (WFE) as surfactant and reductant. The hydrolysis time and the reaction time were systematically investigated. The whole synthesis process must be kept boiling in order to enhance the reducing ability of WFE and decrease the reaction time. Under the optimized hydrolysis time of 10 min, the reaction time just need 5 min. Ag NPs were characterized by means of UV-vis, EDX, TEM, HR-TEM, and SAED. It was found that Ag NPs exhibited the surface plasmon resonance wavelength of 408 nm, a small average size of 12.1 nm, and the face-centered cubic structure. Obtained Ag NPs were used as photocatalyst for the reduction of 4-nitrophenol and revealed a high photocatalytic activity and stability. The rate constant was 0.043 min⁻¹, which suggested the reduction of 4-nitrophenol was fast. Clearly, Ag NPs synthesized in the totally green method have a potential application in the field of the wastewater treatment.

1. Introduction

4-nitrophenol (4-NP), a harmful and toxic pollutant, widely exists in pharmaceutical industry, dyeing industry, food industry, and so on [1, 2]. Traditional wastewater treatment methods are difficult to remove 4-NP with a low concentration [3]. Up to now, photocatalysis is the main method to degrade 4-NP using semiconductor materials such as TiO₂ and WO₃ as photocatalysts [4, 5]. However, most of semiconductor can only absorb ultraviolet light with shorter wavelength due to their relatively wide band gap, indicating a lower utilization of solar energy. In recent years, noble metal nanoparticles (NPs) have attracted wide attention in the field of photocatalysis, which can make full use of solar photons in the visible spectral region [6-8]. Ag NPs can be much more suitable to be chose as the photocatalyst to treat wastewater because of their high photocatalytic properties as well as bactericidal action [9, 10].

At present, several methods, used to synthesize Ag NPs, are divided into physical, chemical and biosynthesis methods. Among these methods, the first two methods rely on complex process, high cost, or strong ligands, which can pose potential environmental and biological risks [11, 12]. Biosynthesis method is regarded as an excellent method due to its simplicity, cost-effectiveness, compatibility for the biomedical and pharmaceutical applications [13]. Especially, the green synthesis methods based on plant extracts provided a promising choice for the preparation of Ag NPs. Nevertheless, only a few kinds of plants, such as Lavandula intermedia, the leaf extract of Cinnamomum tsói, the leaf and bark extract of Syzygium Jambos Alston and the Chinese wolfberry fruits extract (WFE) have been used to synthesize Ag NPs [14-17]. Among these plants, the Chinese wolfberry, an ancient Chinese herbal
medicine, has bactericidal action and a wide distribution in China. Therefore, Ag NPs synthesized by the WFE can possess superior performance in the wastewater treatment. Usually, the reduction of 4-NP is considered as a model to evaluate the photocatalytic properties of biosynthesized Ag NPs in the wastewater treatment [2]. Dong et al. reported the long synthesis time up to 10 h was needed to prepare Ag NPs due to the weak reducing ability of the WFE, which limited their applications in the wastewater treatment [17]. In order to decrease the synthesis time of Ag NPs, the synthesis method based on the WFE must be improved.

In this paper, we tried a fast green synthesis of Ag NPs using the WFE as reductant and surfactant without any chemical agent. The hydrolysis process was adopted to enhance the reducing ability of the WFE and decrease the reaction time. The optimal hydrolysis time was found by the UV-vis spectra. Based on the optimal hydrolysis time, the reaction time was systematically investigated. The composition, morphology and micro-structure of Ag NPs were characterized by UV-vis, EDX, TEM, HR-TEM and SEAD analyses.

2. Experimental methods

2.1. Materials
Silver nitrate (AgNO₃, GR), sodium borohydride (NaBH₄, AR), 4-NP (C₆H₅NO₃, AR) and ethanol (C₂H₅OH, GR) were purchased from Aladdin Reagent Inc. (Shanghai, China) and used directly as the raw materials without further treatment. Deionized water was used throughout this work. In our experiment, the Chinese wolfberry fruits (Lycium barbarum L.) were produced in Ningxia province of China.

2.2. Preparation of the Chinese wolfberry fruits extract
30 g of wolfberry fruits and 250 mL of deionized water were mixed and brought to boiling for 8 min under vigorous stirring. The above boiling solution was cooled in air until to room temperature. Then the cooled solution was centrifuged at 8,000 rpm for 8 min to remove any undesired impurities. The obtained WFE was diluted by deionized water to 10 vol.% for further experiments.

2.3. The synthesis of Ag NPs
Typically, 25 mL of 10 vol.% WFE was taken in a flask and gently heated to boiling with stirring. After the hydrolysis, 5mL of 0.01 mM AgNO₃ solution was added into the above boiling solution. Then the synthesis system was kept boiling with continuous stirring till the end of the reaction. The hydrolysis time was 10 min. The reaction time was set at 5, 10, 15, 20 and 25 min. It could be found that the colour of solution transformed from colourless to brown. In the experiment, the amount of WFE and AgNO₃ solution was fixed as 25 and 5 mL, respectively.

2.4. Characterization of synthesized Ag NPs
Ultraviolet visible spectrum (UV-vis) analysis was carried out on a spectrophotometer (Cary 50, Varian) using deionized water as the dispersing agent to detect the SPR absorption peak of Ag NPs. Energy-dispersive X-ray spectrum (EDX), Transmission electron microscopy (TEM), High resolution transmission electron microscope (HR-TEM), and Selected area electron diffraction (SAED) analyses were performed on a transmission electron microscope (JEM-2100F, JEOL) operated at 200 kV. The sample for TEM was prepared by placing a drop of dilute solution of NPs on an amorphous carbon-copper grid and subsequent evaporation in air at room temperature.

2.5. The reduction of 4-nitrophenol
To investigate the photocatalytic activity of synthesized Ag NPs, the reduction reaction of 4-nitrophenol was used as a model. The reaction was carried out in a quartz cuvette. 3 mL of 1 M NaBH₄ aqueous solution was mixed with 2.5 mL of 10 mM 4-NP. Then 200 μL of 0.1 mM Ag NPs were added into the above mixture. The reduction of 4-NP as a function of time was monitored by
recording the absorption spectra at every 5 min interval in the range of 200-600 nm under sunlight irradiation at room temperature.

3. Results and discussion

3.1. The synthesis of Ag NPs

3.1.1. The effect of hydrolysis time. Keeping the reaction time as 10 min, the effect of the hydrolysis time on the synthesis of Ag NPs was investigated. Figure 1 (a) displays the UV-vis absorption spectra of Ag NPs prepared at different hydrolysis time from 4 to 14 min. It can be seen from figure 1 that the absorption peaks of Ag NPs keep a constant as 407 nm with increasing hydrolysis time. Figure 1 (b) shows the influence of hydrolysis time on the absorbance of the SPR peak of Ag NPs. With the enhancement of the hydrolysis time from 4 to 10 min, the absorbance of SPR peak was gradually increased, indicating that the reduction amount of Ag ions was enhanced. After that, the absorbance of absorption peak tends to be stable even increasing the hydrolysis time from 10 to 14 min, implying the complete hydrolysis of the WFE. As a result, the optimal hydrolysis time is 10 min, which can guarantee the yield of Ag NPs. The main compositions of WFE are polysaccharides and proteins [18], whose hydrolysis products are monosaccharide and amino acids, respectively. It is well known that monosaccharide and amino acids has strong reducing ability, which can benefit for the decrease of the synthesis time.

![Figure 1](image1.png)

**Figure 1.** (a) UV-vis spectra of Ag NPs synthesized at 10 min with different hydrolysis time. (b) Relationship of the hydrolysis time and the absorbance of SPR peak.

![Figure 2](image2.png)

**Figure 2.** UV-vis spectra of Ag NPs synthesized at different reaction time from 5 to 25 min. Inset is the photographs of corresponding Ag NPs.
3.1.2. The effect of reaction time. The reaction time is an important parameter to evaluate the synthesis system to prepare Ag NPs. Under the optimized hydrolysis time (10 min), the effect of the reaction time on the synthesis of Ag NPs was investigated as shown in figure 2. The reaction time was changed from 5 to 25 min. When the reaction time was 5 min, a weak absorption peak had appeared, implying the formation of Ag NPs. Enhancing the reaction time to 15 to 25 min, the absorbance of the SPR peak exhibit a constant value, which suggests the reduction of Ag ions can be totally completed just at 15 min. With increasing reaction time, the absorption peak of Ag NPs is red-shifted from 407 to 412 nm. According to Mie theory, the SPR absorption peak of spherical Ag NPs was red-shifted, indicating the increase of the size of Ag NPs [19]. However, the difference of the SPR absorption peak was only 5 nm, which meant the growth of Ag NPs was slow. Obviously, the WFE was a strong surfactant. Dong et al reported Ag NPs could also be synthesized using the WFE [17]. However, the reaction time reached up to 10 h because of the weak reducing ability shown by the unhydrolyzed WFE. Clearly, the hydrolysis was a key process for the enhancement of the reducing ability of the WFE and the decrease of the reaction time. Therefore, the synthesis system must be kept boiling in order to ensure the sufficient hydrolysis.

3.2. Characterization

Ag NPs synthesized at the optimized reaction conditions were characterized by means of EDX, UV-vis, TEM, HR-TEM and SEAD analyses. The hydrolysis time and the reaction time was fixed at 10 and 15 min, respectively. In order to observe the composition, EDX analysis was carried out. In figure 3a, an intense peak at 22.0 keV and 24.8 keV is shown, which can be ascribe to silver element. Due to the absence of the O element, the product is considered as monometallic Ag NPs. In figure 3b, the SPR absorption peak at 408 nm was further confirm the formation of the spherical Ag NPs [20].

According to Mie, the variety of the size distribution can also be reflected from the half width at half maximum (HWHM) of the UV-vis absorption spectrum [21, 22]. And the HWHM of Ag NPs is only 56 nm, which indicates that the size distribution of synthesized Ag NPs is narrow [23]. The morphology of Ag NPs was further determined by TEM. As can be seen from TEM image (figure 3c), monodisperse and spherical Ag NPs is obtained in the absence of condensation. It can be found from figure 3d, the average size of Ag NPs is 12.1 nm and the standard deviation is 13%, which further
suggests obtained Ag NPs have a narrow size distribution. Obviously, the WFE has a strong surfactant function. Nevertheless, Dong et al reported that Ag NPs synthesized by the WFE without hydrolysis exhibited the average size in the range from 5 to 40 nm. Clearly, Ag NPs synthesized in the boiling WFE showed a smaller size, which could be attributed to the increasing reducing ability of the WFE under the boiling condition. The microstructure of Ag NPs was characterized by HR-TEM and SAED analyses. Figure 3e is the HR-TEM image, which exhibits Ag NPs tend to adopt an icosahedral morphology with a multiple-twinned structure [24]. The interplanar distance is approximately 0.24 nm, corresponding to the (111) lattice planes of the face-centered cubic (fcc) Ag [25]. In fcc metallic NPs with a small size, the multi-twinned icosahedral structure is frequently observed [26]. This multiple-twinned crystalline nature is further indicated via the SAED analysis in figure 3f. The electron diffraction pattern displays four diffuse rings corresponding to (111), (200), (220), and (311) lattice planes of Ag NPs with the fcc structure, confirming the multiple-twinned crystalline nature of Ag NPs.

3.3. The photocatalytic activity of Ag NPs
As shown in figure 4, the photocatalytic activity of Ag NPs was evaluated in the degradation of the 4-NP under sunlight irradiation.

With the addition of NaBH₄ as reductant in 4-NP solution, the UV-vis absorption peak of 400 nm was appeared immediately, implying the formation of nitrophenolate ions. In the absence of the catalyst, the peak at 400 nm remained undiminished even for several hours. However, when Ag NPs were added into the reaction system, the absorbance of the peak at 400 nm was decreased quickly. And the new peak at 300 nm appeared, which implied the formation of 4-aminophenol [27]. When
NaBH₄ is in excess in the reaction system, the rate constant can be assumed to follow pseudo first order and can be described by

\[
\ln(C_i/C_0)=-Kt
\]

Here, \(K\) is the rate constant, \(t\)-reaction time, \(C_i\) and \(C_0\)-concentration of the 4-NP at time \(t\) and \(0\), respectively. The \(C_i/C_0\) ratio is equal to the ratio of the absorbance \(A_t/A_0\). In figure 5, the rate constant is given as 0.043 min⁻¹, which is corresponding to the slope of fitted linear relationship between -ln(Cᵢ/C₀) and the reaction time [28]. Generally, Ag NPs are easily oxidized if the surfactant is weak. In order to observe the stability of Ag NPs, the photocatalytic experiment was repeated every 5 days until 45 days. In figure 6, Ag NPs still show a high catalytic activity after 45 days, which indicates that obtained Ag NPs is stable. Figure 7 is the TEM image of Ag NPs used as catalyst after 45 days. Compared with that of the fresh Ag NPs, it can be found that the morphology of Ag NPs has no obvious change and there are in absence of agglomerates, which ensures a high catalytic activity of Ag NPs after 45 days. Guo et al reported the catalytic performance of hollow porous Au NPs (80 nm) had no significant change after 30 days [29]. Clearly, Ag NPs synthesized by WFE has comparable stability with Au NPs synthesized using chemical reagents as reductant and surfactant. Compared with commercially available Ag NPs, the stability of Ag NPs synthesized by WFE was superior [30]. Based on the high activity and stability, Ag NPs synthesized by the above totally green method have a potential application in wastewater treatment.

4. Conclusions
Ag NPs were synthesized using the WFE as reductant and surfactant without any other chemical reagent in the case of hydrolysis. The hydrolysis was a key process for the enhancement of the reducing ability of the WFE and the decreasing of the reaction time. At the optimal hydrolysis time of 10 min, Ag NPs were synthesized just through 5 min, whose obvious SPR absorption peak could be observed in their UV-vis spectrum. When the reaction time was up to 15 min, Ag ions could be completely reduced. Obtained Ag NPs showed the SPR absorption peak of 408 nm, the average size of 12.1 nm and the multi-twinned icosahedral microstructure. In the degradation of 4-NP, Ag NPs exhibited excellent photocatalytic activity and stability. The rate constant was calculated as 0.043 min⁻¹ according to pseudo first order. The reported green synthesis method is simple and eco-friendly and obtained Ag NPs have the potential applications in the wastewater treatment and the medical field.

Acknowledgement
This work was financially supported by National Natural Science Foundation of China (Grant No. 11404210).

References
[1] Yang Y, Zhang W, Ma X H, Zhao H R and Zhang X 2015 ChemCatChem 7 3454-9
[2] An X, Long Y D and Ni Y H 2017 Carbohydr. Polym. 156 253-8
[3] Ankita G, Ashish K N and Anjali P 2017 Curr. Pollution Rep. 3 17-30
[4] Tian L H, Xu J L, Alnafisah A, Wang R, Tan X Y, Oyler A, Liu L and Chen X B 2017 Chem. Eur. J. 23 5345-51
[5] Hungela Y M, Mahadikb M A, Moholkara A V and Bhosalea C H 2017 Ultrason. Sonochem. 35 233-42
[6] Qin S D, Liu Y C, Zhou Y M, Cha T and Guo J H 2017 J. Mater. Sci. 28 7609-14
[7] Sun H, Zhen S, He Q R, She P, Xu K L and Liu Z N 2017 Dalton Trans. 46 3887-94.
[8] Yin D G, Zhang L, Cao X Z, Chen Z W, Tang J X, Liu Y M, Zhang T T and Wu M H 2016 Dalton Trans. 45 1467-75
[9] Lee T, Chao B K, Kuo Y L and Hsueh C H 2017 Mater. Chem. Phy. 192 78-85
[10] Zhu W Y, Liu J C, Yu S Y, Zhou Y and Yan X L 2016 J. Hazard. Mater. 318 407-16
[11] Pedro Q, Leonor S, Lívia C, Adelaide M, Inês O, Patrícia A. C, Ricardo F and Eulália P 2009 Green Chem. 11 1889-93
[12] Adil S, Assal M, Khan M, Al-Warthan A, Siddiqui M and Liz-Marzán L 2015 *Dalton Trans.* **44** 9709-17
[13] AbdelRahim K, Mahmoud S Y, Ali A M, Almaary K S, Mustafia A E and Husseiny S M 2017 *Saudi J. Biol. Sci.* **24** 208-16
[14] Elemike E, Onwudiwe D, Ekennia A and Katata-Seru L 2017 *Res. Chem. Intermed.* **43** 1383-94
[15] Middi S, Mandal B K and Maddili S K 2017 *J. Photoch. Photobio. B* **167** 236-41
[16] Dutta P, Bordoloi M, Gogoi K, Roy S, Narzary B, Bhattacharyya D R, Mohapatra P K and Mazumder B 2017 *Biomed. Pharmacother.* **91** 567-80
[17] Dong C F, Cao C L, Zhang X L, Zhan Y L, Wang X J, Yang X Z, Zhou K, Xiao X H and Yuan B 2017 *Optik-Int. J. Light Electron Opt.* **130** 162-70
[18] Aiswarya V, Kumar J, Sisodia R, Shakil N A and Walia S 2014 *Ind. Crops Prod.* **55** 202-6.
[19] Jia X W, Shen J Q and Yu H T 2017 *J. Quant. Spectrosc. Radiat. Transfer.* **195** 44-54
[20] Li T, Ma G H and Peng T J 2015 *Rare Metal Mat. Eng.* **44** 1071-74
[21] Wang C, Peng S, Chan R and Sun S H 2009 *Small* **5** 567-70
[22] Zempila M M, Koukouli M E, Bais A, Fountoulakis I, Arola A, Kourermeti N and Balis D 2016 *Atmos. Environ.* **140** 283-97
[23] Shulga Y M, Matyushenko D V, Kabachkov E N, Kolesnikova A M, Kurkin E N, Domashnev I A and Brichkin S B 2010 *Tech. Phys.* **55** 141-3
[24] Malathi S, Ezharasun T, Abiraman T and Balasubramanian S 2014 *Carbohydr. Polym.* **111** 734-43
[25] Deepak S, Niladri S, Gyanaranjan S, Priyanaranjan M and Sarat K S 2017 *Sens. Actuators B: Chem.* **246** 96-107
[26] Raymundo-Pereira P A, Campos A M, Prado T M, Furini L N, Boas N V, Calegaro M L and Machado S A S 2016 *Anal. Chim. Acta* **926** 88-98
[27] Khan F, Asimullah, Khan S, Kamal T, Asiri A, Khan I and Akhtar K 2017 *Int. J. Biol. Macromol.* **102** 868-77
[28] Kumari M M, Jacob J and Philip D 2015 *Spectrochim. Acta A* **137** 185-92
[29] Guo M Z, He J, Li Y, Ma S and Sun X H 2016 *J. Hazard. Mater.* **310** 89-97
[30] Liu W, Zhou Q F, Liu J Y, Fu J J and Jiang G B 2011 *Chinese Sci. Bull.* **56** 27-34