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Research article

Remarkably enhanced thermal properties of tobacco granules with high-thermal-conductivity nanoparticles

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ABSTRACT

Heated tobacco products (HTPs) are a novel type of cigarette that have received extensive attention. The tobacco plug could be made from tobacco granules (TGs), which are heated but not burned during the inhalation process. Thermal conductivity is an important property to evaluate the speed of heating TGs to meet the critical temperature for generating aerosol. Nevertheless, thermal physics properties of TGs is rarely reported. In this study, the thermophysical performance for the tobacco granules is systematically studied. An effective strategy of raising the thermal conductivity of TGs by introducing a small amount of nanoparticles of high-thermal-conductivity-materials (HTCMs, copper, silver, and graphene) is proposed, which not only results in a 35% improvement in the thermal conductivity but also reduces the maximum temperature for generating aerosol. In addition, introducing Cu and Ag particles in the TGs are favorable for improving the antibacterial effect. This method is worth promoting for enhancing the thermal conductivity of other plant-derived heated products.

1. Introduction

Heated tobacco products (HTPs) are a novel type of products, whose tobacco only needs to be heated to release the aerosols, but without the burning process. Therefore, less harmful chemicals would generate in the aerosols for HTPs by comparison of that in cigarette smoke [1]. Currently, there are various trade names of HTPs, including IQOS, Ploom TECH, and glo. Philip Morris International (PMI), the global tobacco giant, launching the IQOS product in Japan and Italy in 2014, which lead the global tobacco market. Two years later, two famous heated tobacco brands of Ploom TECH and glo are launched by the Japan Tobacco (JT) and British American Tobacco (BAT), respectively. For IQOS and glo products, the sticks containing tobacco are inserted into their own heating

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devices, the aerosol gas containing nicotine would generate and then be delivered for inhalation by user when heating to 240–350 °C. For Ploom TECH product, the aerosol containing glycerin and propylene glycol is heated up, which is then forced through branded capsules containing powdered tobacco leaves, again releasing an aerosol that delivers nicotine and other components to the user [2].

The formation and exposure of some harmful and potentially harmful constituents (HPHCs) are significantly reduced by comparison of the standard cigarettes. Although HTPs are prohibited in a few countries, they could be classified as novel tobacco products, smokeless tobacco products, or electronic cigarettes. Some countries use the multiple categories as well [3]. On July 7, 2020, the sale of IQOS Tobacco Heating System is authorized as the modified risk tobacco products (MRTPs) by the U.S. Food and Drug Administration (FDA), whose goal is ensuring that information directed at consumers about decreased risk or decreased exposure from using a tobacco product is supported, and the regulation is expected to benefit the health of the population [4].

Thus far, there are two main heating approaches, i.e., resistive heating and induction heating in the HTP portfolio. Resistive heating relies on the electronic system that is capable of heating the tobacco, the heating temperature could be precisely controlled to avoid burning the tobacco when the current passes through the conductive materials (as blade, needle or cylinder geometry) and releases heat to its surroundings. In this scenario, the material with lower electrical resistance of would generate more heat when the voltage is constant. Induction heating is realized by electromagnetic induction heating, where the heating unit should be the electrically conductive materials that usually are metal. The heating unit is placed in the center of a metal coil. When the electric current goes through the coil, the magnetic field would generate at the center, and this field makes the metal unit at the center heated [1].

Tobacco plug is the key of the HTPs, which is designed and processed for heating. The tobacco plug is mainly consist of tobacco leaves, which are ground and reconstituted into tobacco sheets called cast leaves. In recent years, Chinese manufacturers have launched granular heated tobacco products (GHTPs) and heated herbal (non-tobacco) products (GHHPs). The heated plugs use tobacco or other herbs as raw materials and are made into granules through a granulation and filling process. These granular heated units are compatible with most heating devices on the HTP market. The glycerin content, moisture and size of plant-based granules have significant effects on their thermal conductivity. Due to the inherent low thermal conductivity of plant materials and other additives, the heat efficiency of modern granular heated products is not sufficient, resulting in lower delivery of nicotine and flavor. To improve the thermal conductivity of a specific medium, adding metal materials such as metal particles is a widely used method. Oku et al. described an improvement in the thermal conductivity of carbon materials due to the introduction of metal elements [5]. Wang et al. employed Ag particles to modify the thermal conductivity of a small molecule organic semiconductor [6]. Polymers as the thermal interface materials are often filled with high-thermal-conductivity-materials to strengthen the thermal properties. Lu et al. utilize the molecular dynamics and the two-temperature model in 1 dimension to study the effect of the size of metallic filler on the thermal conductivity enhancement [7]. In addition, as promising fillers, graphite or graphene can improve the thermal performance of thermal interface materials [8]. Recent studies have proved that the antibacterial activities of metal particles and metal composites might stem from several mechanisms, including blistering (blebs), clumping of membranes, and blockage of the electron transport chain [9]. Ag particles commonly own the excellent antimicrobial performance against a variety of microorganisms, such as the viruses, fungi and bacteria. Ag nanoparticles with 10–100 nm size range exhibited high bactericidal activity against bacteria [10].

The target of this study is searching a type of high-thermal-conductivity additive to facilitate the thermal transport in the tobacco granules and to reduce the maximum temperature for releasing aerosol in the meanwhile. Three types of high-thermal-conductivity materials (Cu, Ag and graphene) are added to tobacco granules (TGs). In accordance with the energy dispersive spectroscopy results, metal particles are evenly distributed in the TGs. All three additives (Cu, Ag and graphene) are beneficial for dramatically increasing thermal conductivity of TGs owing to the significantly enhanced phonon transport by the homogeneously distributed high-thermal-conductivity particles. The great effects of introducing Ag and Cu particles on thermal conductivity enhancement in tobacco granule are confirmed. About 35% improvement in thermal conductivity is realized in the TGs-0.1% Cu sample. Whereas the κ of TGs-graphene specimens is slightly lower, which should be ascribed to the porous structure caused by the emission of carbon-based additive at high temperature. In addition, adding Ag particles in TGs could reduce the maximum temperature for releasing aerosol since that Ag could improve the utilization rate of heat so the tobacco granules were heated sufficiently. The safety of utilizing the Ag nanoparticles in tobacco granules is preliminarily proved, Ag particles are almost immobile in the tobacco granules and would not separate from TGs during the inhalation process since that Ag could not be detected in either the filter pads or the filter tip. In the antibacterial test, the nicotine in the TGs was verified to be efficient in inhibiting *E. coli*, *S. aureus* and *P. aeruginosa*, and Ag and Cu particles were capable of further improving the antibacterial activity. Therefore, the addition of only a tiny content of high-thermal-conductivity particles in tobacco granules is capable of accelerating the heat transportation and facilitating the cigarette aerosol production in lower temperature in the meantime. This method is noteworthy for enhancing the thermal conductivity of other types of plant-derived heated products.

2. Experimental

2.1. Tobacco granule preparation

The cured tobacco produced in 2019 was used as raw material and crushed by a grinder, and 80–120 mesh tobacco powder was screened out. After that, 0.1 g of copper (Cu) particles (625 mesh) was mixed with 10 g of tobacco powder adequately, and then the mixture was fully mixed with 90 g of tobacco powder again. Next, 10.5 g of propylene glycol (PG), 24.5 g of glycerin (VG) and 27.5 g of water were added to the Cu-containing tobacco powder above. After being stirred evenly, the tobacco mixture was left at room temperature for 1 h to make the liquid components fully absorbed by the tobacco. After absorption balancing, the material was extruded with a 1 mm aperture at a 45 rpm screw rotation speed in the extruder to form cylindrical tobacco strips. The wet cylindrical tobacco strips are firstly cut into the short strips, and then gradually become the spherical wet tobacco during the rotation process. These two steps are very important for preparation of the tobacco granules. Without the step, the shape and size of the tobacco granules are not uniform, which can affect the preparation of HTP. The rotation is performed at the speed of 1500 rpm for 3 min, and the wet tobacco granules are then obtained. Dry tobacco granules were obtained by drying wet tobacco granules at 90 °C for 60 min. Finally, dry tobacco granules were screened through 16- and 30-mesh sieves, and tobacco granule samples of 16–30 mesh were obtained, labeled "TGs-0.1% Cu". Similarly, samples of tobacco granules (named TGs-0.2% Cu, TGs-0.3% Cu, TGs-0.5% Cu, TGs-0.1% Ag, TGs-0.2% Ag, TGs-0.3% Ag, TGs-0.5% Ag, TGs-0.1% graphene, TGs-0.2% graphene, TGs-0.3% graphene and TGs-0.5% graphene) were prepared by the same method. Tobacco granules without high-thermal-conductivity material were used as control samples called "TGs". The preparation process of tobacco granules is shown in Fig. 1.

2.2. Morphology and composition analysis

The morphology of the tobacco granules were characterized by the field emission scanning electron microscopy (FESEM, Zeiss, Sigma 300, Germany) that matches energy dispersive spectroscopy (EDS, NORAN SYSTEM 7, Thermo, USA) to identify the elemental contents. Elemental contents of the tobacco granules with metal additives were obtained by using an inductively coupled plasma spectrometer (ICP–OES). The tobacco granules were burned to ash and dissolved in hydrochloric acid, and the supernatant was measured by ICP analysis using a centrifuge (TL-4.7 W, SCI, China) for solid–liquid separation. Granule sizes were counted by using ImageJ software. PG and VG were quantified by gas chromatography-mass spectrometry with the internal standard method.

20 ml of isopropyl alcohol containing 1,3-butanediol as the internal standard was added to the flask to reduce the error caused by sample pretreatment. Then the samples of tobacco granules were ground into powders, and 0.2 g of powder was weighed and put into a 50 ml flask. The flask with the sample was shaken at room temperature for 3 h and stood still for 12 h. Subsequently, 2 ml of supernatant was taken and filtered through a 0.45 μm organic filter membrane. Finally, the filtrate was detected by gas chromatography-tandem mass spectrometry (GC–MS). A GC–MS (PerkinElmer Clarus 600T, USA) equipped with a DB-ALC1 column (Agilent, USA, 30 m × 0.32 mm ID, 1.8 μm film thickness) was used to quantify the PG and VG. Helium was introduced as the carrier gas with a flow rate of 1.5 ml/min. The oven program started at 50 °C for 1 min; then, the temperature was increased to 150 °C at 10 °C/min and held for 5 min, and finally increased up to 280 °C at 20 °C/min and held for 10 min. The electron ionization energy was 70 eV. The mass range was m/z 50 to 350, and the ion source temperature was set at 200 °C. The corresponding GC–MS results are shown in Fig. S1. Granular heated tobacco sticks were prepared according to the structure shown in Fig. 2. The preparation process was as follows: (1) one end of the empty paper tube was sealed by sealing paper with white latex; (2) 0.17 g of tobacco granules was filled in the empty paper tube from the open end; and (3) the blocking element and filter tip were placed in the rest of the paper tube in sequence. An IQOS 3.0 Multi device (Philip Morris International, USA) was connected with an e-cigarette smoking machine (PUFFMAN X500E, China) for puffing the granular heated tobacco sticks filled with different tobacco granules. The TPM of the granular tobacco was captured by Cambridge glass-fiber filter PADS and analyzed using the Health Canada Intensive (HCI) Machine-Smoking Protocol [11].

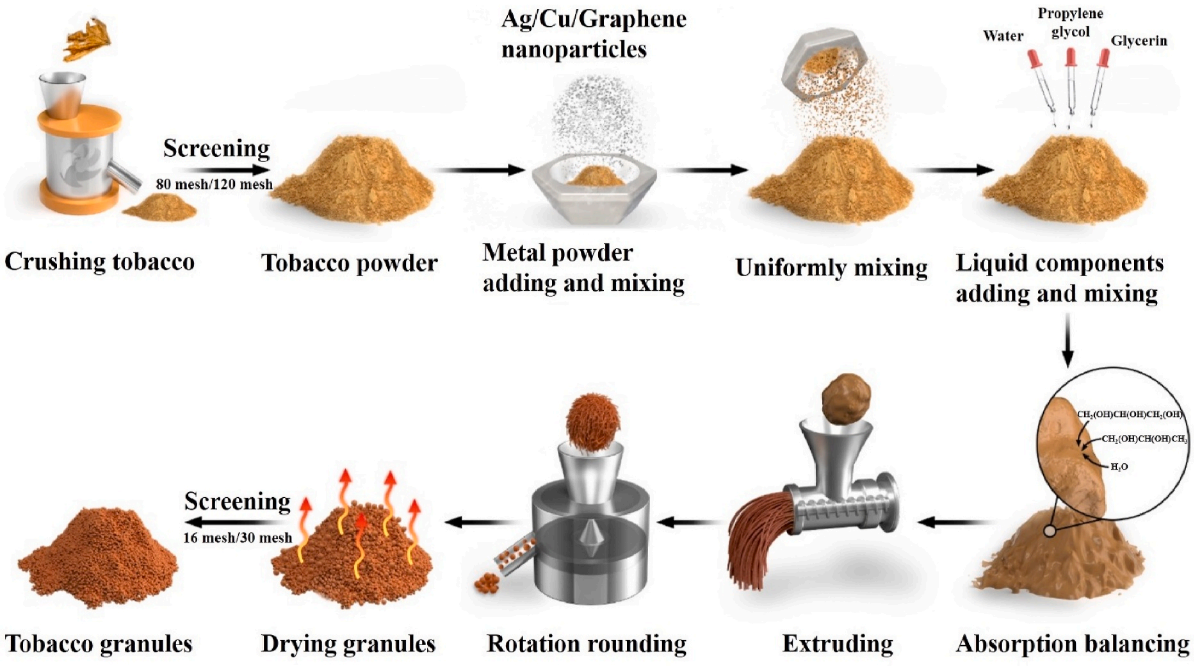

Fig. 1. Flow diagram of tobacco granules preparation procedure.

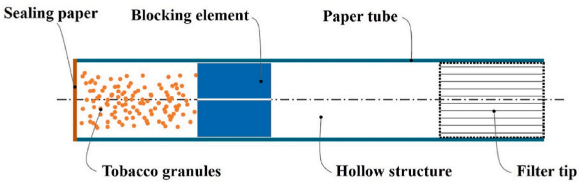

Fig. 2. Schematic diagram of granular heated tobacco stick.

2.3. Thermal physics property characterization

Heat flow meter method is a typical approach to measure the thermal conductivity of the granular materials. In this scenario, the thermal conductivity of the tobacco granules was measured by using a thermoelectric conversion efficiency evaluation system (mini-PEM, Advance Riko, Japan) with the heat flow meter method. The hot-side temperature was set at 313 K, and the temperature of the water cooler was set at 293 K. The Teflon is chosen to be the mold material because of the excellent mechanical strength and the ultralow thermal conductivity by comparison with the tobacco granules. TGs were filled into the hollow Teflon mold to protect granules from compaction, and a very thin wall of 0.5 mm is beneficial for weakening the effect of the mold on the thermal conductivity measurement. The bottom of the mold is designed as 10 mm $\times$ 10 mm to match the size of the heater, and the height is 5 mm. The natural convection process exists in the thermal conductivity measurement. To ensure the effect of void on convection is consistent in each measurement, the tobacco granules with the same mass (0.25 $\pm$ 0.01 g) are filled in the same mold. Thermal conductivity measurements were performed under vacuum conditions. In addition, error bars for thermal conductivity were determined from three test results for each sample. Although it's difficult to accurately measure the thermal conductivity of the granular materials by using this method due to the convection, it's fair to evaluate the impact of high-thermal-conductivity nanoparticles on thermal conductivity enhancement of tobacco granules under the same conditions. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the tobacco granule samples were performed using a differential thermal analyzer (STA449, Netzsch, Germany) in an air atmosphere.

2.4. Antibacterial test

Escherichia coli, *Pseudomonas aeruginosa* and *Staphylococcus aureus* stored in glycerin were inoculated with 50 μL onto Luria-Bertani (LB) solid medium plates and incubated at 37 °C for 12 h. Single colonies were placed in 15 mL of LB liquid medium for 24 h. The bacterial counts of *E. coli*, *P. aeruginosa* and *S. aureus* were estimated by using LB agar medium, and bacteria were placed in 10 mL of LB liquid medium and cultured on a shaker (200 rpm, 37 °C) for 14 h. The dilution factor of all bacterial cultures was 1×10^4. Then, different contents of tobacco granules (1/16: 18.75 mg, 1/32: 9.375 mg, 1/64: 4.688 mg, 1/128: 2.344 mg) with and without 0.1% high-thermal-conductivity materials were weighed and subjected to 0.3 mL of dilute bacterial suspension for 60 min at room temperature. After the reaction, 0.1 mL of the mixed solution was weighed and inoculated on the surface of the nutrient agar plate medium that the bacteria needed, which was then evenly spread and inoculated on 2 plates for each concentration. The culture was incubated in a 37 °C incubator, and the number of colonies was counted after 24 h.

The control sample (TGs) and TGs with high-thermal-conductivity particles were weighed as 187.5 mg and then solubilized with 6 mL of medium. Cell climbing slices were put into a 12-well plate with 1.98 mL of culture medium and 20 mL of corresponding bacteria, and the culture process was carried out for 24 h at 37 °C. The subsequent culture supernatant was discarded, and the culture medium was cleaned by using PBS, which was then fixed with 4% paraformaldehyde for 15 min. After absorbing paraformaldehyde fixative and cleaning with PBS, the culture medium was baked at 37 °C for 30 min. One milliliter of crystal violet staining solution (0.4 g crystal violet powder + 100 mL methanol) was added to each well and stained at room temperature for 20 min. The climbing slices were finally removed and cleaned for observation. Tobacco granules without high-thermal-conductivity material were used as a control sample called "TGs", and the blank sample without TGs was used for comparison.

Table 1
Metal particles (Cu and Ag) contents in TGs.

Sample	Element	Content (%)
Pristine TGs	Cu/Ag	<0.001
TGs-0.1% Cu	Cu	0.08
TGs-0.2% Cu	Cu	0.16
TGs-0.3% Cu	Cu	0.21
TGs-0.5% Cu	Cu	0.39
TGs-0.1% Ag	Ag	0.07
TGs-0.2% Ag	Ag	0.11
TGs-0.3% Ag	Ag	0.16
TGs-0.5% Ag	Ag	0.24

3. Results and discussion

3.1. Composition

Tobacco granules are mainly composed of natural tobacco, glycerin, propylene glycol and water. IR spectra is utilized to characterize the main functional groups of the TGs with metal particles additions, as shown in Figs. S2 and S3. The C–H band locates at 2927 cm^{-1}, and the O–H band locates at 3412 cm^{-1}. The ratio of the bands C–H/O–H (~0.6) is close to that of the midribs [12]. The

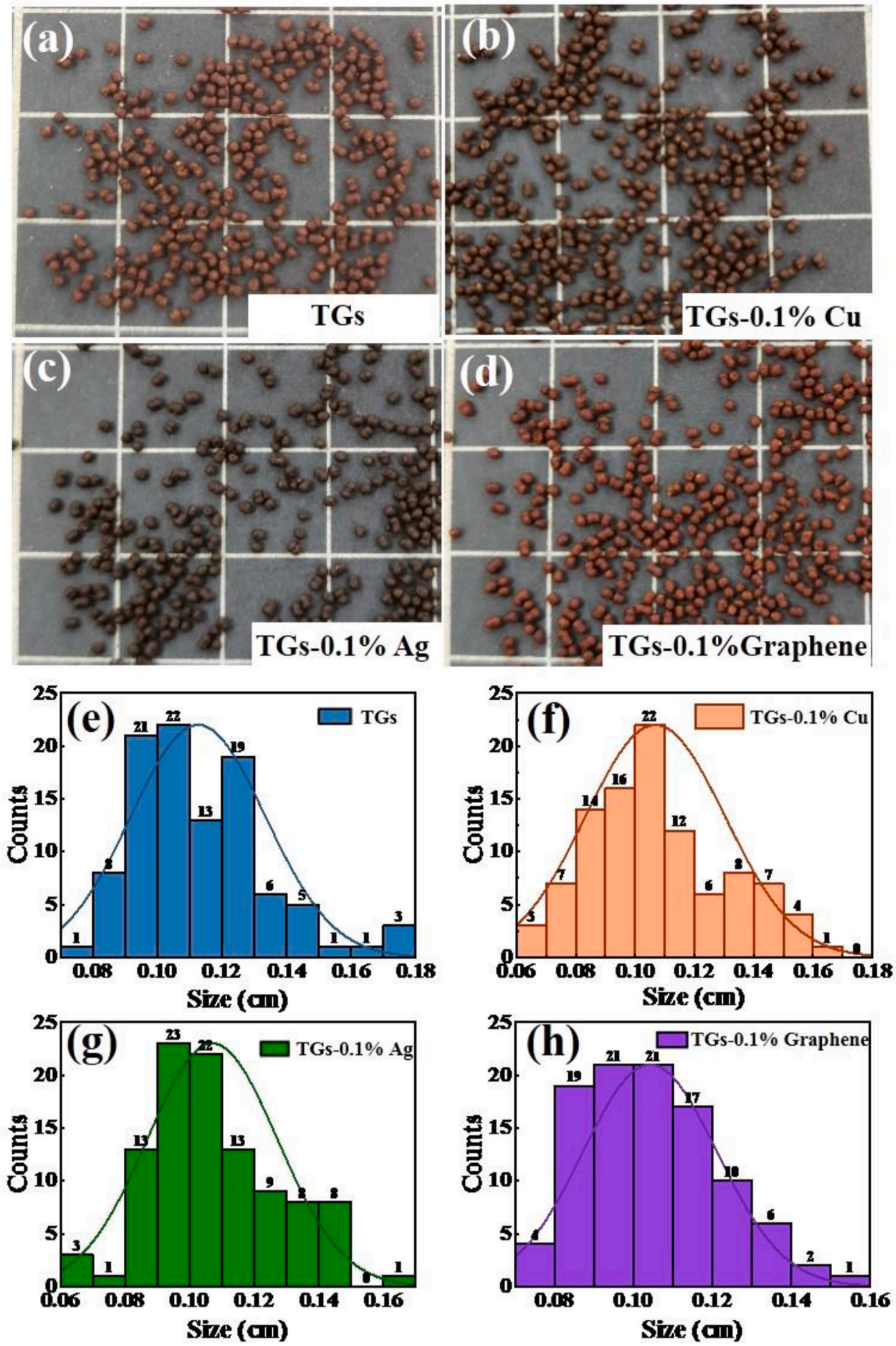

Fig. 3. Morphology of the (a) TGs, (b) TGs with 0.5% Cu, (c) TGs-0.5% Ag and (d) TGs-0.5% grapheme specimen, statistics of size of (e) TGs, (f) TGs-0.5% Cu, (g) TGs-0.5% Ag and (h) TGs-0.5% grapheme sample.

peaks belonging to metal Cu or Ag are invisible due to the tiny content below the detection limit. In addition, the inductively coupled plasma-optical emission spectrometry (ICP–OES) is performed to accurately confirm the metals content in the TGs (Table 1). In accordance with the experimental results, the content of Cu and Ag in the TGs is gradually increased. It is worth noting that the actual content deviates from the nominal ratio since this ratio is calculated according to the dry tobacco powders, and the subsequently added water, propylene glycol and glycerin would result in a decreased weight ratio. Besides, the mass loss during the synthetic procedure is possibly ascribed to the agglomeration of metal particles. Only half of the Ag particles are maintained in the TGs, whereas more Cu particles are preserved (78%) in the TGs when adding the same content of additives, indicating that Cu particles could be better dispersed in the tobacco granules. Thereby, the HTCMs are successfully added into the tobacco granules, which would not change the basic components of the TGs.

3.2. Morphology

The morphology of the synthesized tobacco granules differs from that of natural tobacco, which mainly depends on the synthetic procedure. Regular spherical granules are obtained by combining with the extruding and rotation rounding processes, as shown in Fig. 3(a–d). The size statistics of the tobacco granules are depicted in Fig. 3(e–h), revealing exhibit a tendency close to a normal distribution, resulting in the dense stacking while maintaining appropriate space for the aerosol flow. This distribution of tobacco granules size is therefore beneficial for achieving the higher thermal conductivity [13]. The average size for all tobacco granules concentrates at approximately 0.9–1.1 mm, which is immune to the HTCMs additions. Thus the fabrication method of adding HTCMs in TGs by combining the extruding and rotation rounding process is repeatable, which assists to achieve the products with similar size. Therefore, the effect of granule size on the thermal conductivity measurement is negligible, which is not the key point in this study as well. The microstructure and elemental distribution of TGs were further observed by utilizing field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectrometry (EDS). As exhibited in Fig. S4, the tissue of the synthesized tobacco is dense, which is mainly composed of the C and O elements. The morphology of the tobacco granules with metal particle additions is similar to the pristine specimen (Figs. S5 and S6). According to the EDS mapping results, Cu particles evenly distribute on the surface of the TGs-0.1% Cu specimen, whereas Ag particles prefer to gather in the matrix of TGs-0.1% Ag sample. This result verifies the aforementioned hypothesis for the ICP result that Ag particles are readily to agglomerate in the TGs. Therefore, adding tiny content of HTCMs in TGs would not change either microstructure or macro size, the metal particles could evenly disperse in the tobacco granules, which would greatly affect the thermal physical properties of the TGs.

3.3. Thermal properties

High thermal conductivity (κ) of TGs favors rapidly transferring heat and therefore facilitating more aerosol production in a short time. The κ of TGs with and without the HTCMs additions at 313 K are shown in Fig. 4(a), revealing the great effect of HTCMs on enhancing thermal transport in tobacco granules. Pristine tobacco granules possess the ultralow thermal conductivity of 0.17 $Wm^{-1}K^{-1}$ at 313 K due to the components with low thermal conductivity. Tobacco granules are mainly composed of propylene glycol and glycerin, the thermal conductivity of which is approximately 0.16 $Wm^{-1}K^{-1}$ [14] and 0.27 $Wm^{-1}K^{-1}$ [15] at 313 K, respectively. In this scenario, dispersing Ag, Cu particles and graphene are beneficial for realizing thermal conductivity enhancement, a κ of 0.23 $Wm^{-1}K^{-1}$ at 313 K is obtained for TGs with 0.1% copper additive. Because of the similar shape and size of the pure TGs and that with HCTMs additions, the effects of thermal convection between the granules are regarded as the same for all specimens. The 35% improvement of the thermal conductivity in TGs with HCTMs additions is ascribed to the boosted heat-carrying phonon transport by

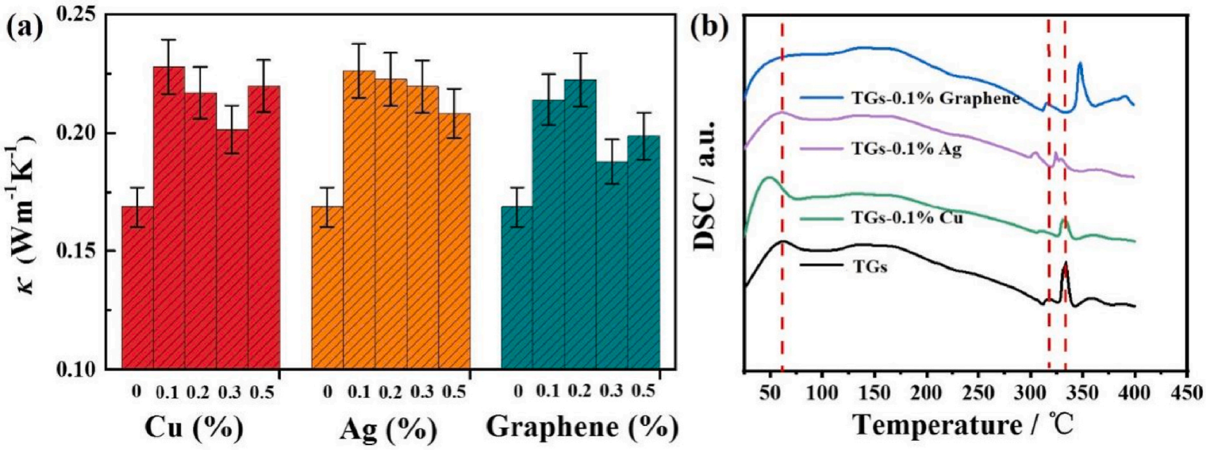

Fig. 4. (a) Thermal conductivity of tobacco granules with different high-thermal-conductivity particles addition, and (b) DSC curves of tobacco granules (TGs) with different high-thermal-conductivity particle addition.

local heat sources in the TGs. As shown in Fig. 5, the dispersed metal particles in the TGs would heat up rapidly during the heating process, which act as the additional heat sources and continue to heat the surrounding TGs [16,17]. The mean free path would be significantly enhanced when the phonon transport close to these local heat sources, resulting in the increased thermal conductivity. According to the results, three kinds of HCTMs are effective to improve the thermal conductivity of the TGs, and introducing 0.1–0.2% mass ratio additives should be the optimum adding content for raising the thermal conductivity of TGs. The thermal conductivity of TGs does not continuously increase with the content of HTCMs. Excessive additives weakened the thermal conductivity improvement, which should be ascribed to the uneven distribution of HTCMs in the TGs. Silver particles agglomeration in the tobacco granules has been observed in the FESEM results, this phenomenon becomes more serious with the increase of additive content, causing the undulated composition and the thermal conductivity. Dispersing nanoparticle in the medium and introducing the mixtures in the tobacco raw materials might further increase the homogeneity.

Enhancing the thermal conductivity of the tobacco granules aims at facilitating the heat transportation to accelerate the aerosol generation. Therefore, the thermodynamic behaviors of TGs with and without 0.1% HTCMs additions are measured through thermal gravimetric analysis and differential scanning calorimetry (DSC), respectively. The weight loss starts to occur at approximately 333 K (Fig. S7), from which (T_s) the aerosol composed of CO, tar, glycerol and glycol gradually generate from TGs, corresponding to each endothermic peaks of the DSC curves (Fig. 4(b)). As the weight gradually decreases with the increase of temperature, the residual mass reflects the content of non-released solid that includes metal particles as well. Ultimately, the residual mass for the pristine TGs is approximately 33.28%, which is lower than those of both TGs with 0.1% Ag (33.54%) and 0.1% Cu (33.41%) particles since that the metal components would not be released at 673 K. It is worth noting that the TGs-0.1% graphene specimen has a higher mass loss of 66.98%, which should be related to the graphene oxidation during the heating process in air. Therefore, dispersing graphene in the TGs is not applicable, as the generation of extra exhaust gas have possibility to be inhaled. Moreover, there is an obvious endothermic peak at approximately 613 K, indicating the highest temperature (T_e) for generating aerosol from TGs. Surprisingly, the T_e of TGs-0.1% Ag sample decreases to approximately 598 K, suggesting that adding Ag particles is beneficial for decreasing the highest temperature for producing aerosol. In comparison, adding copper particles and graphene are immune to the change in T_e of tobacco granules. The work temperature of the HTP heater is close to T_e of TGs in order to promote the production of aerosol and also reduce the energy consumption. Ag particles with higher thermal conductivity would generate more heat to facilitate aerosol generation from TGs in the heating process. The obvious improvement of the thermal conductivity in tobacco granules only needs 0.1 *wt*% metal particles additions. The negligible increase of cost in mass production can bring back the obviously societal interest. The reduced maximum temperature for releasing the aerosol in the TGs might shorten the waiting time for the smoker as well as reduce the energy consumption, less output power is required for the heater.

Although dispersing metal particles favors increasing the thermal conductivity of TGs and reducing the maximum temperature for aerosol generation, it's necessary to investigate whether the metal particles in the TGs would pose a risk of inhalation in order to increase the possibility of practical application. Total particulate matter (TPM) represents the aerosol of particulates/droplets in the cigarette smoke, which is generated by following the HCI smoking regime and collected on a 44 mm diameter Cambridge filter pad (glass fiber). As shown in Fig. S8, the TPM of the pure tobacco granules is approximately 12 mg, which should be the intrinsic component of tobacco. Additionally, the TPM of TGs with the HTCMs additions (Cu or Ag) increased significantly, two reasons might cause the increased TPM: the dispersed metal particles might migrate with the mainstream smoke during the inhalation process, which are finally captured by the glass fiber; another reason is that the dispersed metal particles improve the utilization rate of heat, which promotes the generation of more smoke and therefore the increased TPM of TGs. In accordance with the TPM results, the later should be the reason for the increased TPM. If the metal particles could migrate with the mainstream smoke, more content of metal particles should be captured by the Cambridge filter pad for the TGs with the increased metal additions. Whereas the TPM of the TGs with metal particles additions do not continuously increase with the increase of additive content, though the actual content of metal particles in the TGs is gradually increased. Besides, the tendency of the TPM with metal content is similar to the thermal conductivity results, therefore the effects of metal particles on facilitating heat transport is the main reason for the increased smoke emission, and the optimum content of metal addition is still 0.1%. Nevertheless, it's necessary to explore if the metal particles are really immobile in the TGs during the inhalation process.

To further investigate the metal particles in the TGs are immobile, the Cambridge filter pad and filter tip in the smoking test are

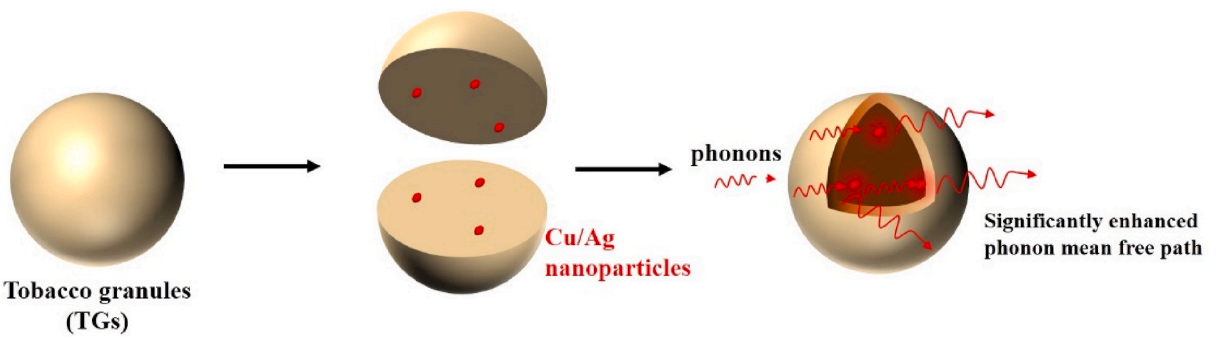

Fig. 5. Schematic diagram of thermal conductivity enhancement on tobacco granules (TGs) with high-thermal-conductivity particles addition.

collected and measured by ICP (Table 2). Metallic Cu is detectable whether in filter pads or the filter tip, but that in the filter tip is significantly greater than that in the Cambridge filter pad, indicating that tiny content of Cu particles might migrate with the mainstream smoke, and the filter tip is effective to capture the Cu particles in the smoke. The remaining Cu content is even lower than that in some natural tobacco leaves [18,19]. It is worth noting that metallic Ag could not be detected in either the filter pads or the filter tip, suggesting that Ag particles could be better stabilized in the tobacco granules and would not separate from TGs during the inhalation process. This result might be attributed to the better adsorption capacity of Ag particles. At the same time, the TPM of the sample slightly decreases with metal particles content, showing a similar variation trend to the thermal conductivity, indicating that the TPM was positively correlated with the thermal conductivity of tobacco granules. Nevertheless, more safety assessments and accurately measurement should be further performed in the subsequent research to judge if this tobacco product is absolutely safe and does not cause any respiratory problems.

In general, adding a tiny content (0.1%) of HTCMs (Cu, Ag, and graphene) results in the approximately 35% thermal conductivity enhancement in tobacco granules since that these particles facilitate the phonon transport in the TGs. But graphene is not stable in the TGs at high temperature in the air, which is adverse to the real application. Ag particles are capable of reducing the maximum temperature for releasing aerosol due to the higher thermal conductivity and local heater effect. Furthermore, Ag is immobile in the TGs during the inhalation process, which further ensures food safety and people's health. Nevertheless, only three kinds of additives are added in the tobacco granules in this study, it's worth trying to disperse other composition or shape of additives that possess high thermal conductivity in order to facilitate the heat transport in tobacco granules. In addition, heat conduction and heat convection simultaneously exist in the tobacco particles during the heating process. This study only focuses on the former, the thermal transport in the tobacco granules. But the actually thermal transport in the tobacco granules is complex, which is related to the size, shape and composition of the granules. Thus the universality of this approach of introducing high-thermal-conductivity particles in other tobacco products to facilitate thermal transport needs to be further studied.

3.4. Antibacterial test

Metal materials are proven to possess the excellent antibacterial properties, thus, the effect of introducing Ag and Cu particles in TGs on the antibacterial properties is worth investigating. Due to the excellent thermal physics performance of TGs with metal particles additions, TGs-0.1% Ag and TGs-0.1% Cu specimens were chosen for the antibacterial test (including *P. aeruginosa*, *S. aureus* and *E. coli*). A crystal violet-stained biofilm of bacteria is observed, as shown in Fig. 6(a), and the obviously darker distribution of bacterial biofilm in the blank specimens is used for comparison. Bacterial growth is inhibited in the sample with tobacco granules, indicating the high antibacterial activity of nicotine in tobacco, which is effective against all three bacteria. In contrast, metal particle addition is beneficial for further enhancing the anti-*P. aeruginosa* and anti-*E. coli* properties of TGs, in particular, the latter one. More details are exhibited in Figs. S9–S11. In addition, the effect of the TGs concentration on the bacteriostatic properties was investigated, as shown in Fig. 6(b–d). In accordance with the colony statistics, the concentration of 1/32 is the optimum inhibitory concentration due to the more stable speed of colony growth in this case. The concentrations of 1/64 and 1/128 resulted in fast colony growth, and that of the specimen with a concentration of 1/16 changed to slow. Furthermore, the normally cultured colony biofilm is thicker than that under the condition of introducing TGs with metal particles added, suggesting a bacteriostatic effect from nicotine as well as Ag and Cu particles. Among them, the effect of TGs with Cu and Ag addition on inhibiting *E. coli* is better, which has been studied in other fields [20–22], therefore, *E. coli* was stained for further observation by using fluorescence confocal microscopy. The 3D reconstruction mapping of *E. coli* biofilms with and without TG addition is displayed in Fig. S12, which reveals the thickness of the biofilm and the distribution and content of dead bacteria. The thickness of the biofilm after adding TGs-0.1% Ag was thinner than that with TGs or TGs-0.1% Cu, and a large number of dead bacteria reunited, indicating a better *E. coli inhibition effect*. In general, nicotine possesses intrinsic antibacterial activity against *P. aeruginosa*, *S. aureus* and *E. coli*, and the effect of Ag and Cu particle addition on the antibacterial activity is selective. Adding Ag particles to tobacco granules is beneficial for inhibiting *E. coli*, which might promote improved food safety.

4. Conclusions

In summary, three typical high-thermal-conductivity materials (HTCMs: Cu, Ag, and graphene) are introduced into tobacco granules (TGs) by combining with extruding and rotation rounding approaches. All these additives are beneficial for dramatically

Table 2
Metal particles (Cu and Ag) contents in filter pad and filter tip after smoking.

Sample	additive	element	content (mg/kg)
filter pads	TGs-0.1% Cu	Cu	0.75
filter pads	TGs-0.2% Cu	Cu	0.31
filter pads	TGs-0.1% Ag	Ag	–
filter pads	TGs-0.2% Ag	Ag	–
filter tip	TGs-0.1% Cu	Cu	3.99
filter tip	TGs-0.2% Cu	Cu	3.11
filter tip	TGs-0.1% Ag	Ag	–
filter tip	TGs-0.2% Ag	Ag	–

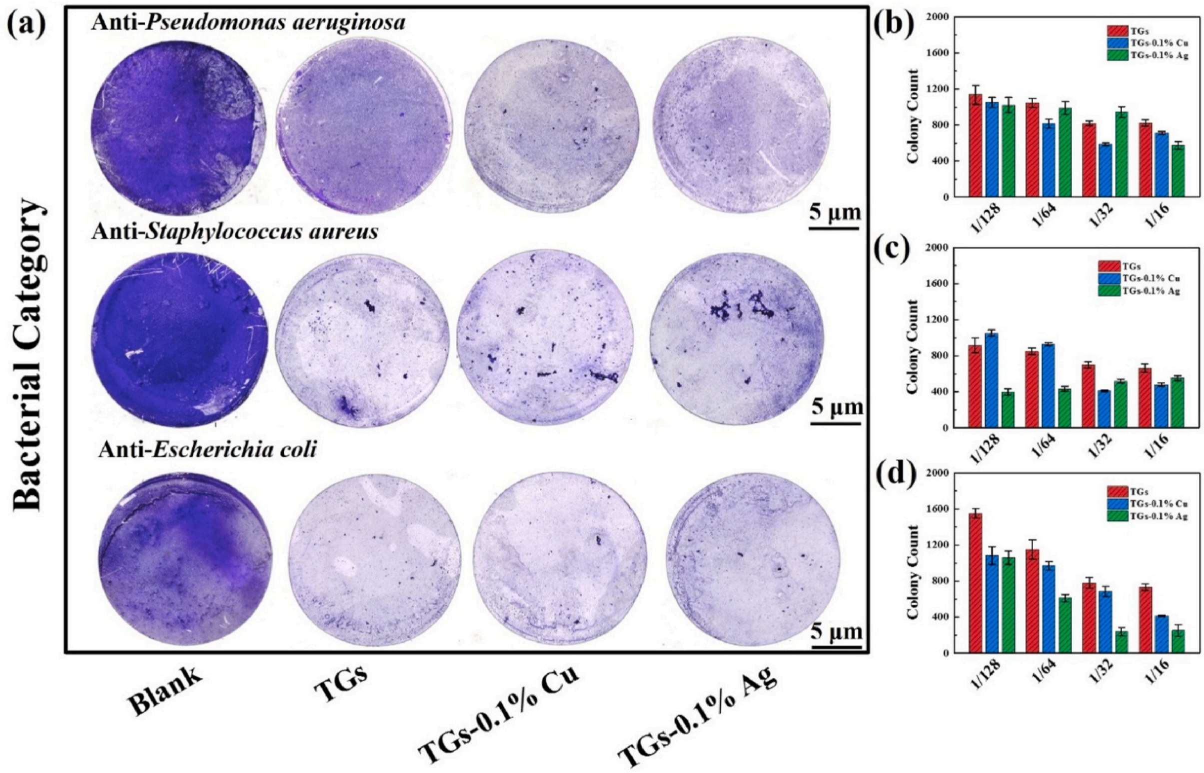

Fig. 6. (a) Effects of tobacco granules with and without metal particles (Cu and Ag) addition on antibacterial by colony observation, different concentration of TGs, TGs-0.1% Cu and TGs-0.1% Ag dependence of colony count after (b) Anti-*Pseudomonas aeruginosa*, (c) Anti-Staphylococcus aureus and (d) Anti-*Escherichia coli* experiment.

increasing thermal conductivity of TGs owing to the shortened phonon mean free path and therefore the significantly enhanced phonon transport by the homogeneously distributed HTCMs. The peak thermal conductivity of 0.23 $Wm^{-1}K^{-1}$ at 313 K is achieved in the TGs-0.1% Cu specimen, the 35% improvement of thermal conductivity in TGs is ascribed to the evenly distributed Cu particles. Interestingly, dispersing Ag particles in TGs could reduce the maximum temperature for releasing aerosol, and the Ag particles are almost immobile in either the heating or smoking process. In the antibacterial test, the nicotine in the TGs was verified to be efficient in inhibiting *E. coli*, *S. aureus* and *P. aeruginosa*, and Ag and Cu particles were capable of further improving the antibacterial activity. Therefore, the addition of only a tiny content of HTCMs in tobacco granules is capable of accelerating the heat transportation and facilitating the cigarette aerosol production in lower temperature in the meantime. Furthermore, Ag particle addition in TGs effectively optimizes the anti-*E. coli* property, which might be an effective strategy to guarantee food safety. Thereby, the strategy of adding tiny content of HTCMs is worth promoting for increasing the thermal conductivity of other types of tobacco products or organic materials.

Author contribution statement

Xiaowei Gong: Conceived and designed the experiments. Yixin Zhang: Performed the experiments; Wrote the paper. Wei Zhao, Yuanxing Duan, Heng Wu, Zilong Zhang, Wei Jiang, Xuemei Li: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data. Yi Han: Conceived and designed the experiments; Wrote the paper. Zhenhua Ge: Conceived and designed the experiments; Analyzed and interpreted the data. Junjie Dong: Conceived and designed the experiments; Performed the experiments. Yunhua Qin: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interest's statement

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2022.e12696.

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