



# Catalytic and antibacterial activities of green-synthesized silver nanoparticles on electrospun polystyrene nanofiber membranes using tea polyphenols



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## ABSTRACT

An efficient and environmentally friendly method has been developed to prepare Ag nanoparticles (AgNPs) coated tea polyphenols/polystyrene (Ag-TP/PS) nanofiber membrane, which combines electrospinning and *in situ* reduction of  $[\text{Ag}(\text{NH}_3)_2]^+$  using TP as the reductant and stabilizer. In this method, TP/Pluronic/PS nanofiber membranes are fabricated by electrospinning and then immersed in the aqueous solution of  $[\text{Ag}(\text{NH}_3)_2]^+$ . While TP is being released from TP/Pluronic/PS nanofibers, the surface of TP/Pluronic/PS nanofibers could function as reactive sites for reduction of  $[\text{Ag}(\text{NH}_3)_2]^+$  without any extra reagents. XRD results indicate that AgNPs thus formed are in metallic form of  $\text{Ag}^0$ . SEM images show that AgNPs can be densely and uniformly coated on the surface of TP/Pluronic/PS nanofibers. The as-prepared Ag-TP/PS nanofiber membranes exhibit excellent catalytic properties for the degradation of methylene blue. Furthermore, the effect of  $[\text{Ag}(\text{NH}_3)_2]^+$  concentration on the morphology and catalytic activity of the membrane is investigated. In addition, the antibacterial assays reveal that Ag-TP/PS nanofiber membrane possesses extraordinary antibacterial activity against both Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* microorganisms. The free-standing membrane is flexible and easy to handle, which is promising for potential applications in catalysis, antibacterial agents and water remediation fields.

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## 1. Introduction

Noble metal nanoparticles have been widely used in various technological applications because of their unique optical, electronic, and catalytic properties [1–5]. Among them, Ag nanoparticles (AgNPs) have attracted much attention due to their distinctive properties, such as good conductivity, chemical stability, catalytic and antibacterial activity [6–12]. A number of efforts have been made to synthesize well-dispersed and size controllable AgNPs [2,13–16]. Chemical reduction is one of the most commonly used methods for the fabrication of AgNPs as stable and colloidal dispersions in water or organic solvents, with borohydride, hydrazine and elemental hydrogen usually used as reductants [3,17,18]. Although those are highly active, their potential to cause environmental problems seriously hinders their practical applications. Thus, an easy and environmentally friendly way to prepare

AgNPs remains a great challenge. The green synthesis of AgNPs includes selection of solvent medium, reductant and non-toxic substance (stabilizer or capping agent) for the stabilization of AgNPs [19]. There have already been many green-chemistry methods for the synthesis of AgNPs, including biological (plant extracts and microorganisms), modified Tollens, irradiation, and polyoxometalates methods [17,20,21]. Among them, utilization of plant extracts is popular owing to its wide variety of sources that are easily accessible and safe to handle. Tea polyphenols (TP) compounds, which are found naturally in tea, are flavonoids and water-soluble reductant. Previous reports showed that they could be exploited for stabilization as well as reduction of metal nanoparticles without any extra reagents or treatment [22,23]. Varma et al. revealed that spherical silver nanoparticles of controllable size distributions could be fabricated by reducing silver nitrate solutions of tea extract or epicatechin of varying concentrations [24]. However, the spontaneous aggregation of AgNPs to minimize their surface energy will cause severe loss of specific surface area and decrease catalytic and antibacterial activities. To overcome this shortcoming, many different strategies have been developed,

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mainly focused on the introduction of AgNPs to high-surface-area matrices [25].

Electrospinning technique provides a versatile approach for the convenient fabrication of continuous fibers with diameters ranging from tens to hundreds of nanometers. The polymer nanofiber membranes obtained by electrospinning are flexible with high porosity and surface-area-to-volume ratio, which are ideal substances for tissue engineering scaffolds, catalytic carriers and filter materials [26,27]. They also possess the advantage of easy manipulation and retrieve over nanoparticle matrices, therefore leading to a wide variety of applications. There are generally two approaches to incorporating AgNPs in/onto nanofibers: one implies the inclusion of AgNPs in polymer during the electrospinning process, and the other relies on the deposition of AgNPs on nanofibers during the post-treatment process [28,29]. For example, Du et al. proposed a green and simple method for preparation of highly uniform and well-dispersed AgNPs (5–7 nm) embedded in electrospun PVA nanofibers by combining electrospinning technique and an *in situ* reduction approach by TP [30]. Zhang et al. showed that AgNPs-filled nylon 6 nanofibers exhibited a steady and long-lasting silver ion release behavior, and robust antibacterial activity [31]. However, immobilization of AgNPs with well-controlled shape, size, and distribution on the surface of electrospun nanofibers still poses a challenge. Therefore, surface modification of nanofibers by deposition or fabrication of AgNPs has received increasing attention, because it is desirable or necessary in certain cases [32,33]. Particularly, the method of deposition of AgNPs on nanofibers via wet-chemistry reactions has several advantages due to the capability to precisely control the size, shape, and assembly of AgNPs [34]. Furthermore, AgNPs immobilized on the surface of nanofibers can exhibit improved performance because of direct contact with the surroundings, compared with AgNPs embedded in nanofibers [35,36]. For instance, flexible and highly sensitive surface-enhanced Raman scattering (SERS) substrates were prepared by electroless plating of AgNPs on the surface of electrospun nanofibers via seed-mediated growth process [37].

Thus, hierarchical nanostructures with a number of prospective applications can be realized by combining the functionalities of AgNPs with the intrinsic properties of electrospun nanofibers, including high surface-area-to-volume ratio. In this work, we present a simple and green method to synthesize AgNPs-coated TP/polystyrene (Ag-TP/PS) nanofibers via electrospinning and *in situ* reduction using TP as the reductant and stabilizer. The membranes thus obtained have large specific surface area and an open structure. Therefore, the membranes exhibit good flexibility, high efficiency and stability as catalysts for the degradation of organic dyes, and excellent performance as antibacterial agents against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). Moreover, the influence of  $[\text{Ag}(\text{NH}_3)_2]^+$  concentration on the morphology and catalytic activity of the membranes is also investigated.

## 2. Experimental

### 2.1. Materials

Polystyrene (PS, Mw = 250,000 g/mol) was purchased from J&K Scientific Ltd. Triblock copolymer poly(ethyleneglycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) (Pluronic P123, Mn = 5800) was commercially obtained from Sigma–Aldrich. Tea polyphenols (TP) were supplied by Xuancheng Baicao Plant Industry and Trade Co., Ltd. All other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further purification.

### 2.2. Preparation of electrospun tea polyphenols/pluronic/polystyrene (TP pluronic/PS) nanofiber membranes

PS and Pluronic (w/w = 7/3) were dissolved in N,N-dimethylformamide (DMF) at a concentration of 12 wt %, and a calculated amount of TP (25 wt % TP/PS-Pluronic) was added to the solution. The mixture was vigorously stirred for 10 h at room temperature to produce a clear brown solution. Then, the solution was transferred into a plastic syringe and fed at a speed of 1.0 mL/h with a distance of 15 cm between the needle tip and collector. The applied voltage was fixed at 14 kV. The fiber membrane was collected on aluminum foil and then peeled off. In addition, PS nanofiber membrane was prepared according to the literature for comparison [38].

### 2.3. Preparation of Ag-TP/PS nanofiber membranes

The as-prepared TP/Pluronic/PS membranes were immersed in a freshly prepared aqueous solution of  $[\text{Ag}(\text{NH}_3)_2]^+$  (0.05, 0.2 and 0.5 mol/L, respectively) at room temperature for 0.5 h. After the reaction, membranes were washed with deionized water for several times and dried overnight in an oven at 40 °C. The samples were labeled as 0.05 M Ag-TP/PS, 0.2 M Ag-TP/PS and 0.5 M Ag-TP/PS, respectively. The whole preparation procedure of Ag-TP/PS nanofiber membrane is schematically shown in Fig. 1.

### 2.4. Characterization

X-ray diffraction (XRD) experiments were conducted on a PANalytical (X'Pert PRO) X-ray diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.1542$  nm) at an acceleration voltage of 40 kV and a current of 40 mA. Scanning electron microscopy (SEM, Tescan) performed at an acceleration voltage of 20 kV was used to observe the morphology of samples. The diameter of electrospun nanofibers and AgNPs was measured by Adobe Photoshop CS3 software from the SEM images. The surface composition of nanofibers was characterized using an energy-dispersive X-ray spectroscopy (EDX) in SEM. Static contact angles were measured using a commercial drop shape analysis system (Data Physics SCA20).

### 2.5. *In vitro* TP release

The dried TP/Pluronic/PS nanofiber membranes were cut into small square pieces (4.0 cm × 4.0 cm, 50–70 μm thick). Each specimen was exactly measured for initial weight (about 15 mg) and immersed in 25 mL of deionized water in vials. At selected time intervals, 3 mL solution was taken out and measured for TP concentrations using a Lambda-35UV–vis spectrophotometer (Perkin–Elmer) at 274 nm. These experiments were conducted in triplicate.

### 2.6. Measurements of the catalytic activities

Methylene blue (MB) was selected as the model dye indicator to evaluate the catalytic properties of the catalysts. The membrane of 1.0 cm × 1.0 cm (4 mg) was immersed into 10 mL of MB solution (5 mg/L) and stored in the dark for 2 h to achieve the adsorption equilibrium for MB. Then, 0.1 mL of 1 mol/L aqueous  $\text{NaBH}_4$  solution was added under nitrogen atmosphere. 3 mL of the above solution was taken out from the reaction system every 10 min and immediately analyzed by UV–vis spectrophotometer. Similar procedures were conducted for the recycling ability tests. The calibration curve of MB was prepared by measuring the absorbance of different predetermined concentrations of the samples. The

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