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Antimicrobial Expanded Polytetrafluoroethylene Film Prepared by γ-ray Radiation Induced Grafting of Poly(acrylic acid)

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The simultaneous γ-ray-radiation-induced grafting polymerization of acrylic acid on expanded polytetrafluoroethylene (ePTFE) film was investigated. It was found that the degree of grafting (DG) of poly(acrylic acid) (PAA) can be controlled by the monomer concentration, absorbed dose, and dose rate under an optimal inhibitor concentration of $[Fe^{2+}]$=18 mmol/L. SEM observation showed that the macroporous structure in ePTFE films would be covered gradually with the increase of the DG of PAA. The prepared ePTFE-g-PAA film was immersed in a neutral silver nitrate solution to fabricate an ePTFE-g-PAA/Ag hybrid film after the addition of $NaBH_4$ as a reduction agent of Ag^+ to Ag atom. SEM, XRD, and XPS results proved that Ag nanoparticles with a size of several tens of nanometers to 100 nanometers were *in situ* immobilized on ePTFE film. The loading capacity of Ag nanoparticles could be tuned by the DG of PAA, and determined by thermal gravimetric analysis. The quantitative antibacterial activity of the obtained ePTFE-g-PAA/Ag hybrid films was measured using counting plate method. It can kill all the *Escherichia coli* in the suspension in 1 h. Moreover, this excellent antibacterial activity can last at least for 4 h. This work provides a facile and practical way to make ePTFE meet the demanding antimicrobial requirement in more and more practical application areas.

Key words: Expanded polytetrafluoroethylene film, Radiation grafting, Poly(acrylic acid), Silver nanoparticles, Antibacterial property

I. INTRODUCTION

The expanded polytetrafluoroethylene (ePTFE) films are obtained by rapidly stretching the polytetrafluoroethylene (PTFE) film in one more directions at 327 °C, then quenching to room temperature to fix the macroporous structure formed during the stretching [1]. ePTFE films are widely used in many areas, not only as water-proof and wind-proof cloth materials [2], filtration films [3], and advanced dielectric materials [4, 5], but also as synthetic blood vessels [6], patches for soft tissue regeneration [7] and surgical sutures [8] for its low toxicity and perfect stability [9, 10]. In spite of these excellent properties, ePTFE still has some problems in practice use. For example, in the application of clothing and water filtration, the antimicrobial property of ePTFE films is urgently needed for the high demand of water quality and human health care [11]. Silver nanoparticles have been proven to have excellent antimicrobial activity so as to be loaded in many kinds of materials as antibacterial agents [12−14]. Commonly, silver ions are first absorbed in the matrix, and then *in situ* reduced and aggregated into silver nanoparticles [15]. However, it is impossible for the direct absorption of silver ions or silver nanoparticles on ePTFE films for its extreme hydrophobic property. Therefore, modifications on ePTFE films should be studied to improve the hydrophilicity so that antimicrobial agents, such as silver nanoparticles, can be loaded in ePTFE film to meet the needs in practical applications.

γ-Ray induced graft copolymerization has been widely applied to surface modification of various polymer materials [16−18]. In our previous work [19], poly(acrylic acid) (PAA) was grafted onto poly(ethylene terephthalate) films, and silver nanoparticles were loaded onto the grafted film successfully. The prepared hybrid film performed excellent antibacterial property against *Escherichia coli* (*E. coli*). The modification of PTFE was generally carried out by chemical etching [20], electron and ion beams irradiation [21, 22], and plasma modification [23]. However, few work refers to the application of γ-ray radiation on the modification of PTFE in literatures because PTFE has been believed to be a typical radiation-degradable polymer, although Tabata group confirmed the radiation induced crosslin-

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king of PTFE under a special irradiation condition, *i.e.*, irradiation around 613 K in inert gas atmosphere or under vacuum [24, 25].

In this work, we first studied the conditions for the graft copolymerization of acrylic acid (AA) on ePTFE film under the radiation of γ-ray. Then, Ag nanoparticles were *in situ* loaded in the grafted PTFE film. Further, the bactericidal activity of the ePTFE-g-PAA/Ag hybrid film was evaluated by the efficiency of killing *E. coli*. The antibacterial efficacy (ABE) of the hybrid film can reach as high as 100%, which meets the antibacterial requirement for the practical use of ePTFE films.

II. EXPERIMENTS

A. Materials

ePTFE films were provided by Xinxiang Xinxingfenghua Membrane Co., Ltd. (Henan, China). Chemical-grade acrylic acid (Sinopharm Chemical Reagents Co., Ltd.) was purified by vacuum distillation and stored at −20 °C before use. Analytical grade reagents including ferrous sulfate hydrate ($FeSO_4{\cdot}7H_2O$), sliver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), and aqueous ammonia ($NH_3{\cdot}H_2O$, 25%−28%) were all purchased from Sinopharm Chemical Reagents Co., China, and used without further purification. Distilled water was used in all the experiments. Mueller-Hinton (MH) Medium was purchased from Xiya Reagent (Chengdu, China). *E. coli* DH5α was used in the antibacterial tests.

B. Preparation of ePTFE-g-PAA film by γ-ray radiation induced grafting polymerization

ePTFE film with a size of 3 cm×3 cm was washed with acetone, and then dried in a vacuum oven overnight at 50 °C. The dried film was immersed in an aqueous solution of AA containing a certain amount of $FeSO_4$. Then the system was exposed to the radiation of ^{60}Co γ-ray (55 kCi, located in University of Science and Technology) at a dose rate of 10 Gy/min for a certain time after being bubbled with nitrogen for 10 min at a speed of three bubbles per second to expel the dissolved oxygen. The grafted films were all washed with water in a Soxhlet extractor for 24 h, to remove homopolymer and unreacted monomers after the grafting polymerization.

C. *In situ* loading Ag nanoparticles on the ePTFE-g-PAA film

The prepared ePTFE-g-PAA film was immersed into a mixture of 100 mL of water and 0.5 mL of $NH_3{\cdot}H_2O$. The system was ultrasonicated for 5 min and continuously agitated at room temperature on a shaking bed (Jingda, WHY2) for another 2 h. Then the film was taken out and washed with water for several times till the pH value of the washing water reached 7.0. Later, the ePTFE-g-PAA film was placed in a beaker containing 20 mL of distilled water. An aqueous solution of $AgNO_3$ (0.5 mol/L, 10 mL) was added under magnetic stirring. The system was agitated at room temperature on a shaking bed for 2 h to reach the absorption equilibrium of Ag^+ ions on the ePTFE-g-PAA film. The aqueous solution of $NaBH_4$ (0.1 mol/L, 10 mL) was then added into the solution under magnetic stirring. The reaction was carried out for 3 h on a bed shaker (200 r/min). Then, the film was cleaned with water ultrasonically for half an hour for 3 times, to remove the residual reduction agent. Finally, the obtained ePTFE-g-PAA/Ag film was dried in a vacuum oven overnight at 50 °C.

D. Characterization

The degree of grafting (DG) of PAA on the ePTFE film is defined by the following Eq.(1):

$$\mathrm{DG} = \frac{m_\mathrm{g} - m_0}{m_0} \times 100\% \tag{1}$$

where m_0 and m_g are the weight of the original ePTFE film and the grafted film respectively. The morphologies of the films were observed with SEM (JEOL JSM-6700F, 5.0 kV). X-ray diffraction (XRD) was recorded on MXP 18 AHF X-ray diffractometer (MAC Science Co., Ltd) with monochromatized Cu Kα radiation (λ=1.54056 Å). X-ray photoelectron spectroscopy (XPS) was recorded with a VG ESCALAB MKII XPS, using a Mg Kα line (1486.6 eV) as the excitation source under high vacuum (5 nPa). Thermal gravimetric analysis (TGA) was carried out under a nitrogen atmosphere at a rate of 10 °C/min with a Shimadzu DTG-60H thermal analyzer.

E. Antibacterial activity tests

E. coli was cultivated in MH medium at 37 °C. All glassware, samples and medium used were sterilized in an autoclave at 121 °C for 20 min before experiment. The bacteria were centrifugally separated from the liquid medium at a speed of 3000 r/min for 10 min. Then the collected cells were washed twice with a sterile phosphate buffer solution (PBS), and redispersed in PBS at a concentration of 10^7 cells/mL. One piece of film with a size of 1 cm×1 cm was immersed into the dispersion and kept at 37 °C on a bed shaker at a speed of 200 r/min. After 1 and 4 h, 1 mL of bacterial culture was sampled respectively, and diluted ten times with PBS serially. Then 0.1 mL of the diluted sample was spread on MH

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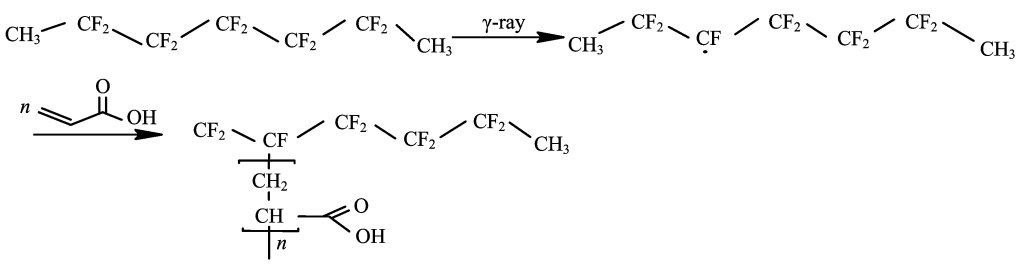

Scheme 1 The main mechanism of simultaneous γ-ray radiation induced grafting of PAA on PTFE.

agar plates. After incubation of the plates at 37 °C for 12 h, the number of colony-forming units (CFU) was counted manually. The mean CFU per milliliter was expressed as the result of multiplying the counted CFU by the dilution factor. ABE of the specimen was calculated according to

$$\mathrm{ABE} = \frac{V_0 - V_\mathrm{t}}{V_0} \times 100\% \qquad (2)$$

where V_0 is the number of CFU in pure PBS buffer solution, and V_t is the number of CFU in the test solution.

III. RESULTS AND DISCUSSION

A. γ-Ray radiation induced graft polymerization of AA on ePTFE film

The main mechanism of simultaneous γ-ray-induced grafting of PAA on ePTFE film are illustrated in Scheme 1 according to previous electron spin resonance studies on free radicals trapped in PTFE irradiated by γ-ray at low temperature or room temperature [26].

Considering the balance of homopolymerization and grafting polymerization of AA monomers and the radiation-induced degradation of PTFE, we first tried the grafting polymerization of AA at a low dose rate (10.4 Gy/min) and absorbed dose (10 kGy), a moderate monomer concentration (15.6wt%), and different inhibitor concentrations ($[Fe^{2+}]$). The results are listed in Table I (run 1−5). When $[Fe^{2+}]$ is lower than 1.8 mmol/L, AA monomers will mainly homopolymerize into a gel, rather than graft polymerize on PTFE film. Once $[Fe^{2+}]$ exceeds 1.8 mmol/L, the homopolymerization of AA could be effectively suppressed. The DG of PAA on ePTFE film starts to increase with $[Fe^{2+}]$ until $[Fe^{2+}]$ reaches 18.0 mmol/L. At this point, the DG of PAA is up to 11.8%. However, it should be noted that Fe^{2+} will not only deactivate homopolymerization but also restraint propagation of the grafting chains. Thus, when $[Fe^{2+}]$ is over 18.0 mmol/L, the DG of PAA decreases rapidly to about 5.0%. Evidently, there is an optimal inhibitor concentration for the grafting of PAA on ePTFE film. So, $[Fe^{2+}]$ is fixed to 18.0 mmol/L during all the following research in this work.

TABLE I The DG of PAA on ePTFE films under different irradiation conditions. Absorbed dose rate in Gy/min, absorbed dose in kGy, $[Fe^{2+}]$ in mmol/L, AA in wt%.

Run	Dose rate	Dose	$[Fe^{2+}]$	AA	DG/%
1	10.4	10	1.8	15.6	Gel
2	10.4	10	3.6	15.6	6.2
3	10.4	10	18.0	15.6	11.8
4	10.4	10	27.0	15.6	5.7
5	10.4	10	36.0	15.6	5.0
6	10.4	1.25	18.0	15.6	2.2
7	10.4	5	18.0	15.6	7.7
8	10.4	15	18.0	15.6	14.9
9	10.4	20	18.0	15.6	20.3
10	5.6	10	18.0	15.6	21.0
11	22.2	10	18.0	15.6	2.6
12	41.6	10	18.0	15.6	2.5
13	10.4	10	18.0	5.2	1.5
14	10.4	10	18.0	10.4	8.1
15	10.4	10	18.0	20.8	13.3
16	10.4	10	18.0	25.9	16.2
17	10.4	10	18.0	31.0	17.1
18	10.4	10	18.0	41.2	Gel

The effect of absorbed dose on the morphological changes of the ePTFE films are displayed in Fig 1. The original ePTFE film (Fig.1(a)) shows a macroporous structure constructed by interlaced PTFE fibers. When the absorbed dose is lower than 10 kGy, some deposits can be seen in Fig.1(b). With the continuous increase of the absorbed dose, the deposits on the fibers become more and more, and gradually block in Fig.1 (c) and (d). Finally, the deposits fill up all the pores in the film when the absorbed dose is as high as 20 kGy. This morphological change is in accordance with the corresponding DG of PAA that grows with the absorbed dose, as listed in Table I (run 3 and 7−9), indicating that the deposits should be the grafted PAA. The FTIR spectra of the ePTFE-g-PAA film with a DG of 11.8% (run 3) and 20.3% (run 9) are shown in Fig.2(b), with a comparison with that of the original ePTFE film in Fig.2(a). Besides the characteristic absorption peaks of PTFE, *i.e.*, 502 cm^{-1} (CF_2 wagging), 555 cm^{-1} (CF_2 defor-

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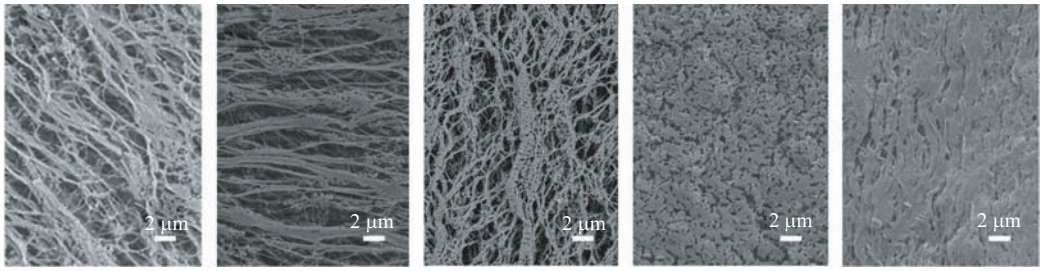

FIG. 1 SEM images of the ePTFE film after irradiated by γ-ray at different absorbed dose (a) 0 kGy, (b) 5 kGy (run 7), (c) 10 kGy (run 3), (d) 15 kGy (run 8), and (e) 20 kGy (run 9).

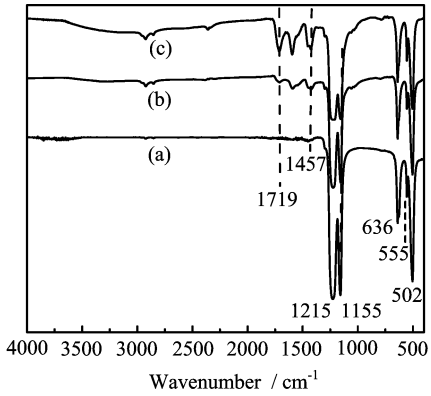

FIG. 2 FTIR spectra of (a) original ePTFE film, ePTFE-g-PAA film with a DG of (b) 11.8% (run 3), and (c) 20.3% (run 9).

mation), 636 cm^{-1} (CF_2 rocking), 1155 cm^{-1} (ν_{asC-F}), and 1215 cm^{-1}(ν_{sC-F}) [27], new absorption peaks contributed by AA structural units at 1719 cm^{-1} ($\nu_{C=O}$), ~2900 cm^{-1} (ν_{C-H}), and 1457 cm^{-1} (δ_{C-H}) appear. The intensities of these bands also become stronger as the DG of PAA increases. All the above results verify that PAA can be successfully grafted on ePTFE film initiated by γ-ray irradiation at the appropriate conditions.

The DG of PAA also depends on the dose rate under a constant absorbed dose. As listed in Table I (run 3 and 10−12), the DG of PAA decreases rapidly from 21% to 2.5% when the dose rate increases from 5.6 Gy/min to 41.6 Gy/min. This phenomenon was caused by two reasons. First, the radical concentration will increase with the dose rate so that the possibility of radical termination rises. Secondly, the high degree of gelation in the system at high dose rate results in a high viscosity of the grafting system, which makes the diffusion of monomers difficult so as to inhibit the grafting reactions.

It is also found that excessive monomer concentration may not be good for the grafting of PAA, as shown in Table I (run 3 and 13−18). The DG of PAA commonly increases with AA concentration. However, the gelation induced by the crosslinking of the PAA chains in the solution also becomes more and more serious with the increase of AA concentration. When the AA concentration rises up to 41.6%, the whole system becomes a gel and the ePTFE film even cannot be separated.

B. Loading silver nanoparticles onto ePTFE-g-PAA films

Compared with the raw ePTFE film, ePTFE-g-PAA film has an improved hydrophilicity due to the grafted hydrophilic carboxyl groups. The aqueous solution of $AgNO_3$ can permeate into the ePTFE-g-PAA film. When pH equals to 7.0, Ag^+ ions can be adsorbed on the grafted PAA chains through strong electrostatic interaction between Ag^+ and COO^- ions. At the time, the absorbed Ag^+ ions can be reduced into silver atom by the addition of $NaBH_4$. The produced silver atoms further *in situ* aggregate into silver nanoparticles to form ePTFE-g-PAA/Ag hybrid film. Since silver ions are immobilized by COO^- ions, the as-prepared silver nanoparticles will also be fixed and distributed along the PAA chains so that the loading capacity of silver nanoparticles can be tunable by the DG of PAA. Figure 3(a) is a typical surface morphology of the prepared ePTFE-g-PAA/Ag hybrid film. It can be clearly seen that particles with a size of several tens of nanometers to 100 nanometer are absorbed on the film. Figure 3(b) shows the XRD pattern of the corresponding hybrid film in Fig.3(a). Three peaks located at 2θ values of 38.26°, 44.34°, and 64.57° correspond to (111), (200), and (220) reflection of fcc structure of metallic silver respectively [28]. This demonstrates that the produced nanoparticles are the crystals of silver 3c (JCPDS card No.04-0783). The full width at half maximum of the peak at 2θ of 38.26° is 0.561. So according to Scherer equation [29], the size of the crystalline silver nanoparticles can be calculated as 15 nm, which is much less than the observed particle size in Fig.3(a). This result indicates that the loaded Ag nanoparticles are the aggregates, rather than individual nano-Ag grain.

The chemical state of the silver nanoparticles loaded on the ePTFE-g-PAA film can also be verified by XPS analysis, as shown in Fig.4(a). The peaks of 368.3 eV ($3d_{5/2}$) and 374.1 eV ($3d_{3/2}$) indicate that the metallic

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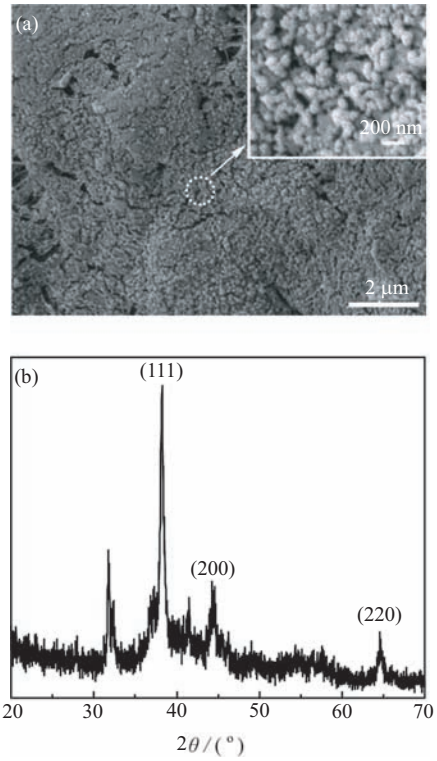

FIG. 3 (a) SEM image and (b) XRD spectrum of ePTFE-g-PAA/Ag hybrid film prepared from run 9 in Table I. The inset in (a) is the SEM image with high magnification.

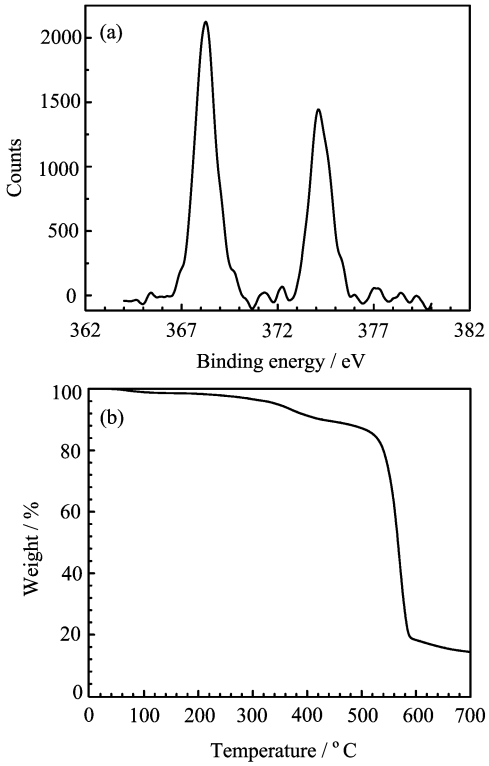

FIG. 4 (a) XPS spectrum and (b) TGA curve of ePTFE-g-PAA/Ag hybrid film prepared from run 3.

state silver (Ag^0) atoms are formed. The loading capacity of Ag nanoparticles can be determined by TGA analysis, as shown in Fig.4(b). Two distinct weight losses corresponding to decomposition of PAA and PTFE could be detected at 240−450 and 470−650 °C, respectively. There is a 14.4% of residual weight fraction at above 650 °C, which corresponds to the load capacity of silver nanoparticles. Meanwhile, the 9.2% of weight loss of PAA in the hybrid film equals to a 10.8% of PAA in the pure ePTFE-g-PAA film, which is very close to the DG measured by the weighing method, *i.e.* 11.8%.

C. Antibacterial activity of ePTFE-g-PAA/Ag hybrid films

The quantitative antibacterial activity of the prepared ePTFE-g-PAA/Ag hybrid films was measured using counting plate method. The numbers of viable *E. coli* cells in the suspensions in contact with the different sample films are listed in Table II, as well as shown in Fig.5. For the original ePTFE film, the ABE is only 45.3% after 4 h. Grafting of PAA on ePTFE film could make a little improvement on the film, *i.e*, the ABE rises to 63.6%. However, ePTFE-g-PAA/Ag hybrid films show very effective antibacterial activity against *E. coli* no matter what the DG of PAA is. Both of them can kill all the bacteria in the suspension in 1 h, *i.e.*, the ABE is 100%. Moreover, this excellent antibacterial activity can last at least for 4 h.

TABLE II Antibacterial effect of ePTFE, ePTFE-g-PAA, and ePTFE-g-PAA/Ag hybrid films against *E. coli*.

Film	DG/%	CPU/10^7			ABE[c]/%
		0 h	1 h	4 h	
ePTFE	0	6.4	4.2	3.5	45.3
ePTFE-g-PAA	20.3	6.4	2.8	2.2	63.6
ePTFE-g-PAA/Ag[a]	11.8	6.4	0	0	100
ePTFE-g-PAA/Ag[b]	20.3	6.4	0	0	100

[a] Film prepared from run 3.
[b] Film prepared from run 9.
[c] ABE after 4 h.

IV. CONCLUSION

In this work, the grafting polymerization of AA has been successfully conducted on ePTFE film using simultaneous γ-ray-radiation-induced grafting method under the appropriate conditions including an optimal inhibitor concentration [Fe^{2+}], low dose rate, low absorbed dose, and moderate monomer concentration. The DG of PAA can be controlled by the monomer concentration, absorbed dose, and dose rate. The pores in ePTFE films could be filled with the increase of the

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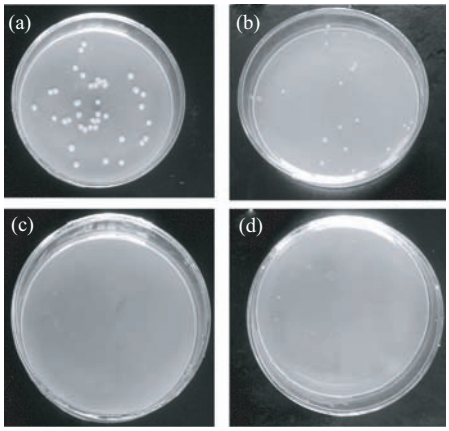

FIG. 5 The antibacterial effect against *E. coli* after 4 h of (a) original ePTFE film, (b) ePTFE-g-PAA film with a DG of 20.3%, (c) ePTFE-g-PAA/Ag hydrid film with a DG of 11.8%, (d) ePTFE-g-PAA/Ag hydrid film with a DG of 20.3%.

DG of PAA. SEM, XRD, and XPS results prove that the grafted PAA chains can immobilize silver ions in a neutral silver nitrate solution, and further *in situ* fix the produced Ag nanoparticles on ePTFE film in the presence of reduction agent, $NaBH_4$. The loading capacity of Ag nanoparticles could be tuned by the DG of PAA, and determined by TGA. The prepared ePTFE-g-PAA/Ag hybrid film exhibits excellent and lasting antibacterial activity. It can kill all the *E. coli* in the suspension in one hour, *i.e.*, the ABE is 100%. Moreover, this excellent antibacterial activity can last at least for 4 h. This technique provides a facile strategy for the preparation of effective antibacterial ePTFE film, which has great significance on expanding the practical applications of ePTFE in the field of antibactericidal and biomedical materials.

V. ACKNOWLEDGMENTS

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