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Full Length Article

# Temperature-controlled cross-linking of silver nanoparticles with diels-alder reaction and its application on antibacterial property

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ABSTRACT

Sliver nanoparticles (AgNPs) were synthesized and functionalized with furan group on their surface, followed by the reverse Diels-Alder (DA) reaction with bismaleimide to vary the particle size, so as to give different antibacterial activities. These nanoparticles were characterized using Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Ultraviolet-Visible (UV–vis), Nanoparticle Size Analyzer and X-Ray Photoelectron Spectroscopy (XPS). It was found that the cross-linking reaction with bismaleimide had a great effect on the size of AgNPs. The size of the AgNPs could be controlled by the temperature of DA/r-DA equilibrium. The antibacterial activity was assessed using the inhibition zone diameter by introducing the particles into a media containing Escherichia coli, Listeria monocytogenes, and Staphylococcus aureus, respectively. It was found that these particles were effective bactericides. Furthermore, the antibacterial activity of the nanoparticles decreased orderly as the particle size enlarged.



## 1. Introduction

Over the past few decades, the investigations on the antibiotics, especially the surveys on the antibacterial activity of silver nanoparticles (AgNPs), have largely increased [1–5]. Great attention has been focused on the employment of AgNPs in the biomedical field (e.g., paper [6], textile fabrics and wound dressing [7], food storage containers [8], catheters [9], bandages, drinking waters sterilization [10], household antibacterial coatings [11] and dental resin composites [12]). For medicine, the antibacterial properties of silver held considerable promise due to its extraordinary usefulness as a broad-spectrum antibacterial agent, which was reviewed extensively as well [13].

Silver ion is highly toxic to bacteria such as Escherichia coli, Listeria monocytogenes and Staphylococcus aureas [14], but it has a low toxicity to animal cells [10]. Furthermore, silver ions and silver-based materials are highly poisonous to almost all microorganisms. That is due to the emergence of antibiotic resistance. That is, most of the bacteria fail to develop immunity to silver. Recently, Durán et al. [7] reported a mixture of AgNPs with amphiphilic hyperbranched macromolecules that could be used for antibacterial surface coating, and the introduction of silver to infected keratinocytes in a humid healing environment enhanced the benefit ratio as compared to wound dressing without silver.

The antibacterial activity of AgNPs is mainly generated from the $Ag^+$ associated with the soluble complexes [15–18]. The mechanism is that the surface of AgNPs can easily absorb silver ions, which bind biological thiol groups in enzymes, such as NADH degydrogenase, and disrupt the bacterial respiratory chain by generating reactive oxygen species (ROS) that can lead to oxidative stress and cell damage.

However, there are some limitations of the silver antibacterial materials, such as restricted perdurability of antibacterial efficiency, and perhaps, lack of intrinsic recoverability. For example, organic antiseptics can easily realize controlled drug release that are widely used in the areas of drug delivery, tissue engineering, and molecular imaging [19,20]. However, it is very hard to adjust the bioactivity of silver-contained materials after it is ready to use. Recently, Xiu et al. [11] reported that AgNPs with different morphological performance could dominantly affect the release behavior of silver ion, which would be useful to prepare silver-contained antibacterial materials with controlled release behavior.

In this paper, another easy approach is reported to control the antibacterial activity of AgNPs, which is based on the controlled aggregation of AgNPs so as to get different particle size and surface area. That is, AgNPs with furan groups reacted with bismaleimide to generate cross-linked aggregates by the reverse Diels-Alder (DA) reaction. Thus, AgNPs with different size were achieved by controlling the built-in reversibility based on the use of heat as an

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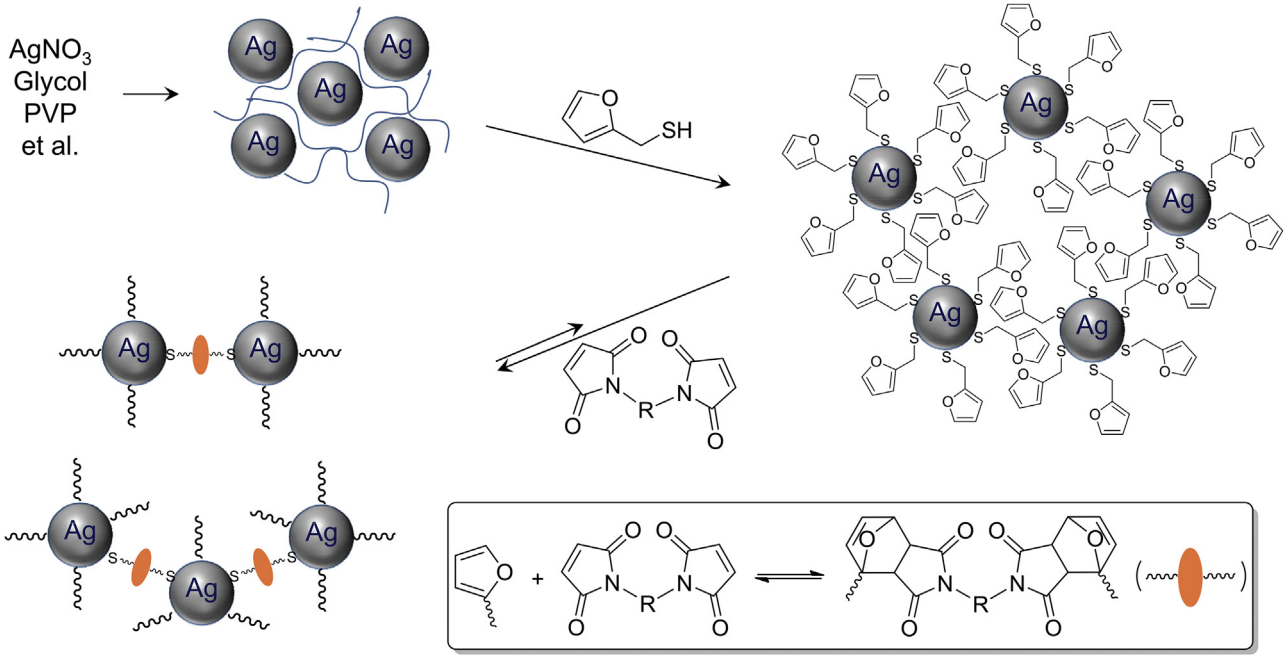


**Fig. 1.** Synthesis, functionalization, and controlled cross-linking of silver nanoparticles.

**Table 1**
The preparation of the different samples.

| Runs | $AgNO_3$ | PVP | $C_2H_6O_2$ | Furfuryl thiol | Bismaleimide | Cross-linkingTemperature |
|---|---|---|---|---|---|---|
| 1 | 1.5g | 10.5g | 49.8 ml | – | – | – |
| 2 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | – | – |
| 3 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | 0.04g | 60 °C |
| 4 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | 0.04g | 70 °C |
| 5 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | 0.04g | 80 °C |
| 6 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | 0.04g | 90 °C |
| 7 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | 0.04g | 100 °C |
| 8 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | 0.04g | 110 °C |
| 9 | 1.5g | 10.5g | 49.8 ml | 0.011 ml | 0.04g | 120 °C |
| 10 | – | 10.5g | 49.8 ml | 0.011 ml | 0.04g | – |

external trigger. Our effort is to achieve different surface area of AgNPs by varying the particle size since the surface area determined the release rate of $Ag^+$ from AgNPs and generate different antibacterial performance.

## 2. Experimental section

### 2.1. Materials and chemicals

$AgNO_3$, Polyvinylpyrrolidone (PVP), glycol, Furfuryl thiol, N,N-dimethyl formamide (DMF), N,N'-(4,4′-methylenediphenyl) dimaleimide (BMI) were of the highest purity available and used as received without further purification. Three bacterial strains, E.coli, L.monocytogenes and S.aureus, were purchased from J&K Scientific Ltd.

### 2.2. Preparation of AgNPs

According to a former process [21], a glycol solution (49.8 ml) containing PVP (10.5 g) was heated to 60 °C. Then, $AgNO_3$ (1.5 g) was added into the solution and heated at 120 °C for 1.5 h. The AgNP solution was obtained after the reaction was cooled to room temperature.

### 2.3. Functionalization of the AgNPs with furfuryl thiol

The AgNPs solution (15 ml) was dissolved in 45 ml glycol solution. Then, a DMF solution (15 ml) containing furfuryl thiol (0.011 ml) was added into the above mixture. (Furfuryl thiol (1.1 ml) was added to a 100 ml flask and made up to a final volume with DMF). After stirred at 120 °C for 3 h, the reaction mixture was then allowed to cool down to room temperature.

### 2.4. Controlled cross-linking of the furan-functionalized AgNPs

N,N′-(4,4′-methylenediphenyl) bismaleimide (0.04 g) was dissolved in DMF (9 ml), To that was added the furan-functionalized AgNPs solution. The mixture was respectively allowed to stir at 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C for 4 h.

### 2.5. Materials characterization

For the analysis of UV and Nanoparticle size analyzer, the AgNPs solutions were diluted to adequate concentration. The UV spectra were recorded by an UV spectrophotometer (UV-2550,Japan) in the region of 350–650 nm. Size and distribution of the AgNPs were obtained using Nanoparticle Size Analyzer (Zetasizer Nano S90).

For the X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and X-Ray Photoelectron Spectroscopy (XPS), the AgNPs solutions were centrifugated, washed with acetone for three times,