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AgNPs/PVA and AgNPs/(PVA/PEI) hybrids: preparation, morphology and antibacterial activity

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Abstract
Two strategies are demonstrated to fabricate AgNPs/PVA and AgNPs/(PVA/PEI) nanofibre hybrids. In the first approach, we synthesized AgNPs in poly(vinylalcohol) (PVA) solution and then electrospun the AgNPs/PVA solution into the AgNPs/PVA nanofibres. In the other one, the polyethylenimine (PEI) was introduced to improve the water-stability of PVA and then the AgNPs were immobilized on electrospun PVA/PEI nanofibres to fabricate the AgNPs/(PVA/PEI) nanofibres. Field-emission scanning electron microscopy, transmission electron microscopy, ultraviolet–visible spectroscopy and x-ray photoelectron spectroscopy (XPS) were utilized to investigate the morphology and the growth mechanism of the hybrids. The investigations demonstrate that both of the obtained AgNPs/PVA hybrids and AgNPs/(PVA/PEI) hybrids exhibit good water-stability and good antibacterial activity against *E. coli* and *S. aureus*.

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, with the steady and fast-growing field of nanoscience and nanotechnology, nanosized noble metal particles have attracted plenty of attention because of their tempting properties in physics (such as electronic and optical devices), biotechnology (such as biosensing and antimicrobial agents), chemistry (such as catalyst and initiator) and so on [1–3]. Among them, Ag nanoparticles (AgNPs) are efficient and cost-effective noble metal nanoparticles; their special structure makes them possess particle effect, surface effect, quantum size effect and macroscopic quantum tunnelling effect, all of which allow AgNPs to have wide applications in many fields. Due to the marked interaction with biopolymer (such as enzyme, DNA, cell wall and cell membrane) effectively in bacteria, AgNPs exhibit excellent applications especially in biotechnology, such as antimicrobial agent. Weiss and Kriegel *et al* have already demonstrated a number of applications of the antibacterial activity of AgNPs [4, 5].

However, naked AgNPs are easily oxidized during storage and tend to aggregate due to their high surface energy [6, 7], resulting in a remarkable reduction in their antibacterial activity. Therefore, much attention has been focused on the synthesis of small-size and highly dispersed AgNPs [8]. As we know, essentially, there are two strategies that have been used to obtain small-size AgNPs with high dispersion: one is the introduction of AgNPs on/into solid supports (including polymeric membrane, metal oxide, carbon and so forth) [8–11] with different nanostructures (such as nanotubes, fibres, spheres and so on) [8, 12–17] to form composite structure. The other strategy is to put the small-size AgNPs into colloidal solutions containing complexes or surfactants with polymer ligands [8, 18, 19]. However, this process can cause loss in the activity of AgNPs. Meanwhile, the small-size AgNPs can lead to difficulty in sedimentation from the solution, so their recycling is not satisfactory for large-scale applications. Therefore, the first method seems to be better. Nanostructures materials, such as nanotubes and spheres are time-consuming and costly, which make them unsuitable for

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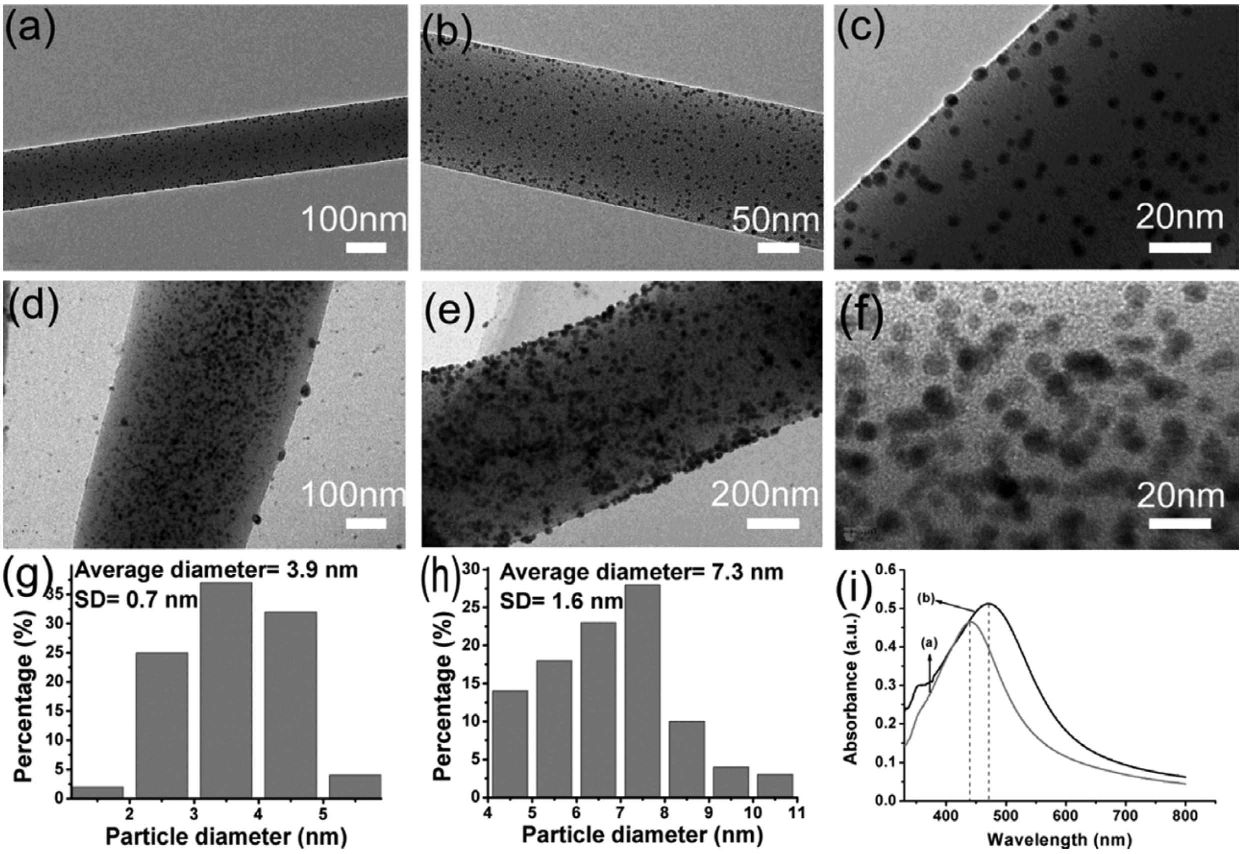

Figure 1. (*a*), (*b*), (*c*) TEM images of the AgNPs/PVA hybrids and (*g*) the corresponding particle distribution of AgNPs; (*d*), (*e*), (*f*) TEM images of the AgNPs/(PVA/PEI) hybrids and (*h*) the corresponding particle distribution of AgNPs; (*i*) The UV–Vis spectra of (*a*) AgNPs/PVA hybrids and (*b*) AgNPs/(PVA/PEI) hybrids.

practical application. From the relevant research, we know polymeric membrane is not only easy to obtain, but can also control AgNPs to release effectively. Therefore, the fabrication of Ag-based membraniform antibacterial agents might be very promising in antibiosis.

During the last few decades, electrospinning has been developed to be a remarkably simple, efficient and versatile technique, which has been exploited to process polymer, metal oxide materials and gelation into 1D nanofibres [20]. The resulting nanofibres have high surface area that make them potential candidates for a variety of fields, such as membrane technology [21, 22], drug delivery system [23], enzyme immobilization [24], electronics [25] and sensors [26]. Obviously, this method provides an approach to bridge the dimensional and property gap between macroscale engineering materials and nanoscale materials [8].Through the wonderful technology, 2D membraniform nanostructure could be easily fabricated. Poly(vinylalcohol) (PVA) is an easily electrospun polymer that can be used as the solid support of AgNPs. Its high polar, water-soluble, biocompatibility, processability and hydrophilicity [22, 27–29] have led to its industrious use in areas such as membranes [30], adhesives [31], paints and coating [22, 31].

Based on the advantages of electrospun PVA nanofibres, we adopted the nanofibres mat to support AgNPs. To improve the water-stability of PVA, we selected glutaraldehyde [32–34] as chemical cross-linkers to reduce its water solubility. We modified PVA with polyethylenimine (PEI), which has abundant amine groups on the molecular chains, and they should be an ideal polymer for the fabrication of a polycationic nanofibre reactor [35].

In the present investigations, two procedures are employed to fabricate AgNPs/PVA and AgNPs/(PVA/PEI) nanofibre hybrids. In the first approach, we synthesized AgNPs in the PVA solution and then electrospun the AgNPs/PVA solution into the AgNPs/PVA nanofibres. In the other one, PEI was introduced to improve the water-stability of PVA and then the PVA/PEI nanofibres were functionalized by thiols groups to fabricate the AgNPs/(PVA/PEI) nanofibres. Our investigations indicate that the two kinds of obtained hybrids exhibited pretty good antibacterial activity.

2. Experimental sections

2.1. Chemicals and materials

Polyvinylacohol (PVA, 88% hydrolyzed, $M_w = 88\,000$) was supplied by Sigma Aldrich. Silver nitrate ($AgNO_3$, 99.8%) was obtained from Shanghai Reagent Factory. PEI (50%, $M_w = 70\,000$) was acquired from Aladdin Chemistry Co., Ltd. Epigallocatechin gallate (EGCG, 98%) was collected from Xuancheng BaiCao Plant Industry and Trade Co., Ltd Glutaraldehyde (GA, 25%) was bought from Kermel, Tianjin Chemical Reagent Co., Ltd (3-Mercaptopropyl) triethoxysilane (MPTES, $C_9H_{22}O_3SSi$, 95%) was gained from TCI (Shanghai) Development Co., Ltd. Absolute ethyl alcohol (C_2H_5OH) was from Hangzhou Gaojing Fine Chemical Industry. Deionized water was prepared by an ultra-pure water purifier system. All chemicals were used as received without further purification.

2.2. *Synthesis of AgNPs embedded in PVA nanofibres by an in situ reduction method*

10 ml 12 wt% PVA was put in a breaker at 65 °C and stirred by magnetic force for 30 min. 0.027 g $AgNO_3$ dissolved in 4 ml deionized water was added to the mixture, and after 1 h, 0.003 g EGCG dissolved in 1 ml purified water was dropped into the above mixture for 2 h. Thus, the solution with 0.024 wt% Ag was obtained. The solutions with 0.030 wt% Ag and 0.040 wt% Ag were acquired through the same method. The above solutions were electrospun under a fixed voltage of 15 kV, the products were collected for 5 h on a piece of aluminum foil at a distance of 12 cm, meanwhile, the velocity of flow was set at 0.3 ml h^{-1}. The mat was cross-linked by GA vapour at 60 °C for 24 h.

2.3. *Synthesis of AgNPs immobilized on PVA/PEI nanofibres*

14 g 12 wt% PVA and 1.12 g PEI were placed in a breaker and then stirred for 12 h at a proper rate. The mixture was electrospun for 5 h to acquire a piece of mat with the following related parameters: 18.6 kV, 15 cm, 0.3 ml h^{-1}. Then the nanofibre mat was cross-linked by the above-mentioned method. The cross-linked nanofibre mat was functionalized by the mixture of 3 ml MPTES and 45 ml ethanol in a immersion oscillator at 40 °C for 12 h, followed by being placed in a beaker containing silver nitrate solution for 1 h and put into EGCG solution for 2 h in sequence. The mass fraction of Ag was in correspondence with the AgNPs embedded in PVA nanofibres, respectively.

2.4. *Antibacterial activity evalution*

The antibacterial activity of the hybrids was appraised against the bacteria of Gram-negative *Escherichia coli* (*E. coli*) ATCC 25922 and Gram-positive *Staphylococcus aureus* (*S. aureus*) ATCC 6538 by the nonwoven fabric attachment method [40–42]. The two kinds of microorganism were cultivated in sterilized Luria–Bertain (LB) broth and then incubated overnight at 37 °C with shaking before use. 100 μl bacterial suspensions were spread uniformly over the agar plates. The two kinds of prepared hybrids were cut into small pieces with a diameter of 2 cm. After that, these circular pieces of AgNPs/PVA and AgNPs/(PVA/PEI) hybrids were placed over the solidified agar gel in different Petri dishes. In the end, the inoculated agars in the Petri plates were kept for incubation at 37 °C, and after 12 h and 20 h, the breadth of inhibition zone was recorded, respectively.

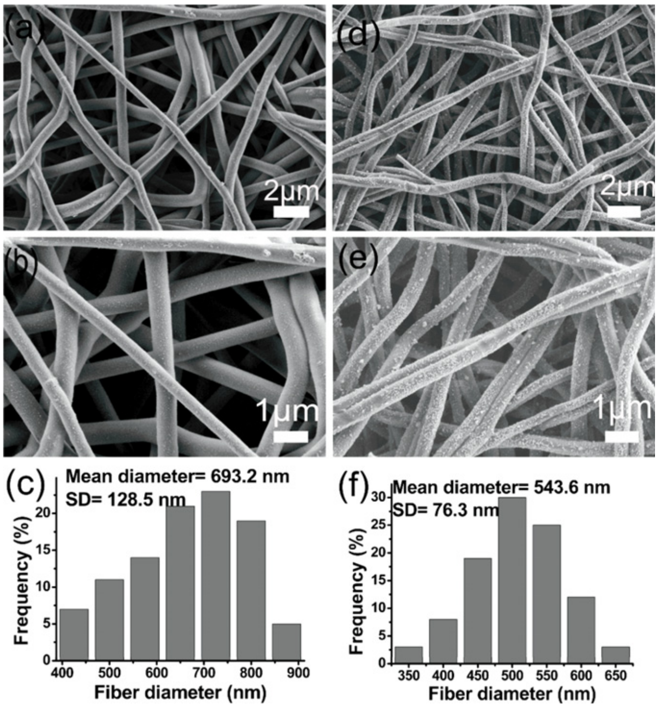

Figure 2. (*a*), (*b*) FE-SEM images of AgNPs/PVA hybrids and (*c*) the corresponding diameter distribution of nanofibres; (*d*), (*e*) FE-SEM images of AgNPs/(PVA/PEI) hybrids and (*f*) the corresponding diameter distribution of nanofibres.

2.5. *Characterization*

Two pieces of the two kinds of hybrids were placed in absolute ethyl alcohol, then ultrasonified for about ten minutes, dropped on the ultra-thin carbon-coated copper grid and dried under infrared lamp for five minutes, respectively. The images were acquired using a JSM-2100 transmission electron microscopy (TEM, JEOL, Japan) at an accelerating voltage of 200 kV. The spectra of AgNPs/PVA and AgNPs/(PVA/PEI) hybrids were collected by a Lambda 900 ultraviolet–visible (UV–Vis) spectrophotometer (Perkin Elmer, USA). All the spectra were collected over a wave length range of 200–800 nm. The morphology of the AgNPs/PVA and AgNPs/(PVA/PEI) hybrids were observed by an ULTRA-55 field-emission scanning electron microscope (FE-SEM, JOEL, Japan). X-ray photoelectron spectra of PVA nanofibres, AgNPs/PVA hybrids, PVA/PEI nanofibres and AgNPs/(PVA/PEI) hybrids were recorded by using an x-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with aluminum (mono) K_α source (1486.6 eV). The aluminum K_α source was operated at 15 kV and 10 mA. The high-resolution survey (pass energy = 48 eV) was performed at spectral regions relating to silver, oxygen and sulfur.

3. Results and discussion

3.1. *Morphology and structure of AgNPs/PVA and AgNPs/(PVA/PEI) hybrids*

TEM images of the AgNPs/PVA hybrids are shown in figures 1(*a*)–(*c*). As described in the figure, the AgNPs

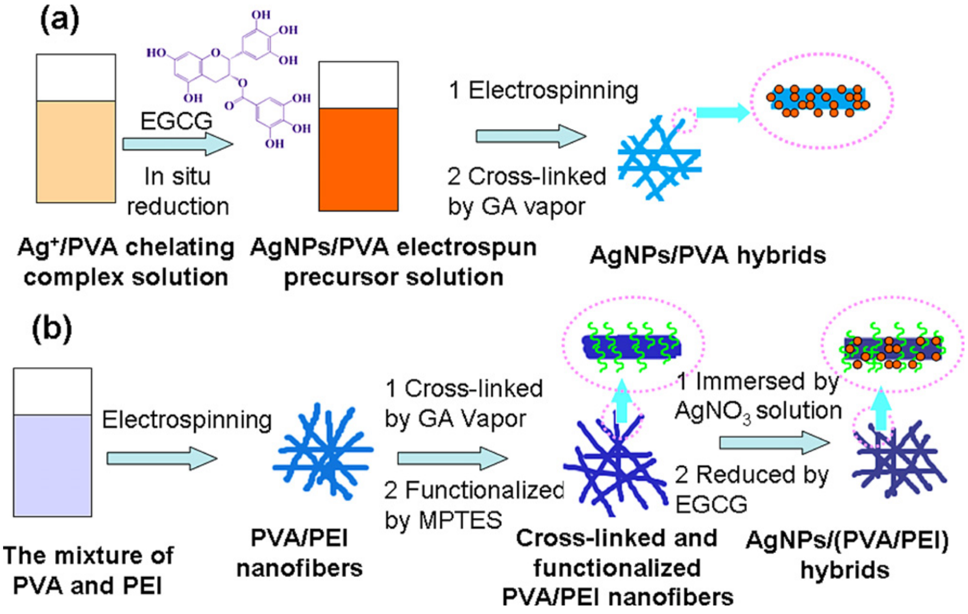

Figure 3. A schematic illustration of the procedure for the fabrication of (*a*) the AgNPs/PVA hybrids and (*b*) AgNPs/(PVA/PEI) hybrids.

are uniformly dispersed in PVA nanofibres and have a relatively narrow particle diameter distribution about 3.9 nm (figure 1(*g*)). The morphology of the AgNPs immobilized on PVA/PEI nanofibres are shown in figures 1(*d*)–(*f*), and it can be seen that the AgNPs with an average diameter of 7.3 nm (figure 1(*h*)) distributed on PVA/PEI nanofibres evenly. Compared with the AgNPs embedded in PVA nanofibres, the average diameter of the AgNPs on PVA/PEI nanofibres is much larger and the diameter distribution of AgNPs is broader. The UV–Vis absorption spectra of the AgNPs/PVA hybrids and AgNPs/(PVA/PEI) hybrids are shown in figure 1(*i*). Obviously, the band in curve (b) around 467 nm is broader than the band in curve (a) around 437 nm, indicating that the AgNPs on PVA/PEI nanofibres are larger than the AgNPs in PVA nanofibres and have a relatively higher polydispersity, which is corresponds well with the TEM results. Typically, the intensive surface plasma resonance (SPR) band of AgNPs has a hypsochromic shift from 415 to 386 nm. The shift of SPR is attributed to the competition between the growth of AgNP size (which leads to the bathochromic shift) and electron transfer (which results in a change in free electron concentration of Ag and may cause bathochromic shift or hypsochromic shift of SPR peak) [39, 42].

Figure 2 shows the FE-SEM images of the hybrids via electrospinning technique. As can be seen from figures 2(*a*) and (*b*), a large quantity of AgNPs are well-dispersed in PVA nanofibres, which have a mean diameter of 693.2 nm and posses relatively smooth surface. Obviously, through the *in situ* approach, AgNPs can be generated in PVA by the reduction of Ag^+ which is dissolved in the electrospun precursor solution [4, 36–38]. As illustrated in figures 2(*d*)–(*f*), it is apparent that quite a number of AgNPs grow on the outside of modified PVA nanofibres. Evidently, most of the AgNPs have good dispersion, apart from a few of them stuck together. Thus, AgNPs can be homogenously immobilized on the mat through a silver–sulfur bonding interaction after the introduction of thiol groups from MPTES [43]. As can be seen from the chart (figure 2(*f*)), the mean diameter of the PVA/PEI nanofibres is 543.6 nm, which is much smaller compared with that of PVA nanofibres. What's more, the former has a narrow distribution of diameter.

Figure 3(*a*) summarizes the procedure for the preparation of AgNPs/PVA hybrids. $AgNO_3$, which was selected as the source of Ag ions, was added to the PVA solution first, and then the Ag^+ was *in situ* reduced by EGCG. Thus, the AgNPs/PVA electrospun precursor solution was obtained. Afterward, the above solution was electrospun and subsequently cross-linked by the vapour of GA, during which the reaction between the hydroxyl groups of PVA and the aldehyde groups of GA happened, so as to enhance the water-stability of PVA [32, 43]. With the above procedures, the AgNPs/PVA hybrids were acquired. It is believed that the concentration of PVA polymer is higher than water and it may restrict the free growth of AgNPs and direct the particular arrangements of AgNPs. Therefore, in the fabrication process of the AgNPs, the polymer solution may play a crucial role for the diameter and distribution of the AgNPs. In figure 3(*b*), the PVA/PEI nanofibres were achieved through the process of electrospinning. After this, the PVA/PEI nanofibres were cross-linked by the GA vapour and then functionalized by MPTES, during which high-density -SH groups were introduced onto the surface of the PVA/PEI nanofibres, allowing a number of Ag^+ to be immobilized via the interaction between Ag ions and SH groups [43]. Then, the SH groups functionalized PVA/PEI nanofibres were immersed in $AgNO_3$ solution, followed by reducing with EGCG and then the AgNPs/(PVA/PEI) hybrids were obtained. According to the literature, EGCG is an excellent bidentate ligand to bond with Ag^+ by forming a stable five-member chelating ring. Afterward, the chelated Ag ions were reduced into Ag element as well as a part of the phenolic hydroxyls of EGCG being oxidized to the corresponding orthoquinone and

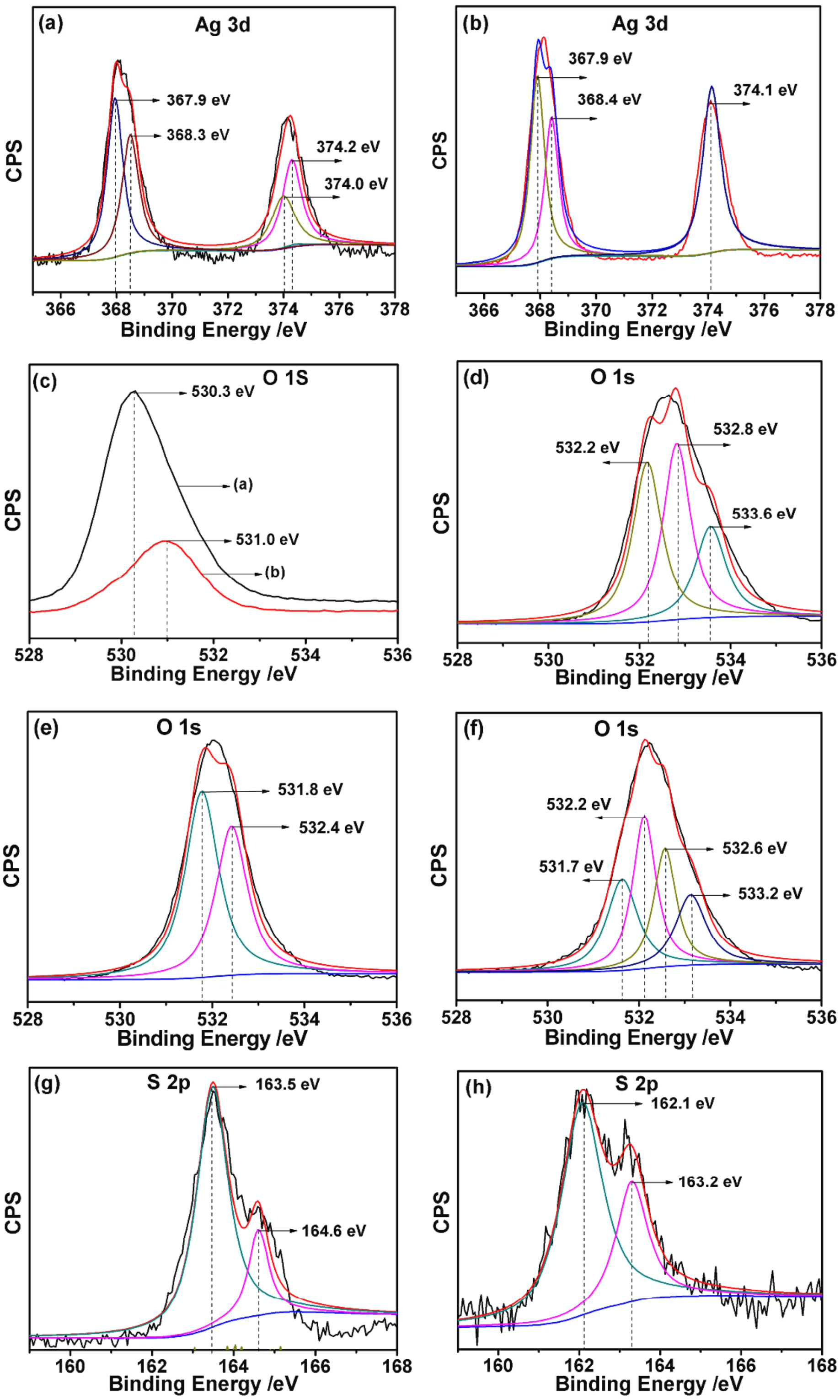

Figure 4. XPS spectra of Ag, oxygen, and sulfur atoms. (*a*) Ag 3d of AgNPs/PVA hybrids; (*b*) Ag 3d of AgNPs/(PVA/PEI) hybrids; (*c*) (*a*) O 1s in pure PVA; (*b*) O 1s in EGCG; (*d*) O 1s in AgNPs/PVA hybrids; (*e*) O 1s in PVA/PEI nanofibres; (*f*) O 1s in AgNPs/(PVA/PEI) hybrids; (*g*) S 2p of PVA/PEI nanofibres; (*h*) S 2p of AgNPs/(PVA/PEI) hybrids.

carbonyl groups. The formed carbonyls and free hydroxyls are both able to stabilize AgNPs by the interaction between the surface Ag atoms of AgNPs and oxygen atoms of EGCG [39, 44, 45, 48, 49]. Hence, it is concluded that chelating effects of AgNPs with hydroxyls in PVA and sulfhydryls in MPTES play an important role in the formation of AgNPs/PVA and AgNPs/(PVA/PEI) hybrids, which will be demonstrated by x-ray photoelectron spectroscopy (XPS).

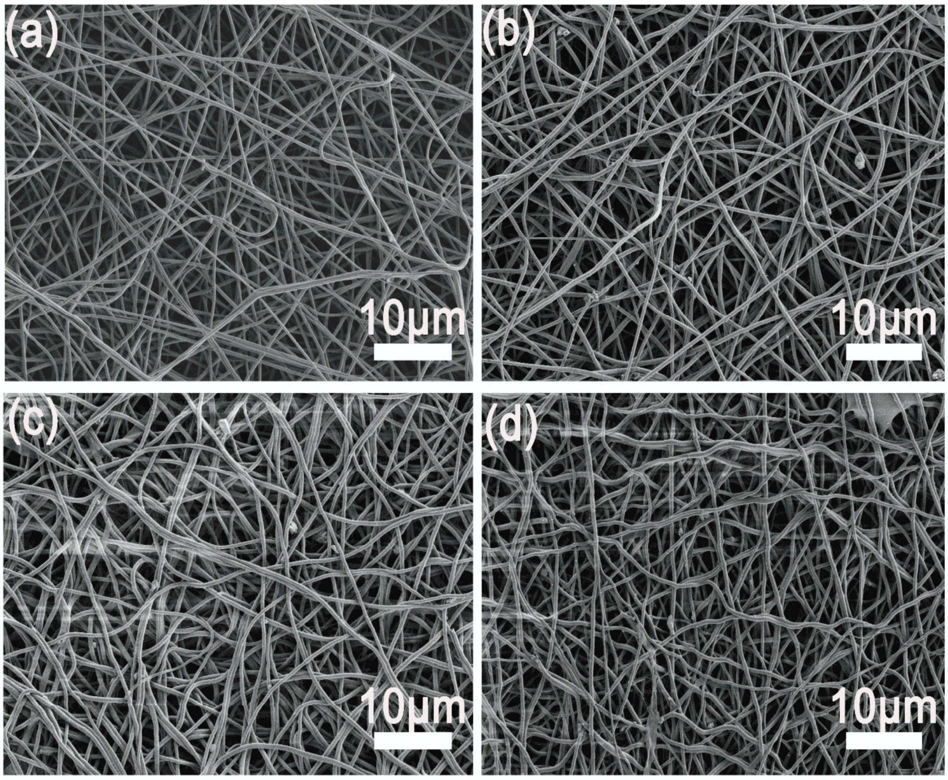

Figure 5. FE-SEM images of the AgNPs/PVA hybrids immersing in water for different times (*a*) 0 h (*b*) 12 h (*c*) 24 h (*d*) 48 h.

The XPS characterization was used to further characterize the fabrication process of the hybrids. Figure 4(*a*) shows the XPS spectrum in the Ag 3d region of the AgNPs/PVA hybrids. These peaks observed at 368.3 eV and 374.2 eV are ascribed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ of the bulk Ag, respectively. The other two peaks located at 367.9 and 374.0 eV are attributed to the chelating effects of Ag with hydroxyls in PVA. As can be seen in figure 4(*b*), the binding energy of Ag $3d_{5/2}$ shifts to 368.4 eV, while the binding energy of Ag $3d_{3/2}$ shifts to 374.1 eV, which is assigned to the interaction between AgNPs and hydroxyls [45, 47]. The peak located at 367.9 eV is ascribed to the interactions between AgNPs and sulfhydryl group.

As shown in figure 4(*c*), the peak at 530.3 eV and 531.0 eV are assigned to the O 1s in PVA and EGCG molecules, respectively. After the addition of EGCG and the formation of AgNPs, as can be seen in figure 4(*d*), the O 1s peak in AgNPs/PVA hybrids possesses three peaks at 532.2, 532.8 and 533.6 eV, which are mainly attributed to the involvement of hydroxyls in PVA and the vibration of phenolic hydroxyls in EGCG. In figure 4(*e*), the peaks at 531.8 eV and 532.4 eV are ascribed to the O 1s in PVA and MPTES molecules, respectively. The binding energy of O 1s in PVA shifts to a higher value, indicating the chemical changes in the environment. After being immersed in $AgNO_3$solution and reduced by EGCG, as shown in figure 4(*f*), the O 1s peak in AgNPs/(PVA/PEI) hybrids are divided into four peaks. The peaks at 531.7 and 532.6 eV are assigned to the involvement of hydroxyls in PVA, which is the result of the chelating effects between AgNPs and hydroxyls. The peak at 532.2 eV is ascribed to the O 1s in MPTES, the variation indicates the change of its existing chemical environment. The peak at 533.2 eV also implies the vibration of phenolic hydroxyls in EGCG [39, 42].

The XPS spectra of the S 2p in PVA/PEI nanofibres and AgNPs/(PVA/PEI) hybrids are shown in figures 4(*g*) and (*h*). It can be clearly seen that S 2p spectra have an S $2p_{3/2,1/2}$ doublet structure. The peaks located at 163.5 eV and 164.6 eV shift to 162.1 eV and 163.2 eV, respectively, which may result from the chemical bond formation between sulfur and Ag. As is known from the literature, the sulfur attached to metal would lead to lower electronegativity, and the decrease of binding energy of S 2p [46, 50]. Based on the above data, it can be concluded that the interactions among AgNPs, hydroxyls and sulfhydryls play a significant role in the formation process of AgNPs/PVA and AgNPs/(PVA/PEI) hybrids.

As we know, the PVA is a kind of water-soluble polymer, and it is important to improve the water-stability of PVA for widely practical applications. To testify the water-stability of the obtained AgNPs/PVA hybrids, the nanofibres mats immersed in water for different times are provided. As shown in figure 5, with the increase of the soak time, there are nearly no changes of the morphology of the nanofibres, indicating that the cross-linking of the hybrids by the GA vapour is effective way to improve the water-stability of the nanofibres.

3.2. Antibacterial activity

Traditionally, the antibacterial effects of the materials could be qualitatively determined by the length of the inhibition zones. Figures 6 and 7 show the experimental results of the antibacterial tests for the AgNPs/PVA and AgNPs/(PVA/PEI)

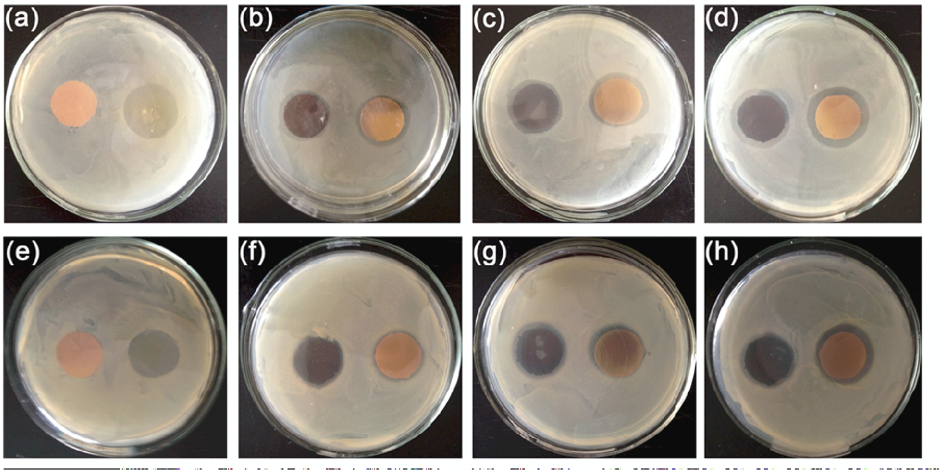

Figure 6. Pictures of inhibition zone test of hybrids after 12 h.

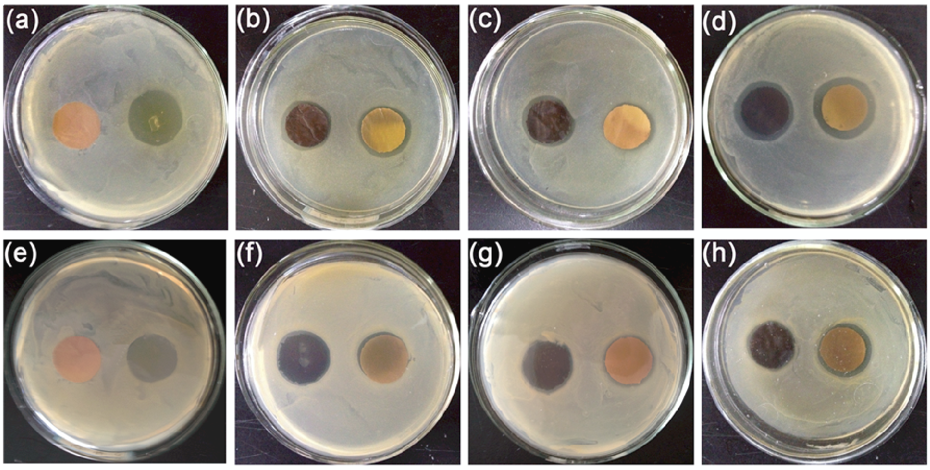

Figure 7. Pictures of inhibition zone test of hybrids after 20 h.

hybrids. As observed clearly from figures 6 and 7, the pure PVA nanofibre mat and pure PVA/PEI nanofibre mat exhibit no bacterial properties against *E. coli* and *S. aureus* at all. On the other hand, for the AgNPs/PVA hybrids and AgNPs/(PVA/PEI) hybrids, with the increase of AgNPs, the length of the inhibition zones become bigger. Meanwhile, there was no significant difference between the two different kinds of hybrids, indicating that both AgNPs/PVA hybrids and AgNPs/(PVA/PEI) hybrids can control AgNPs to release effectively. What's more, the two kinds of hybrids contained low content of AgNPs, implying that the two kinds of methods are both facile and effective.

The hybrids in the first line are against *E. coli*, in the second line are against *S. aureus*: (a) pure PVA, pure AgNPs/(PVA/PEI); (b) 0.024 wt% AgNPs/PVA, 0.024 wt% AgNPs/(PVA/PEI); (c) 0.030 wt% AgNPs/PVA, 0.030 wt% AgNPs/(PVA/PEI); (d) 0.040 wt% AgNPs/PVA, 0.040 wt% AgNPs/(PVA/PEI).

4. Conclusion

In summary, two strategies are demonstrated to fabricate AgNPs/PVA and AgNPs/(PVA/PEI) nanofibre hybrids. In the first approach, we synthesized AgNPs in the PVA solution and then electrospun the AgNPs/PVA solution into the AgNPs/PVA nanofibres. In the other one, the PEI were introduced to improve the water-stability of PVA and then the PVA/PEI nanofibres were funtionalzed by thiols groups to fabricate the AgNPs/(PVA/PEI) nanofibres. The experimental results demonstrated that both of the as-prepared AgNPs/PVA hybrids and AgNPs/(PVA/PEI) hybrids exhibited good water-stability and good antibacterial activity against *E. coli* and *S. Aureus*. Moreover, these strategies are significant with respect to the synthesis of nanocomposites that have potential applications in catalysts, sensors and so forth.

Acknowledgments

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