Synthesis of Antibacterial Polypropylene Film with Surface Immobilized Polyvinylpyrrolidone-Iodine Complex

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ABSTRACT: A novel antibacterial material with surface immobilized polyvinylpyrrolidone-iodine complex was synthesized facilely by a two-step approach. First, *N*-vinylpyrrolidone (NVP) was photografted onto polymeric substrates, and subsequently the surface-grafted polyvinylpyrrolidone (PVP) underwent complexation of iodine. In the UV-induced photografting process, PVP was efficiently grafted onto the polypropylene (PP) film surface by a unique film interlayer photopolymerization (FIP) technique; the grafting yield (Y_g) could be controlled by varying the irradiation time or the monomer concentration. Further, we demonstrated that the grafted PVP chains could readily perform the complexation reaction with iodine as the homopolymer PVP does, which was characterized by UV–vis spectroscopy. The antibacterial activity of the modified polymer against *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans* was investigated. The results show that the modified PP film with surface-immobilized PVP-I complex has a desirable antibacterial property, with broad spectrum and high efficiency. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2026–2031, 2005

Key words: antibacterial materials; functionalization of polymers; photopolymerization; polyvinylpyrrolidone; surfaces

INTRODUCTION

Antibacterial materials have been used in a wide variety of applications, such as biomedical products, packing materials, filters of air-conditioning systems, and so forth. Up to now, the predominant approach to obtain antibacterial material has been to incorporate or adsorb some bactericides, including heavy metals, halogens, phenols, and antibiotics, into the existing matrix.[1–7] But this technique usually requires a large quantity of bactericides, thus leading to cost increase as well as the damage of bulk property. Furthermore, the antibacterial substances added may gradually release from inside the material to the environment, resulting in fast invalidation of the antibacterial action.

Chemical immobilization of antibacterial reagents onto the material's surface is an alternative, attractive method to solve the above problems. Many polymerizable bactericides, such as quaternary ammonium salts,[8–10] quaternary phosphonium salts,[11–15] pyridinium salts,[16–23] and so forth, have been grafted onto film or fabric surfaces by various means, resulting in the desirable antibacterial property.

It has been recognized that polyvinylpyrrolidone-Iodine (PVP-I) complex, commercially named "povidone iodine," is a promising bactericide with various attractive merits, such as broad spectrum, high efficiency, nonirritation, and persistence.[24–28] However, few attempts have been made to introduce the PVP-I complex onto the polymer surface, by which a novel antibacterial material is to be created. Moreover, due to the biocompatibility of the PVP-grafted surface, this antibacterial material may be extended to the manufacture of biomedical devices.

In a series of photografting studies, we have facilely grafted various vinyl monomers onto polymer surfaces by a unique film interlayer photopolymerization (FIP) technique.[29–34] This study aims at photografting PVP onto polypropylene film first, and subsequently having the surface-grafted PVP undergo complexation of iodine, thus resulting in a novel antibacterial material with surface immobilized PVP-I complex (Scheme 1). The chemical principle of surface photografting is also illustrated in Scheme 1: under UV irradiation, the excited benzophenone (BP) abstracts hydrogen from the substrate surface, thus resulting in a surface free radical (grafting point). Consequently, the surface graft po-

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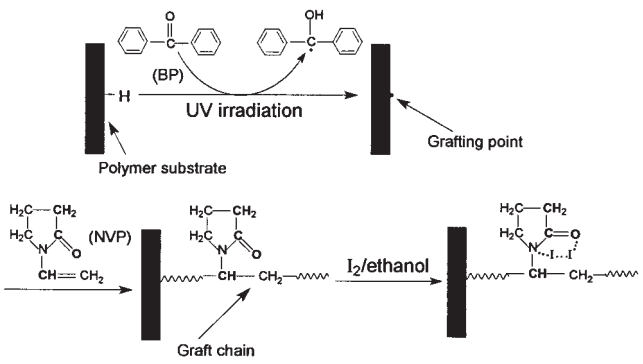

Scheme 1 Synthesis route of surface immobilized PVP-I complex by surface photografting of NVP and the subsequent complexation of iodine.

lymerization will occur in the presence of vinyl monomers like NVP.[30]

EXPERIMENTAL

Materials

Commercial casting polypropylene (PP) film was used as a model polymeric substrate, which was first cut into 5 × 5 cm sheets, then Soxhlet-extracted with acetone for 48 h to remove the additives and impurities.

NVP was distilled at reduced pressure to eliminate the inhibitor. BP and iodine were of analytical grade and used without further purification. Acetone, ethanol, and *n*-heptane were of analytical grade and used as received. All reagents were purchased from Beijing Chemical Reagents Company.

Escherichia coli (*E. coli*), *Staphylococcus aureus* (*S. aureus*), and *Candida albicans* (*C. albicans*) were obtained from the American Type Culture Collection (ATCC 8099, ATCC 6538, and ATCC 10,231, respectively).

Surface photografting procedure

The apparatus and procedure of surface photografting have been described in detail in our previous articles.[29–34] Briefly, a predetermined amount of NVP solution containing BP was deposited between two overlapping films with a microsyringe and spread into an even and very thin liquid layer (about 3 μm) under suitable pressure from a top quartz plate. Then the assembled unit was irradiated under UV light (high-pressure mercury lamp, 1kW) from the top side at room temperature for 0.5–4 min. After irradiation, the top and bottom films were separated and put into a vacuum chamber, then kept at room temperature for 24 h to vaporize the residual monomer and solvent. Afterwards. the grafted films were subjected to Soxhlet extraction with water for 12 h to remove the ungrafted homopolymer of PVP.

The surface photografting parameters—grafting yield (Y_g), percent conversion of NVP to the overall photopolymerization (C_p), and percent conversion of NVP to the photograft polymerization (C_g)—were obtained by the following equations:

$$C_p = (W_p/W_m) \times 100\% \quad (1)$$

$$C_g\text{-}(W_g/W_m) \times 100\% \quad (2)$$

$$Y_g = (W_g/W_f) \times 100\% \quad (3)$$

where W_p is the weight of total PVP formed, including grafted PVP and homopolymerized PVP, W_m the weight of monomer added, W_g the weight of grafted PVP, and W_f the weight of virgin substrates. All the gravimetric analysis was performed with an electronic balance (Sartorius BP211D, Germany) with accuracy of 0.00,001 g.

Iodine complexation

The grafted samples were impregnated in iodine solution (100% ethanol as solvent) at various iodine concentrations and temperatures for some certain time, then thoroughly rinsed with *n*-heptane to remove the adsorbed iodine. The samples were dried in air at room temperature.

Characterization

The chemical composition of the grafted surface was measured by a Fourier transform infrared (FTIR) spectrometer (ThermoNicolet Nexus 670), equipped with a variable-angle attenuated total reflection (ATR) accessory (PIKE ATRMax II) with ZnSe (n = 2.43) as the internal reflection element wafer. The chemical structure of the grafted samples after iodine treatment was determined by a UV–vis spectrometer (GBC Cintra 20, Australia).

Antibacterial activity test

A colony of *E. coli*, *S. aureus*, or *C. albicans* grown on an agar slant was inoculated in 5 mL of nutrient broth. The culture was incubated at 37°C for 18–20 h with gentle agitation on a rotary shaker (300 rpm). Then the cells were diluted serially with 0.03 mol L^{-1} phosphate buffered saline (PBS: 7.13 g × L^{-1} Na_2HPO_4 × $12H_2O$, 1.36 g × L^{-1} KH_2PO_4, pH 7.2) to a desired concentration. The virgin and modified films were incubated with 20 mL of cell suspension at 37°C for different times with 300 rpm agitation. Afterwards, 1 mL of the cell suspension was taken out, diluted serially, and placed on an agar plate for incubation at 37°C for 72 h. The number of viable cells was determined as

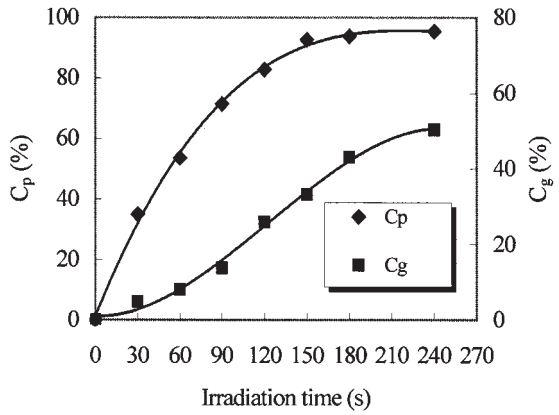

Figure 1 Evolutions of the overall photopolymerization (C_p) and surface photograft polymerization (C_g) of NVP. Monomer concentration, 2.0 mol L^{-1}; BP concentration, 0.05 mol L^{-1}; UV intensity, 6800 μW cm^{-2}.

colony forming units (CFU). The original number of cells used for a given experiment was determined by standard serial dilution.

The morphology of the bacteria cells after contact with the virgin and modified samples was observed by a scanning electron microscope (FEI Quanta 200). The samples were first washed with PBS immediately after the incubation period, then immersed into 2.5 vol % glutaraldehyde and kept at 4°C for 5 h for cell fixation. The samples were again washed with PBS, followed by step dehydration with 30%, 50%, 70%, 85%, 95%, and 100% ethanol for 15 min each. Finally, the samples were dried under supercritical CO_2 and sputter-coated with a thin film of gold for imaging purposes.

RESULTS AND DISCUSSION

Surface photografting of NVP

With PP film as substrate and BP as photoinitiator, the evolutions of overall photopolymerization and surface photograft polymerization of NVP were investigated. The results are presented in Figure 1.

It can be seen that NVP could readily undergo photopolymerization under UV irradiation. Due to the fairly thin monomer solution between two overlapping films, the photografting process here reported could proceed much more rapidly in comparison with the conventional vapor- or liquid-phase procedures.[35,36] Within 2 min, C_p could reach more than 80%, and the corresponding C_g was around 25%. Within 3 min, nearly 95% of the total monomer had participated in photopolymerization, 42% of which was grafted onto the polymer surface. Later, the increase of C_p slowed down while C_g still increased, which means that some ungrafted homopolymer chains could be eventually grafted onto the film surface by coupling reactions.[33] The ultimate grafting efficiency (defined as W_g/W_p) of this photografting system was more than 60%. The UV-induced surface photografting is, therefore, a facile technique for rapid surface modification of commercial polymeric materials.

Figure 2 shows the grafting yields at various irradiation times and monomer concentrations. In accordance with the evolution of C_g, the grafting yield increased along with the irradiation time. Moreover, it can be seen that higher monomer concentration led to higher Y_g at a fixed irradiation time, which provides an alternative way to control the density of surface graft chains in addition to the irradiation time. The ease of Y_g control is of great significance in that the surface concentration of PVP-I complex, which has effective antibacterial property, would strongly depend on the density of surface-grafted PVP chains. As estimated from the gravimetric analysis, the ultimate surface density of pyrrolidone groups could be 0.39 μmol cm^{-2} for 2.0*M* monomer concentration and 0.72 μmol cm^{-2} for 4.0*M* concentration. Our previous study has shown that over 1% of the grafting yield, the film surface was entirely covered with a layer of graft chains.[32] Therefore, the present grafted surface with such high Y_g may have a multilayer of graft chains, from which high surface concentration of PVP-I complex is expected to be obtained after the iodine complexation procedure.

Characterization of the grafted surface

The success of surface photografting of NVP can be further ascertained by comparing the IR spectra of the grafted film with those of virgin film, as shown in Figure 3. The IR spectra of pure PP and homopolymer PVP are also presented.

In the pure PVP spectrum, the wide absorption band at around 1680 cm^{-1} indicates carbonyl groups

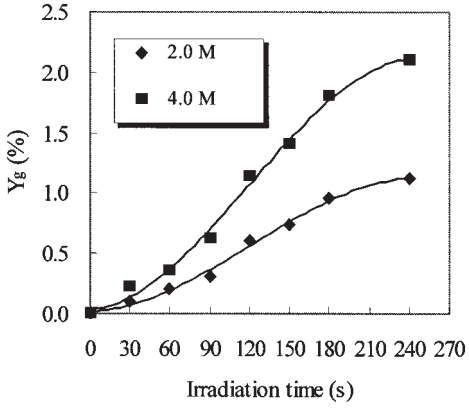

Figure 2 Evolution of surface grafting yield (Y_g) at different monomer concentrations. BP concentration, 0.05 mol L^{-1}; UV intensity, 6800 μW cm^{-2}.

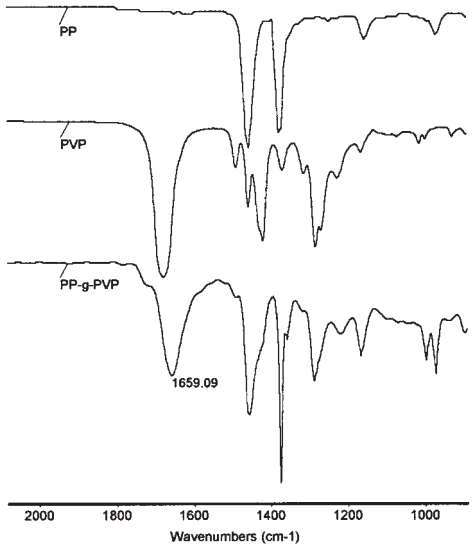

Figure 3 ATR-FTIR spectra of virgin PP, homopolymer PVP, and surface-grafted PP film.

(C═O) in pyrrolidone units, and 1290 cm^{-1} is assigned to the vibration absorption of the C-N bond. Comparing the spectrum of grafted PP with that of pure PP, it can be seen that a specific absorption band appeared at around 1659 cm^{-1}. This band, with a small shift towards lower wavenumbers in comparison with that of pure PVP, corresponds to the existence of PVP graft chains on the film surface.

Complexation of iodine onto surface grafted PVP

There is reason to suppose that the grafted PVP on the polymer surface would perform complexation reactions as the homopolymer PVP does. So far, no reports have ever concerned the complexation of iodine onto the surface-grafted PVP. After being impregnated in iodine solution and completely washed away, the adsorbed iodine with heptane (heptane dissolves free iodine but does not dissolve the iodine in complex[37]), the grafted film became reddish-brown, which suggested that iodine had chemically attached (not adsorbed) onto the PVP-grafted surface. The change of chemical composition on the film surface after iodine treatment was determined by UV–vis spectroscopy, as shown in Figure 4.

The absorption band at around 295 nm is assigned to the pyrrolidone units on the PVP-grafted film surface. Further, it can be seen that a specific absorption peak appeared at around 365 nm in the iodine-treated films, which corresponds to the formation of PVP-I complex.[37]

The kinetics of iodine complexation were further investigated, as shown in Figures 5 and 6. It can be seen that the extent of the complexation reaction gradually increased along with the reaction time. More-

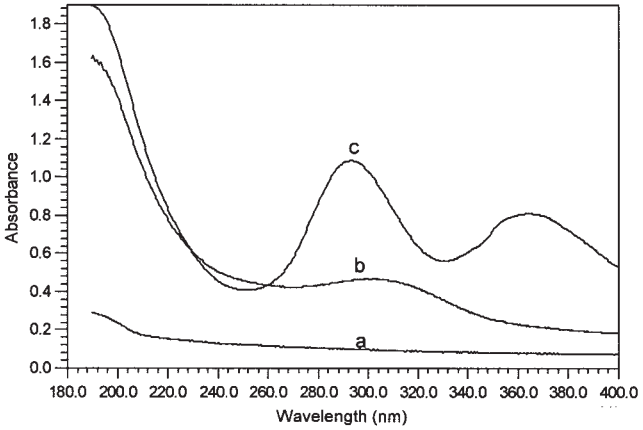

Figure 4 UV absorption spectra of (a) virgin film, (b) PVP-grafted film (Y_g = 2.1%), and (c) PVP-grafted film after complexation of iodine.

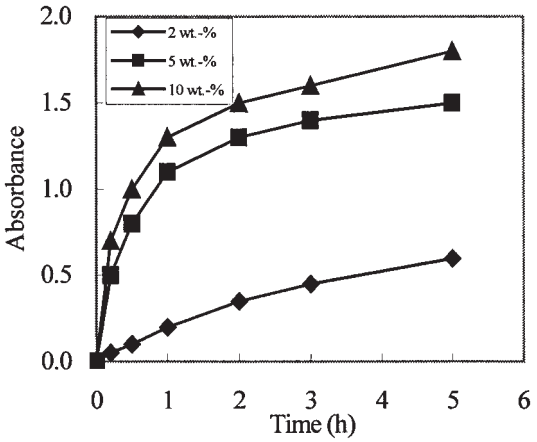

Figure 5 UV absorbance at 365 nm of PVP-grafted film (Y_g = 2.1%) after being treated at various concentrations of iodine solution at 70°C.

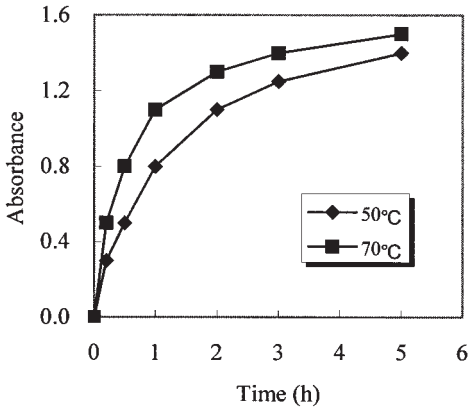

Figure 6 UV absorbance at 365 nm of PVP-grafted film (Yg = 2.1%) after being treated with 5 wt % iodine solution at different temperatures.

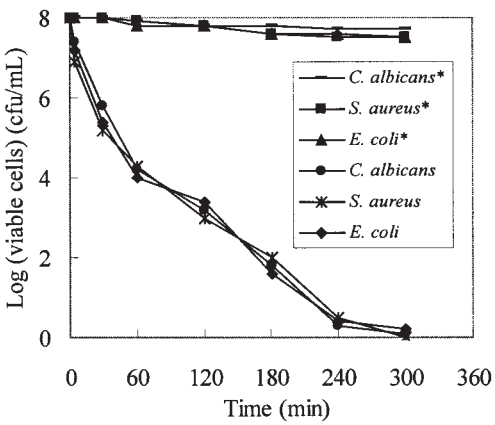

Figure 7 Change of the viable cell number of *E. coli*, *S. aureus*, and *C. albicans* after contact with the virgin and modified film surfaces for different times. *E. coli**, *S. aureus**, *C. albicans**: the microorganisms contacting with the virgin films.

over, the complexation process was greatly affected by iodine concentration and reaction temperature. Figure 5 shows that the complexation of iodine was speeded up by enhancing the iodine concentration, which was in agreement with a basic thermodynamic principle that high iodine concentration would favor the shift of the complexation equilibrium towards the PVP-I complex. Figure 6 shows that higher temperature resulted in deeper complexation at a fixed reaction time. This may reveal a fact that the complexation between PVP and iodine is an endothermic reaction; hence, higher temperature is favorable to this complexation reaction.

As for the chemical structure of the PVP-I complex, there still exists some controversy in literature (one possible model is Scheme 1).[25–28] Most researchers referred to the formation of the hydrogen bond between the triiodide ions ($H^+I_3^-$) and the oxygen atoms in pyrrolidone groups. However, the structure of the PVP-I complex is affected by preparation conditions. In solid or nonaqueous-solution preparations, the iodic species in the PVP-I complex may mostly be molecular iodine. The issue is beyond the emphasis of this study; here we just extend the known complexation reaction to the chemical immobilization of iodine onto the PVP-grafted surface, thus resulting in a unique antibacterial material.

Antibacterial activity

With three types of microorganisms, *E. coli* (gram-negative bacterium), *S. aureus* (gram-positive bacte-

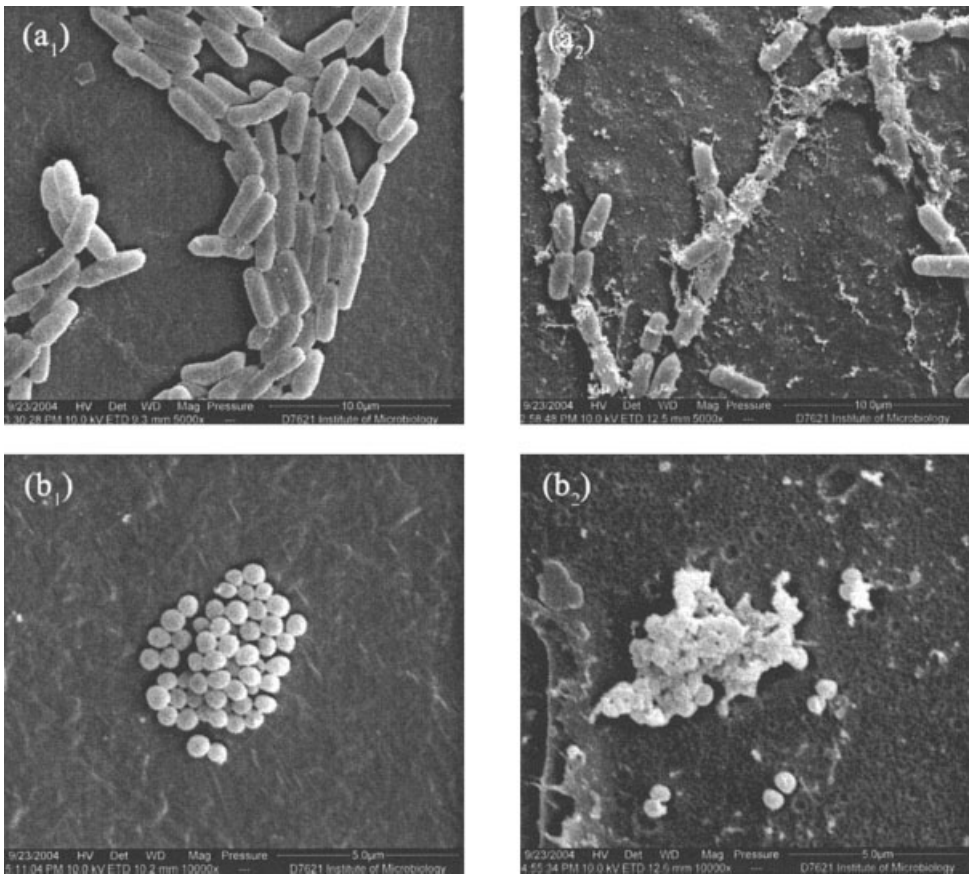

Figure 8 SEM morphologies of (a_1, a_2) *E. coli* and (b_1, b_2) *S. aureus* after contact with (a_1, b_1) virgin films and (a_2, b_2) modified films for 30 min.

rium), and *C. albicans* (fungus), the antibacterial activity of the modified film with surface immobilized PVP-I complex was examined, as shown in Figure 7.

It can be seen that within several minutes (~ 5 min) of contact with the modified films, the number of viable cells of all types of microorganisms sharply decreased to less than 10%. With the contact time increased, nearly 99.999% of the microorganisms could be eliminated. This indicates that the modified surface with PVP-I complex exhibits an excellent antibacterial action. Because the antibacterial material could kill both gram-positive and gram-negative bacteria as well as fungus, it is reasonable to expect that a broad spectrum of microbial species will be susceptible.

The morphologies of *E. coli* and *S. aureus* after contact with the virgin and modified films for 30 min were observed by SEM, as shown in Figure 8.

It can be seen that both of the bacteria on the virgin films kept the natural, regular cell shapes with clean and smooth surfaces, which indicated the living state. In contrast, the bacteria cells exposed on the modified films changed remarkably. The cell shapes turned to be irregular, flat, and even cracked at some positions. Moreover, the bacterial surfaces became indistinct and covered with a layer of slime. These appearances meant that the bacteria had been killed.

It has been recognized that the antibacterial activity of the PVP-I complex is essentially attributed to the iodine ingredient, which may exist as IO^-, I^-, or I_3^- species in the aqueous media.[28] So the sterilization of the antibacterial film may result from the penetration of various iodine species into the bacterial cell, and subsequently lead to halogen-induced denaturation of protein and the relative enzymes, followed by the disruption of the cell membrane and leakage of the intracellular contents.

CONCLUSIONS

NVP was readily photografted onto polymeric substrates and subsequently performed complexation reaction with iodine; thus, a novel antibacterial material with surface immobilized PVP-I complex was synthesized. The photografting of NVP can be completed within several minutes of UV irradiation, and the grafting yield could be controlled by irradiation time or monomer concentration. The surface-grafted PVP could readily form complex with iodine, as the homopolymer PVP does. The viable count method and SEM images confirmed that the modified film with surface PVP-I complex has a desirable antibacterial property, with a broad spectrum and high efficiency.

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