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Luminescent composite polymer fibers: *In situ* synthesis of silver nanoclusters in electrospun polymer fibers and application

Wenran Gao [a], Xumei Wang [b], Weiqing Xu [a], Shuping Xu [a,*]

[a] State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University, Changchun 130012, PR China
[b] Chinese National Petroleum Corporation Bohai Drilling Engineering Company Limited, Tianjin 300457, PR China

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ABSTRACT

The purpose of this study is to prepare multifunctional polymer fibers. We report a simple and controllable method for in situ synthesis of Ag nanoclusters (NCs) in electrospun polymer fibers *via* a photochemical reaction. The prepared composite polymer fibers emit pink luminescence and the luminescence property can be optimized by pH and Ag(I) precursor concentration. The as-prepared Ag NCs in electrospun polymer fibers were mainly Ag_{2-5} with a quantum yield of 6.81% and a lifetime of 2.29 ns. The *in situ* growth of Ag NCs avoids excessive surface modifications which may cause the aggregation of Ag NCs in many *ex situ* assembly methods. The combination of Ag NCs with polymer fibers greatly improves the stability of Ag NCs and broadens their applications. The storage of Ag NCs becomes facilitative due to the formation of bulky mat. Furthermore, these luminescence composite polymer fibers show strong antibacterial activity against *Staphylococcus aureus* (*S. aureus*).

1. Introduction

Ultra-small fluorescent noble metal nanoclusters (the size is smaller than 2 nm) have been a source of immense interest because of their novel electrical, optical and chemical properties, which are significantly different from those of noble metal nanoparticles [1,2]. These unique properties arise from their high aspect ratio and quantum size effect, which result from their ultra-small sizes approaching the Fermi wavelength of an electron (ca. 0.5 nm for Au and Ag) and discrete energy levels [3–5]. Metal nanoclusters have wide potential applications in the fields of fluorescent bio-labeling [6], single-molecule microscopy [7], chemical sensing [8–13], catalysis [14,15], data storage [16] and antibacterial agents [17–20], etc. [21–23]. However, the synthesis of metal nanoclusters has always been a challenge since they are so small and easy to aggregate. Therefore, during preparation, templates and stabilizers are often required to prevent the formation of large-sized metal aggregates, especially for Ag nanoclusters (Ag NCs). Reported templates for preparations of Ag NCs include deoxyribonucleic acid (DNA) [11,12,24–27], thiols [14], cyclodextrin [18], dendrimers [21], polymers [28–33], and proteins [34–36], etc [37,38]. Even with stabilizers, the stability of Ag NCs is usually poor in water. For example, Ag NCs stabilized by DNA in water can only last for several days [24]. It is worth noting that Ag NCs in solution may limit their applications as solid materials such as test paper and surface patterning [39,40].

To achieve highly stable metal nanoclusters and widen their applications, a feasible way to combine metal nanoclusters with bulk materials is adopted. Among other methods, electrospinning is the simplest and most effective technique to obtain fibrous bulk materials from various materials including polymers and composites [41,42]. Diameters of electrospun fibers can vary from nanometer to micrometer scales and the type of polymers is widely optional [41]. Electrospun polymer membranes have been widely applied in many fields because of their unique structural features including high surface area per unit volume, small fiber diameter, low weight and prospect to incorporate active chemistry properties [42].

In this paper, we report on an effective and easy method to *in situ* synthesize luminescent Ag NCs in carboxylic group-rich electrospun polymer fibers to form multifunctional composite polymer fibers. In present study, we electrospun a kind of poly(methyl methacrylate)–poly(methacrylic acid) (PMMA–PMAA) nanospheres to prepare carboxylic group-rich electrospun polymer fibers. Through an ion exchange process between the hydrogen ions of carboxylic groups and Ag ions, Ag ions were captured and enriched in the fibers and then they were *in situ* reduced to Ag(0) by a photochemical reduction reaction. Consequently, novel Ag NC composite polymer fibers were

Abbreviations: NCs, nanoclusters; DNA, deoxyribonucleic acid; PMMA, poly(methyl methacrylate); PMAA, poly(methacrylic acid); UV–vis, ultraviolet–visible; XPS, X-ray photoelectron spectroscopy; SEM, field-emission scanning electron microscopy; EDX, energy dispersive X-ray spectroscopy; LDI-ToF-MS, laser desorption ionization time-of-flight mass spectroscopy; MMA, methyl methacrylate; MAA, methylacrylic acid; DMF, dimethyl formamide; CFU, colony forming units; IR, infrared; FT, Fourier transform; *S. aureus*, *Staphylococcus aureus*.

* Corresponding author at: State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Ave., Changchun 130012, PR China. Tel.: +86 431 85168505; fax: +86 43185193421.
E-mail addresses: gaoshang5566@126.com (W. Gao), wxmddp@163.com (X. Wang), xuwq@jlu.edu.cn (W. Xu), xusp@jlu.edu.cn (S. Xu).

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achieved and they exhibited a bright pink luminescence. This in situ growth method endows Ag NCs with an excellent, long-term optical stability due to the protection of the solid polymer matrix. In addition, we found that these luminescent fibers presented antibacterial activity, which can be a promising candidate as a class of antibacterial membrane materials.

2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$, 99.8%) was purchased from Shanghai Reagent No. 1 Plant. Methyl methacrylate (MMA, 99.0%), methylacrylic acid (MAA, 99.0%) and dimethyl formamide (DMF) were obtained from Tianjin Guangfu Fine Chemical Reagent Plant. Potassium persulfate ($K_2S_2O_8$) was purchased from Tianjin Fuchen Chemical Reagent Plant.

2.2. Preparation of the electrospinning solution

The electrospinning solution is DMF solution containing PMMA–PMAA nanospheres, which was synthesized by soapless seeded emulsion polymerization as described in the literature [43]. First, 3.7 mL of MMA, 100 mL of ultrapure water and 0.0841 g of $K_2S_2O_8$ were added in a flask. After continuous stirring for 40 min under N_2 gas at 70 °C, we obtained the PMMA nanospheres with a size of 250 nm. Second, 20 mL of the prepared PMMA nanosphere solution, 1.5 mL of MAA and 1.5 mL of MMA were added in sequence in a flask and stirred to mix for 30 min. 77 mL of water and 0.048 g of $K_2S_2O_8$ were introduced and constantly stirred for 40 min under N_2 atmosphere protection at 70 °C. After that, the PMMA–PMAA nanospheres were yielded and their size was about 320 nm. The polymer nanospheres were centrifuged and dried in an oven at 70 °C. Third, the PMMA–PMAA particles were dissolved in DMF solution under vigorous stirring for 12 h under room temperature to obtain the electrospinning solution with a mass fraction of 20%.

2.3. Electrospinning

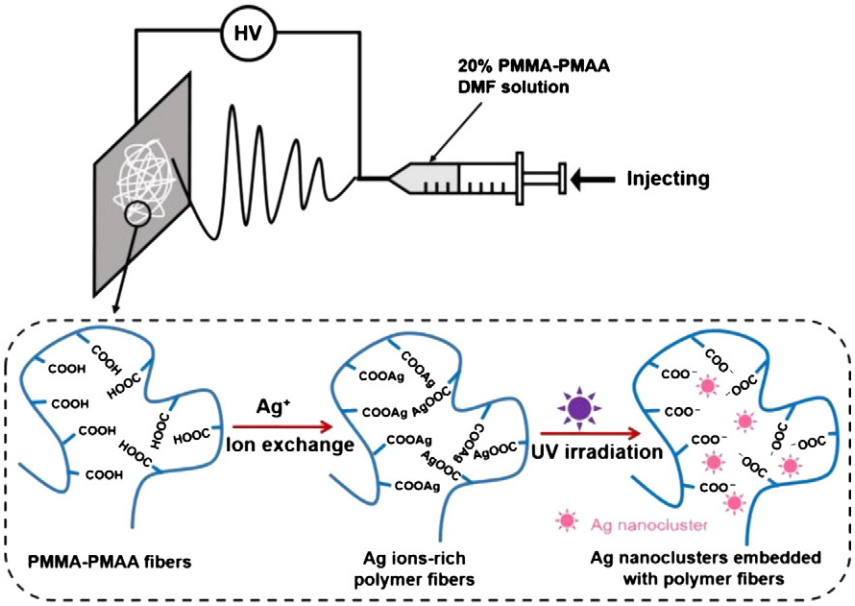
A fibrous membrane of PMMA–PMAA was electrospun by a lab-made electrospinning setup which consists of a precise programmable microprocessor based infusion syringe pump, a high-voltage DC power supply with the highest voltage of 20 kV and a collector plate. The collector plate is a square plate of aluminum foil which is laid vertically against the needle to collect fibers. Both the infusion syringe pump (Baoding Longer Precision Pump Co., Ltd., model LSP01-1A) and collector plate are kept in a custom-made chamber, which has a plastic cabinet with two front windows. The high-voltage power supply with a power of 10 W was model PS 375/20 kv and purchased from Stanford Research Systems Inc.

In a typical electrospinning process, the electrospun solution was transferred into a plastic syringe (capacity of 1 mL) with a metal needle. In the present study, the positive voltage, the needle-to-collector distance and the flow rate of the solution were set respectively as 15 kV, 15 cm and 0.15 mL/h. Under these conditions, the obtained electrospun polymer fibers were typically 600 nm in diameter. After 4 h electrospinning, a PMMA–PMAA fiber membrane was obtained on the collector plate, and was further detached prior to use.

2.4. Ag NC formation

Scheme 1 shows the synthesis of the composite polymer fibers. First, the electrospun fiber membrane was immersed into a silver nitrate aqueous solution with a certain concentration and pH for 15 min. In this process, there was an ion exchange between the hydrogen ions of carboxyl groups and Ag ions. Meanwhile, the Ag ion(I)-rich electrospun polymer fibers were obtained. Second, the Ag ion-rich electrospun polymer fibers were irradiated under a 365 nm UV lamp (power = 6 W) for tens of minutes. The electrospun polymer fibrous membrane changed its color from white to pink with the extending of irradiation time, which indicates the generation of Ag NCs.

Various pH values and Ag(I) concentrations were chosen to optimize the synthetic conditions. We immersed the electrospun polymer fiber membrane (about 0.1 g with similar area) into $AgNO_3$ solutions with a concentration of 0.10 M, 0.05 M, 0.025 M, 0.01 M, 5.0 mM, 2.5 mM and 1.0 mM under the same pH of 5.62 to evaluate the effect of Ag(I) concentration. To detect the pH effect on the formation of Ag NCs, we changed the pH of $AgNO_3$ solution (0.01 mol/L) by adding HNO_3 or NaOH, and the pH were adjusted to 3.92, 4.88, 5.62, 6.89 and 7.56 to *in situ* synthesize Ag NCs.



Scheme 1. The strategy for preparing luminescent composite polymer fibers.