Electronic Supplementary Information

Sustained release of Ag⁺ confined inside polyoxometalates for long-lasting bacterial resistance

Zhewei Xu,^a Kun Chen,^{*bc} Mu Li,^b Changying Hu^{*ad} and Panchao Yin^{*bc}

a. Packaging Engineering Institute, Jinan University, Zhuhai 519070, P. R. China.

b. South China Advanced Institute for Soft Matter Science and Technology, South China University of Technology, Guangzhou 510641, P. R. China.

c. State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510641, P. R. China.

d. Department of Food Science and Engineering, Jinan University, Guangzhou 510632, P. R. China.

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Experimental Procedures

Materials

PVA (degree of polymerization: 1799 and alcoholysis degree: 99%), sodium tungstate, phosphoric acid and silver standing solution (1000 μ g/mL in 1% HNO₃), silver nitrate were obtained from Aladdin Reagent Ltd. (China). Transferrin, bovine serum albumin, nutrient broth and Mueller-Hinton Broth was obtained from Beijing Solarbio Science & Technology Co., Ltd. Water used in the experiment were prepared using water purified system (Water Purifier) to a specific resistance of 18.2 MΩ cm.

K₁₃Na[AgP₅W₃₀O₁₁₀] (AgP₅W₃₀) was synthesis according to the method of Kato¹, and the product was confirmed by ³¹P nuclear magnetic resonance (NMR) (Bruker AVANCE III spectrometer, 500 MHz) spectra and infrared spectra (IR) (Bruker, VERTEX 33 spectrometer).

Release of silver from AgP₅W₃₀

To monitor the ion exchange, 10 mg of AgP_5W_{30} was dissolved in deuterated saline with different concentration of NaCl (the molar ratio of AgP_5W_{30} to the added Na⁺ is 1:276, 1:138, 1:69, 1:14, 1:2, 1:1, 1:0.5, respectively, and the mass concentration of NaCl is 2%, 1%, 0.5%, 0.1%, 0.015%, 0.007%, 0.0036%, respectively), and ³¹P NMR spectra of AgP_5W_{30} was measured at different interval.

To study the selectivity of ions exchange and stability of AgP_5W_{30} , 10 mg of AgP_5W_{30} was dissolved in deuterated saline and deuterated saline with 1% CaCl₂, 1% ZnCl₂, 1% sodium acetate, 5 µM transferrin (Tf) and 5 mM bovine serum albumin (BSA), respectively. ³¹P NMR spectra of AgP_5W_{30} was tested after 4 days of incubation at room temperature. The intensity of spectra was normalized by the peak area. In the calculation of the conversion rate, the spectral interferences from original Na⁺ to the spectra of AgP_5W_{30} and NaP_5W_{30} were corrected by the background correction.

Ions exchange kinetics

As the result of proton exchange reported by Kim, the exchange reaction proceeds in two steps.² And we think the ions exchange reaction also takes places in two steps:

 $\begin{bmatrix} AgP_5W_{30} \end{bmatrix} + \begin{bmatrix} Na^+ \end{bmatrix} \rightarrow \begin{bmatrix} NaAgP_5W_{30} \end{bmatrix}$ $\begin{bmatrix} NaAgP_5W_{30} \end{bmatrix} \rightarrow \begin{bmatrix} NaP_5W_{30} \end{bmatrix} + \begin{bmatrix} Ag^+ \end{bmatrix}$

the ions exchange rate is only influenced by the concentration of AgP_5W_{30} and sodium ions, second-order reaction rate equation was used to describe the exchange behavior. When $[AgP_5W_{30}] = [Na^+]$

When $[AgP_5W_{30}] = kt + \frac{1}{[AgP_5W_{30}]_0}$ When $[AgP_5W_{30}] \neq [Na^+]$ $\ln \frac{[AgP_5W_{30}]}{[Na^+]} = -kt([Na^+]_0 - [AgP_5W_{30}]_0) + \ln \frac{[AgP_5W_{30}]_0}{[Na^+]_0}$

Where k is the exchange rate constant, $[Na^+]$ and $[AgP_5W_{30}]$ are the concentration of sodium ions and AgP₅W₃₀ at the time *t*, $[Na^+]_0$ and $[AgP_5W_{30}]_0$ are the initial concentrations of Na⁺ and AgP₅W₃₀.

Persistent bacteriostasis of AgP₅W₃₀

Bacterial strains of *Escherichia coli* (*E. coli*) (ATCC 8739), *Staphylococcus aureus* (*S. aureus*) (ATCC 6538) were provided by Shanghai Luwei Technology Co. Ltd in a form of agarslantculture-medium. All the tested bacteria were freshly incubated in nutrient broth (NB) at 37 °C for 16 hours. Then the cultures were centrifuged at 4500 g for 15 min and the supernatant was removed, then the precipitate was resuspended in normal saline. Bacteria used for experiment were of $O.D_{600}=1$ (10^9 CFU/mL) and further diluted to desired concentration. For persistent bacteriostasis, the bacteria were incubated in NB with the antibacterial agent which concentration is lower than the minimal inhibitory concentrations (MICs), and the concentration of AgP₅W₃₀, K₁₂Na₂[NaP₅W₃₀O₁₁₀] (NaP₅W₃₀), and silver nanoparticles were 200 ppm, 200 ppm and 2.81 ppm (same silver concentration), respectively. Then, the bacteria were subcultured using the NB with the same concentration of antibacterial agent as described above.

MICs of antibacterial agents against bacteria with different subculture round was tested using broth dilution method. The antibacterial agents were diluted to the setting concentration using Mueller-Hinton Broth (MHB), and the last test tube was used as the blank control. Then the bacteria were added and the final bacterial concentration in every test tube was 5×10^5 CFU/mL. After 24 hours of incubation, the MICs was confirmed according to the condition of bacterium growth. The MICs of AgNO₃ was test using the bacteria without subculturing.

Film preparation, thickness and the opacity property.

The active film was prepared according to the method of Chen³ with minor modifications. Briefly, 30 g of PVA was mixed with 250 mL water at 95 °C under vigorous stirring until the liquid was homogeneous. After the temperature of the PVA solution lowered to 50 °C, 0, 0.15, 0.3 and 0.9 g of AgP₅W₃₀ (0, 0.5%, 1% and 3% w/w relative to PVA on a dry basis) was dissolved in 20 mL water and mixed with the PVA solution to prepare the film forming solution. The film forming solutions were degassed in the vacuum drying oven overnight. The films were prepared by casting the mixed solutions onto a glass plate using a film steel spreader, then the film forming solution were dried onto flat heating stage at 50 °C for 1 h, and the film was peeled from the casting surface. The prepared films were marked as PVA0, PVA0.5, PVA1, PVA3 which corresponding to the films incorporated with 0%, 0.5%, 1%, 3% AgP₅W₃₀, respectively. The prepared films were stored in the constant temperature and humidity test chamber (Temperature: 25 °C, RH: 50%) for a week before the characterization of the films.

Thickness of the films was measured at five random points of each film sample using a digital micrometer (Shanghai Measuring & Cutting Tool Works Co., Ltd, China) with an accuracy of 0.002 mm, and the average thickness was calculated. The opacity of prepared films was tested using Ultraviolet-Visible (UV-Vis) spectrum (Shimadzu UV-1800 spectrometer), and the transmittance of the films were recorded.

Antibacterial activity of the films

The antibacterial activity of the composite films was studied by agar-diffusion method with minor modifications⁴. Briefly, 0.2 mL of fresh cultured bacterial solution at the concentration of 10^8 CFU/mL was applied on the agar medium and the prepared films (1.5 cm in diameter) were place on the surface of the agar. Then the inhibition zone diameters were measured after 24 h of incubation at 37 °C.

X-ray analysis

Wide-angle X-ray scattering was performed using Rigaku D/max-III-A with Cu-Kα radiation, and the scattering vector scale was calibrated using a silicon powder.

Thermogravimetric analysis and differential scanning calorimetry

The thermal property of the prepared films was carried out using a thermal analyzer (TA TGA5500). The film samples were cut into pieces, and about 6 mg sample was inserted into a crucible. The sample was heated from ambient temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with the flow rate of 50 mL/min.

The differential scanning calorimetry of the prepared films was carried out using differential scanning calorimeter (TA DSC 2500). The film samples were cut into pieces and about 5 mg of samples were loaded into a crucible. The samples were initially heated from 40 to 200 °C and then cooled to 0 °C to remove previous thermal history. The second heating scan was subsequently performed from 0 to 200 °C. Both the heating and cooling rates were 10 °C/min under a nitrogen atmosphere with the flow rate of 50 mL/min. The glass transition temperatures were obtained in the second heating run.

Scanning electron microscopy (SEM)

The surface and the cross-section morphologies of the prepared films was studied by SEM (Phenom G2 pro, Netherlands) operating at 5 kV acceleration under moderate vacuum. The film samples were fractured in liquid nitrogen for cross-section morphology observation and sputtered with gold layer prior to visualization.

Mechanical properties

The tensile strength (TS), Yong modulus (Y), and percentage of elongation at break (EAB) of the prepared films were determined using an electromechanical universal tester (Shenzhen Labsans Testing Machine Co., Ltd., China) according to the ASTM D638-08. The films were cut into dumbbell forms (50×4 mm) and clamped in the self-aligning grips of the device. The stretching speed was 50 mm/min and ten samples were tested for each film with different concentration of AgP₅W₃₀.

The release of AgP_5W_{30} into the food simulation

The release of AgP_5W_{30} was tested according to EU 2016/1416. Briefly, the films were cut into 3 × 3 cm squares and individually immersed in 15 mL water in a tightly sealed vessel. The samples of solution were sampled at different time interval, and the concentration of released silver ion was measured by inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 8000, PerkinElmer). The study of the AgP_5W_{30} release from PVA films was performed at 20 °C and the release experiments were performed in triplicate. To measure the initial AgP_5W_{30} concentration in the films (M_f), the prepared films were dissolved in hot water, and the concentration of Ag was measured by ICP-OES.

Kinetic of AgP₅W₃₀ release and partition coefficient

Fick's second law was used to describe the diffusion pattern of AgP₅W₃₀ into the food simulation, and the analytical solution of Fick's second diffusion equation for one-dimensional diffusion and limited volume of food simulant was used⁵.

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} exp^{\frac{1}{1+\alpha}} [\frac{-Dq_n^2 t}{L^2}]$$

Where M_t and M_{∞} are the amount of AgP_5W_{30} released from the film at time t (s) and at equilibrium, respectively, α is mass ratio of equilibrated migrant in food to that in packaging material, D (cm²/s) is the diffusion coefficient of the AgP_5W_{30} through the film and L (m) is the thickness of film. q_n is the positive roots of the transcendent equation of tan q_n =- αq_n . For α <<1, $q_n \approx n\pi/(1+\alpha)$, and for other α values $q_n \approx [-\alpha/2(1+\alpha)]$ equation, the value remains unchanged considerably after the n=50; therefore, the summation terms until n=50 were calculated in the equation.

The partition coefficient (K) was calculated according to the definition:

 $K = \frac{C_{s,\infty}}{C_{F,\infty}}$

Where K is the partition coefficient, $C_{s,\infty}$ and $C_{F,\infty}$ are the AgP₅W₃₀ concentration in the food simulation and in the film at equilibrium.

Results and Discussion

Characterization of AgP₅W₃₀

According to the report of Kato¹, AgP₅W₃₀ was synthesized in two steps by hydrothermal method. The IR spectra of synthesized K₁₂Na₂[NaP₅W₃₀O₁₁₀] (NaP₅W₃₀) and K₁₂Na₂[AgP₅W₃₀O₁₁₀] (AgP₅W₃₀) are shown in Fig. S1A. Three main characteristic peaks for NaP₅W₃₀ are assigned as follows: P-O (1164/1085 cm⁻¹), *v*_{as} (W-O_d, 983/936 cm⁻¹), *v*_{as} (W-O_b-W, 910 cm⁻¹); O_b is the bridged oxygen of two octahedrons sharing a corner, and O_d is the terminal oxygen⁶. The IR spectra of AgP₅W₃₀ indicate the existence of the Preyseler-type POM structures (as marked with the red dotted lines). IR spectra of AgP₅W₃₀ and NaP₅W₃₀ are almost identical to each other (Fig. S1), as well as the IR spectra of AgP₅W₃₀ is consistent with Ag-O^{7, 8} in the cavity of Preyseler structure. This peak becomes weaker after ion exchange indicate the release of Ag⁺ from the cavity. ³¹P NMR spectrum of NaP₅W₃₀ and AgP₅W₃₀ are shown in Fig. 1A. The chemical shift of NaP₅W₃₀ is consistent with previous report⁹, which demonstrates the success synthesis of the product of AgP₅W₃₀.



Fig. S1. IR spectrum of NaP_5W_{30} and AgP_5W_{30} .

Stability of AgP₅W₃₀ in pure water



Fig. S2. ^{31}P NMR spectrum of AgP₅W₃₀ dissolved in pure D₂O.

IR spectrum of AgP_5W_{30} before and after ions exchange



Fig. S3. IR spectrum of AgP_5W_{30} before and after the 24 days of ion exchange in solution containing 10 mg/mL of sodium chloride.

Inhibition zone of AgNO₃ and NaP₅W₃₀ against *E. coli* and *S. aureus*



Fig. S4. Antibacterial activities of AgNO₃ and NaP₅W₃₀ against *E. coli* (A) and *S. aureus* (B) after 24 h of incubation.

Ions exchange kinetics

Preyssler-type phosphotungstate is a doughnut-shaped molecule which consists of five PW_6O_{22} units, and the cavity in the molecule could encapsulate various cations⁹. In most of the cases, only one cation could be encapsulated in one Preyssler molecule. In that, we think that the essence of the ions exchange behavior is the competition of the cavity volume between the sodium ions and silver ions. The exchange rate is influenced by the concentration of sodium ions and the anion of AgP_5W_{30} , so that the limitation of the exchange rate is subjected to the rate of sodium ions or silver ions diffusion through the Preyssler molecule. The exchange rate constant is shown in Table S1. The fitting results showed good correlation (R^2 >0.95) between molar ration and the concentration of NaCI, and the variation trend of *k* demonstrated that the reaction rate could be accelerated by increasing the reactant concentrations.

		U		
Molar ratio:		k/	R ²	
	AgP5W30:	(L/(mol∙min)		
	NaCl			
	1:0.5	0.082117	0.9570	
	1:1	0.053052	0.9691	
	1:2	0.033023	0.9729	
	1:14	0.006587	0.9864	
	1:69	0.001227	0.9874	
	1:138	0.000608	0.9876	
	1:276	0.000300	0.9894	

 Table S1. Exchange rate constant of the ion exchange reaction with different concentration of NaCl.

Film opacity

The UV-Vis absorption of the composite films is shown in Fig. S5. As the amount of AgP_5W_{30} increasing, the films became less transparent due to the low compatibility between polymers and inorganic POM metal salts, potassium and sodium salts, which would result in the aggregation and crystallization of AgP_5W_{30} . Compared with the pure PVA films, in the visible region, the transmittance of the film incorporating with AgP_5W_{30} was attenuated obviously due to the aggregation of AgP_5W_{30} . Moreover, most of the POMs have strong absorption in

ultraviolet region, and the characteristic absorption in ultraviolet region indicates the incorporation of AgP_5W_{30} in PVA.



Fig. S5. UV-Vis spectra of AgP₅W₃₀-composite films.

X-ray analysis

The dispersion of POMs in PVA is similar to the dissolving of POMs in solvents (e.g. water). When the concentration of the POMs is lower than the solubility (ca. 1% wt), POMs will be soluble in PVA and stay as discrete clusters. POMs will be counted as in amorphous state in PVA. When the concentration of the POMs is higher than the solubility, the excess amount of POMs will form micro-crystals in polymer matrix. Therefore, the co-existence of both discrete POM and POM micro-crystals can be observed at high loading amount of POMs in PVA.

X-ray analysis is employed to confirm the aggregation and crystallization of AgP_5W_{30} . XRD patterns of AgP_5W_{30} and the composite films are shown in Fig. S6. The peak at 2θ =19.5° (101) indicated the semi crystallization of PVA under effect of the rich hydroxyl groups of PVA in its side-chain^{10, 11}. The AgP_5W_{30} POM show admirable solubilities (ca. 1 % wt) in PVA media. When the concentration of POM in PVA is lower than the critical concentration, POMs are well-dissolved in PVA, and only the form factor of single POM particle can be observed. For the films containing more than 1% AgP_5W_{30} , POMs will partially crystallize as micro-crystals in PVA media. It explains that their XRD data shows relatively sharp diffraction peaks of AgP_5W_{30} at 2θ = 6.6° which could be interpreted as the crystalline interplanar spacing of 1.3 nm. The crystalline of AgP_5W_{30} observed in PVA matrix also agreed with the result of UV-Vis transmittance.



Fig. S6. XRD patterns of AgP₅W₃₀ and composite films.

SEM image of films

SEM images of the surfaces and cross-sections of the PVA films incorporated with different amount of AgP_5W_{30} show that these composite films are smooth and continuous (Fig. S7). No obvious agglomeration and phase separation were observed. Under the relative low magnification view, PVA showed good compatibility with AgP_5W_{30} , which could be attributed to the rich hydrogen bonds between AgP_5W_{30} and side chains of PVA. These results also provided evidence to support the promising mechanical properties of the composite films (Fig. S9 in supporting information) that was homogeneous and processable for further applications.





Fig. S7. SEM image of the surfaces (A) and cross-sections (B) of AgP₅W₃₀-composite films.

Thermogravimetric analysis and differential scanning calorimetry

Thermal stability of the prepared films was evaluated by thermogravimetric analysis. The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) results are shown in Fig. S8A and B. All the films incorporated with different amount of AgP₅W₃₀ decomposed in a similar three-step degradation manner, corresponding to three temperature ranges: 35-130 °C, 230-330 °C, and 400-500 °C. The first step with about 6% weight loss was caused by the loss of water in the films. The second step with about 75% weight loss was caused by the degradation of PVA side chain^{3, 12}. The weight loss during the third step was mainly caused by the degradation of PVA main chain. As showed in Fig. S8B, the side chain decomposition of pure PVA started at 286 °C, and the initial decomposition temperature increased to 289 °C with the addition of AgP₅W₃₀, which indicated the thermal stability of PVA films was slightly improved. The thermal stability improvement could be interpreted as the forming of the hydrogen bonds between hydroxyl on the PVA side chain and AgP₅W₃₀. The results of differential scanning calorimetry (DSC) are shown in Fig. S8C and D. The glass-transition temperature of the prepared films all maintained at 77 °C. Since the content of AgP₅W₃₀ was small, the glass-transition temperature was almost unchanged.





Fig. S8. TGA (A), DTG (B), DSC (C), and the derivative of DSC curve (D) of AgP_5W_{30} -composite films.

Mechanical properties

The mechanical properties of all the films are showed in Table S2. Since inorganic materials could provide entanglement points to the polymer chains, it is generally believed that the addition of inorganic materials can increase the tensile strength of polymers. Moreover, hydrogen bonds between PVA side chains and AgP₅W₃₀ could make PVA easier to crystallize, so that the tensile strength (TS) and Young modulus (Y) of PVA film generally increased with the increasing of AgP₅W₃₀, while the elongation at break (EAB) slightly decreased with the increasing of AgP₅W₃₀. Compared with the pure PVA films, TS of the films incorporated with 3% AgP₅W₃₀ increased 26.14%, and the EAB decreased 6.59%. and the results were consistent with the findings by adding inorganic materials into PVA matrix, such as ZnO nanoparticle-PVA¹³ and ZrO₂-PVA¹⁴. In general, the composite films keep their good mechanical properties and have further application potentials.



Fig. S9. Stress-strain curve of the different PVA films.

	Table S2. Thickness and mechanical properties of PVA films.			
	Thickness/mm	TS/MPa	Y/GPa	EAB/%
PVA0	0.040±0.003	73.34±4.39	3.38±0.24	81.39±6.44
PVA0.	0.056±0.003	80.32±5.64	4.35±0.11	79.66±7.13
5				
PVA1	0.041±0.005	85.24±4.07	4.45±0.07	76.57±4.37
PVA3	0.042±0.007	92.51±3.82	4.61±0.39	76.03±6.81

Release of AgP₅W₃₀ from PVA films

Studying the release of active ingredients contributes to the evaluation of antimicrobial properties. The release profile of AgP_5W_{30} from PVA films are shown in Fig. S10. The initial burst release phenomenon could be ascribed to the swelling behavior of PVA in water. The swelling behavior could allow the entrapped AgP_5W_{30} in the inner core to move through the polymer networks easily. The partition coefficient (D) and diffusion coefficient (K) of AgP_5W_{30} are shown in Table S3. D increased with the increase of AgP_5W_{30} concentration, which indicates that the AgP_5W_{30} diffusivity through composite films was concentration dependent. Moreover, the release percentage with different concentration of AgP_5W_{30} was close to each other. These results indicated that the hydrophilia of the composite films were similar to each other.



Fig. S10. Release profile of Ag from PVA films

Fable S3. Initial concentration in films,	diffusion coefficient, partition	coefficient and release	percent of AgP ₅ W ₃₀ .
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	Initial	K×10 ²	D×10 ¹³ /(cm ² /s)	R^2	M∞/M _f
	concentration/ppm				
PVA0.	68.45±4.10	1.67	3.50	0.752	0.84
5					
PVA1	136.62±2.70	1.13	2.76	0.903	0.81
PVA3	404.83±32.67	0.28	0.49	0.797	0.86

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