Research Article

Effect of Microwave Irradiation on Polyvinyl Alcohol as a Carrier of Silver Nanoparticles in Short Exposure Time

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Microwave heating of Ag^+ in polyvinyl alcohol (PVA) is an effective method to synthesize silver nanoparticles (AgNPs), a broad-range antibacterial agent. However, the microwave may cause PVA solution to dry out and degrade. This study is aimed at investigating the effect of microwave irradiation on different concentrations of PVA in PVA/ Ag^+ solution in short periods of exposure. Fourier-transform infrared (FTIR) spectroscopy was employed to evaluate chemical changes of samples with different exposure times and PVA concentration. The results confirm the redox reaction of Ag^+ with PVA. In addition, Ag^+ reduces the rate of hydrolysis of PVA, and the ether bridges are limited by the spatial structure.

1. Introduction

Antibiotic resistance has become one of the most significant health threats because microbes evolve rapidly against our antibiotics while the development of new antibiotics takes decades. Consequently, the old drugs—including metal and their salts that were used to treat infections before the era of antibiotics dominance—have once again become the research focus [1]. Among metals such as silver, copper, zinc, or gold, silver, whose applications have been widely studied [2, 3], has a broad range of antibacterial properties and has relatively low toxicity. Silver nanoparticles (AgNPs)—whose scale is from 1 to 100 nm—also exhibit good biological interaction. However, many studies proved that inappropriate size and concentration of AgNPs are toxic to mammalian cells [4–6]. Therefore, rather than using pure AgNPs, a carrier or stabilizer to control the size and enhance the surface interaction is generally necessary [7–11].

Polyvinyl alcohol (PVA)—a hydroxy polymer with the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$ —possesses many excellent features such as biocompatibility, biodegradability,

water-solubility, and gel-forming. However, they are thermally unstable. During the heat treatment, two major stages occur: elimination reactions and chain scission and cyclization [12]. Elimination reaction produces reactive carbon atoms along the polymer chain, which makes PVA highly reactive to other chemicals during the thermal process. Taking the advantages of this phenomenon, adding Ag^+ ions in PVA solution will cause a redox reaction between Ag^+ , an oxidant, and reactive PVA, a reductant. In previous studies, PVA was proven to be a potential carrier/stabilizer for the synthesis of AgNPs [9]. Moreover, thermal stimulation of PVA could occur without the need of additional catalyst or cross-linker that may induce harmful effects to the body [9].

There are two primary techniques to induce reactions: conventional heating and microwave heating. Compared with conventional heating, microwave heating is a more versatile and economical method with reduced reaction times [13]. Bernal et al. investigated the effect of microwave on PVA with ethylene glycol as the solvent from 4 min to 60 min [12]. However, overexposure of microwave irradiation causes parching and total degradation of PVA. In the

TABLE 1: List of samples.

Abbreviation	PVA concentration (%)	Exposure time (s)	AgNO ₃ added
P8	8	0	No
P8T60	8	60	No
P8T90	8	90	No
P6T60Ag	6	60	Yes
P8T60Ag	8	60	Yes
P10T60Ag	10	60	Yes
P6T90Ag	6	90	Yes
P8T90Ag	8	90	Yes
P10T90Ag	10	90	Yes

FIGURE 1: FTIR spectra of (a) P6T60Ag, P8T60Ag, and P10T60Ag and (b) P6T90Ag, P8T90Ag, and P10T90Ag.

application as a carrier of AgNPs, the exposure time of microwave for PVA is a significant factor, and its effects have not been well-understood yet.

In this study, we investigate the effect of microwave irradiation on different concentrations of PVA in PVA/Ag⁺ solution in short periods of exposure.

2. Materials and Methods

2.1. Materials. Polyvinyl alcohol (PVA; hydrolysis degree of 99.0–99.8%) was purchased from Sigma-Aldrich, USA. Silver nitrate (AgNO₃ ≥ 99%) was obtained from Guangdong, China. The microwave oven is a magnetron MM250 (Whirlpool Corp., USA).

2.2. Sample Preparation. Typically, aqueous solutions of 6 wt%, 8 wt%, and 10 wt% of fully hydrolyzed PVA were prepared by dissolving PVA in distilled water at 75°C. The 1% silver nitrate solution was added to the PVA solution so that the silver concentration was up to 120 ppm. Subsequently,

the PVA solution was microwaved at 800 W for determined periods. All samples are listed below in Table 1.

2.3. FTIR Measurement. Samples were freeze-dried into powder in order to avoid the interference of the hydrogen bonding of water molecules. Then, their FTIR spectra were obtained using a FTIR analyzer (PerkinElmer Spectrum GX, USA).

3. Results and Discussion

The original PVA was characterized with a broad, strong O-H stretching within the range 3700–3000 cm⁻¹, a medium aliphatic C-H stretching peak within the 2920–2930 cm⁻¹ region, and along with C=O stretch (around 1640 cm⁻¹), C-O stretch (1088 cm⁻¹), and CH₂ and CH₃ bending (1438 cm⁻¹). All the peaks of PVA spectrum reappeared in other samples (Figures 1 and 2), which proved that the effects occurred partially in the PVA structure and PVA can still maintain its properties under microwave in short periods of exposure.

FIGURE 2: FTIR spectra of (a) P8, P8T60, and P8T60Ag and (b) P8, P8T90, and P8T90Ag.

Figure 3 displays the FTIR spectra of microwaved and nonmicrowaved of freeze-dried of 8 wt% PVA solution. As the time of microwave exposure increases, the absorbance of O-H stretch, C-H stretch, and CH_2/CH_3 bend decreases. This reproduces the results in previous reports that PVA molecule undergoes elimination reaction and hydroxyl groups decrease [9, 12]. Subsequently, some C-OH groups theoretically form double bonds $\text{C}=\text{O}$ causing the reduction of CH_2 and C-H stretch, while some may lead to polymer dehydration with the formation of ether groups between PVA molecules, which is shown by the changes in peak around C-O stretch. Here, $\text{C}=\text{O}$ stretching of the P8 sample shows the existence of acetate groups. PVA is the product of the hydrolysis process of polyvinyl acetate. This means that the reaction may be incomplete leaving residual acetate groups [12]. Therefore, the changes at this peak may be the replacement of acetate group with ketone or aldehyde group. Notably, the absorbance of C-O stretch does not follow the order of exposure time. This phenomenon expresses the relationship between the reduction of C-OH groups and the formation of C-O groups with respect to time of exposure. To be specific, when PVA is treated with microwave, an increase of $\text{C}=\text{O}$ groups parallelly reduces C-OH group, thus lowering the absorbance; however, after 90 s of microwave exposure, ether group C-O form and its absorbance of light is higher and enhances the absorbance at peak 1088 cm^{-1} .

Figure 1 depicts the FTIR spectra of freeze-dried PVA/silver nitrate solution with the concentration of 6 wt%, 8 wt%, and 10 wt% under different periods of microwave irradiation. The intensities of O-H bonds as well as other bonds correlate with the concentration of PVA in the microwaved PVA/silver nitrate solutions, except for C-O peaks after 90 s of microwave exposure. It can be considered that the cross-linking reaction of PVA molecules is limited even when the concentration of PVA increases. As mentioned above, after 90 s of microwave exposure, the ether bridges between PVA molecules form. However, compared between 60 s and 90 s

FIGURE 3: FTIR spectra of P8, P8T60, and P8T90.

of microwave exposure, the PVA/Ag^+ solution is provided with more energy after being treated with microwave for 90 s; however, C-O peak of P8T90Ag matches that of P10T90Ag. The reason could be that the spatial structure of conjugated PVA prevents themselves from further intermolecular reaction. In other words, the O-H group is continuously broken, but the rate of C-O ether group formation is decreased, causing the equal transmittance at peak 1088 cm^{-1} (as shown in Figure 2).

Figure 2 illustrates the FTIR results of PVA at 8 wt% under microwave irradiation at 60 s and 90 s with or without adding the AgNO_3 solution. After 60 s or 90 s of microwave exposure, the transmittances of O-H stretching of samples having Ag^+ (P8T60Ag and P8T90Ag) are lower than those

of samples not having Ag (P8T60 and P8T90). This means that at the same time of microwave exposure, Ag^+ in PVA solution prevents the degradation of PVA. It may be caused by the redox reaction of Ag^+ and PVA when part of the energy provided by microwave process may be used for the redox reaction. Moreover, the existence of Ag does not affect the formation of ether bridges as shown in the C-O stretching of those samples.

Stability of nanoparticles is strongly dependent on the viscosity of the gels. When PVA is considered itself, the crosslinking between PVA molecules by ether groups is the only chemical parameter; however, it plays a minor role due to its limitation of spatial complexity. This promotes the combination of PVA with other polymers to crosslink instead of PVA itself.

4. Conclusion

The aim of this work is to investigate the chemical changes in PVA/ Ag^+ solution under a short period of microwave irradiation. The results have shown that PVA under microwave is a potential method to synthesize AgNPs. Within a short period of time, PVA still maintains O-H groups, which is the basis of its properties. Ether bridges, intermolecular bonds, are considered minor impacts on PVA crosslinking because of their limitation in spatial structure. The existence of Ag^+ reduces the rate of hydrolysis of PVA.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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