Electronic Supplementary Information

Sustained release of Ag\textsuperscript{+} confined inside polyoxometalates for long-lasting bacterial resistance

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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 μg/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 AgP₅W₃₀ was dissolved in deuterated saline with different concentration of NaCl (the molar ratio of AgP₅W₃₀ 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 AgP₅W₃₀ was measured at different interval.

To study the selectivity of ions exchange and stability of AgP₅W₃₀, 10 mg of AgP₅W₃₀ 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 AgP₅W₃₀ 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 mixture of AgP₅W₃₀ and NaP₅W₃₀ 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 place in two steps:

\[ [A\text{g}\text{P}_5\text{W}_{30}] + [N\text{a}^+] \rightarrow [N\text{aAgP}_5\text{W}_{30}] \]

\[ [N\text{aAgP}_5\text{W}_{30}] \rightarrow [N\text{aP}_5\text{W}_{30}] + [A\text{g}^+] \]

the ions exchange rate is only influenced by the concentration of AgP₅W₃₀ and sodium ions, second-order reaction rate equation was used to describe the exchange behavior.

When \([A\text{gP}_5\text{W}_{30}] = [N\text{a}^+]\)

\[
\frac{1}{[A\text{gP}_5\text{W}_{30}]} = kt + \frac{1}{[A\text{gP}_5\text{W}_{30}]}_0
\]

When \([A\text{gP}_5\text{W}_{30}] ≠ [N\text{a}^+]\)

\[
\ln \left( \frac{[N\text{a}^+]}{[A\text{gP}_5\text{W}_{30}]} \right) = -kt([N\text{a}^+]_0 - [A\text{gP}_5\text{W}_{30}])_0 + \ln \left( \frac{[A\text{gP}_5\text{W}_{30}]}{[N\text{a}^+]_0} \right)
\]

Where k is the exchange rate constant, \([N\text{a}^+]\) and \([A\text{gP}_5\text{W}_{30}]\) are the concentration of sodium ions and AgP₅W₃₀ at the time \(t\), \([N\text{a}^+]_0\) and \([A\text{gP}_5\text{W}_{30}])_0\) 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.D₆₀₀=1 (10⁹ 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 5×10⁵ 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 10⁸ 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 AgP₅W₃₀ into the food simulation

The release of AgP₅W₃₀ 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 AgP₅W₃₀ release from PVA films was performed at 20 °C and the release experiments were performed in triplicate. To measure the initial AgP₅W₃₀ concentration in the films (Mᵢ), the prepared films were dissolved in hot water, and the concentration of Ag was measured by ICP-OES.
Kinetic of AgP$_5$W$_{30}$ release and partition coefficient

Fick’s second law was used to describe the diffusion pattern of AgP$_5$W$_{30}$ 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 used$^5$.

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

Where $M_t$ and $M_\infty$ are the amount of AgP$_5$W$_{30}$ released from the film at time $t$ (s) and at equilibrium, respectively, $\alpha$ is mass ratio of equilibrated migrant in food to that in packaging material, $D$ (cm$^2$/s) is the diffusion coefficient of the AgP$_5$W$_{30}$ through the film and $L$ (m) is the thickness of film. $q_n$ is the positive roots of the transcendent equation of $\tan q_n = -\alpha q_n$. For $\alpha << 1$, $q_n \approx n\pi/(1+\alpha)$, and for other $\alpha$ values $q_n \approx [-\alpha/2(1+\alpha)]$, 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 AgP$_5$W$_{30}$ concentration in the food simulation and in the film at equilibrium.

Results and Discussion

Characterization of AgP$_5$W$_{30}$

According to the report of Kato$^1$, AgP$_5$W$_{30}$ was synthesized in two steps by hydrothermal method. The IR spectra of synthesized K$_{12}$Na$_2$[NaP$_5$W$_{30}$O$_{110}$] (NaP$_5$W$_{30}$) and K$_{12}$Na$_2$[AgP$_5$W$_{30}$O$_{110}$] (AgP$_5$W$_{30}$) are shown in Fig. S1A. Three main characteristic peaks for NaP$_5$W$_{30}$ are assigned as follows: P-O (1164/1085 cm$^{-1}$), $\nu_{as}$ (W-O$_b$, 983/936 cm$^{-1}$), $\nu_{as}$ (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 oxygen$^6$. The IR spectra of AgP$_5$W$_{30}$ indicate the existence of the Preyssler-type POM structures (as marked with the red dotted lines). IR spectra of AgP$_5$W$_{30}$ and NaP$_5$W$_{30}$ are almost identical to each other (Fig. S1), as well as the IR spectra of AgP$_5$W$_{30}$ before and after ion exchange (Fig. S3). The peak at 1384 cm$^{-1}$ in the IR spectra of AgP$_5$W$_{30}$ is consistent with Ag-O$^7,8$ in the cavity of Preyssler structure. This peak becomes weaker after ion exchange indicate the release of Ag$^+$ from the cavity. $^{31}$P NMR spectrum of NaP$_5$W$_{30}$ and AgP$_5$W$_{30}$ are shown in Fig. 1A. The chemical shift of NaP$_5$W$_{30}$ is consistent with previous report$^9$, which demonstrates the success synthesis of the product of AgP$_5$W$_{30}$. 
Fig. S1. IR spectrum of NaP₅W₃₀ and AgP₅W₃₀.

Stability of AgP₅W₃₀ in pure water

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

IR spectrum of AgP₅W₃₀ before and after ions exchange

Fig. S3. IR spectrum of AgP₅W₃₀ before and after the 24 days of ion exchange in solution containing 10 mg/mL of sodium chloride.
Inhibition zone of AgNO$_3$ and NaP$_5$W$_{30}$ against *E. coli* and *S. aureus*

Fig. S4. Antibacterial activities of AgNO$_3$ and NaP$_5$W$_{30}$ 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$_6$O$_{22}$ units, and the cavity in the molecule could encapsulate various cations$^9$. 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$_5$W$_{30}$, 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 NaCl, and the variation trend of $k$ demonstrated that the reaction rate could be accelerated by increasing the reactant concentrations.

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

<table>
<thead>
<tr>
<th>Molar ratio: AgP$<em>5$W$</em>{30}$:NaCl</th>
<th>k/(L/(mol·min))</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.5</td>
<td>0.082117</td>
<td>0.9570</td>
</tr>
<tr>
<td>1:1</td>
<td>0.053052</td>
<td>0.9691</td>
</tr>
<tr>
<td>1:2</td>
<td>0.033023</td>
<td>0.9729</td>
</tr>
<tr>
<td>1:14</td>
<td>0.006587</td>
<td>0.9864</td>
</tr>
<tr>
<td>1:69</td>
<td>0.001227</td>
<td>0.9874</td>
</tr>
<tr>
<td>1:138</td>
<td>0.000608</td>
<td>0.9876</td>
</tr>
<tr>
<td>1:276</td>
<td>0.000300</td>
<td>0.9894</td>
</tr>
</tbody>
</table>

Film opacity

The UV-Vis absorption of the composite films is shown in Fig. S5. As the amount of AgP$_5$W$_{30}$ 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$_5$W$_{30}$. Compared with the pure PVA films, in the visible region, the transmittance of the film incorporating with AgP$_5$W$_{30}$ was attenuated obviously due to the aggregation of AgP$_5$W$_{30}$. Moreover, most of the POMs have strong absorption in
ultraviolet region, and the characteristic absorption in ultraviolet region indicates the incorporation of \( \text{AgP}_5\text{W}_{30} \) in PVA.

![UV-Vis spectra of AgP\(_5\)W\(_{30}\)-composite films.](image)

**Fig. S5.** UV-Vis spectra of \( \text{AgP}_5\text{W}_{30}\)-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 POM in PVA.

X-ray analysis is employed to confirm the aggregation and crystallization of \( \text{AgP}_5\text{W}_{30} \). XRD patterns of \( \text{AgP}_5\text{W}_{30} \) and the composite films are shown in Fig. S6. The peak at \( 2\theta=19.5^\circ \) (101) indicated the semi crystallization of PVA under effect of the rich hydroxyl groups of PVA in its side-chain\(^{10,11} \). The \( \text{AgP}_5\text{W}_{30} \) 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% \( \text{AgP}_5\text{W}_{30} \), POMs will partially crystallize as micro-crystals in PVA media. It explains that their XRD data shows relatively sharp diffraction peaks of \( \text{AgP}_5\text{W}_{30} \) at \( 2\theta = 6.6^\circ \) which could be interpreted as the crystalline interplanar spacing of 1.3 nm. The crystalline of \( \text{AgP}_5\text{W}_{30} \) observed in PVA matrix also agreed with the result of UV-Vis transmittance.

![XRD patterns of AgP\(_5\)W\(_{30}\) and composite films.](image)

**Fig. S6.** XRD patterns of \( \text{AgP}_5\text{W}_{30} \) 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$_5$W$_{30}$ 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$_5$W$_{30}$, which could be attributed to the rich hydrogen bonds between AgP$_5$W$_{30}$ 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.
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 AgP$_5$W$_{30}$ 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. 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 AgP$_5$W$_{30}$, which indicated the thermal stability of PVA films was slightly improved. The thermal stability improvement could be interpreted as the forming of hydrogen bonds between hydroxyl on the PVA side chain and AgP$_5$W$_{30}$.

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 AgP$_5$W$_{30}$ was small, the glass-transition temperature was almost unchanged.
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.

![Stress-strain curve](image)

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

**Table S2.** Thickness and mechanical properties of PVA films.

<table>
<thead>
<tr>
<th></th>
<th>Thickness/mm</th>
<th>TS/MPa</th>
<th>Y/GPa</th>
<th>EAB/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA0</td>
<td>0.040±0.003</td>
<td>73.34±4.39</td>
<td>3.38±0.24</td>
<td>81.39±6.44</td>
</tr>
<tr>
<td>PVA0.5</td>
<td>0.056±0.003</td>
<td>80.32±5.64</td>
<td>4.35±0.11</td>
<td>79.66±7.13</td>
</tr>
<tr>
<td>PVA1</td>
<td>0.041±0.005</td>
<td>85.24±4.07</td>
<td>4.45±0.07</td>
<td>76.57±4.37</td>
</tr>
<tr>
<td>PVA3</td>
<td>0.042±0.007</td>
<td>92.51±3.82</td>
<td>4.61±0.39</td>
<td>76.03±6.81</td>
</tr>
</tbody>
</table>
Release of AgP$_5$W$_{30}$ from PVA films

Studying the release of active ingredients contributes to the evaluation of antimicrobial properties. The release profile of AgP$_5$W$_{30}$ 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$_5$W$_{30}$ in the inner core to move through the polymer networks easily. The partition coefficient (D) and diffusion coefficient (K) of AgP$_5$W$_{30}$ are shown in Table S3. D increased with the increase of AgP$_5$W$_{30}$ concentration, which indicates that the AgP$_5$W$_{30}$ diffusivity through composite films was concentration dependent. Moreover, the release percentage with different concentration of AgP$_5$W$_{30}$ 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](image)

Table S3. Initial concentration in films, diffusion coefficient, partition coefficient and release percent of AgP$_5$W$_{30}$.

<table>
<thead>
<tr>
<th>Initial concentration/ppm</th>
<th>$K \times 10^2$</th>
<th>$D \times 10^{13}/(\text{cm}^2/\text{s})$</th>
<th>$R^2$</th>
<th>$M_\infty/M_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA0.5</td>
<td>68.45±4.10</td>
<td>1.67</td>
<td>0.752</td>
<td>0.84</td>
</tr>
<tr>
<td>PVA1</td>
<td>136.62±2.70</td>
<td>1.13</td>
<td>0.903</td>
<td>0.81</td>
</tr>
<tr>
<td>PVA3</td>
<td>404.83±32.67</td>
<td>0.28</td>
<td>0.797</td>
<td>0.86</td>
</tr>
</tbody>
</table>

References

7. C. M. Corp, Spectrum, [https://www.spectrumchemical.com/chemicals/Silver-Oxide](https://www.spectrumchemical.com/chemicals/Silver-Oxide).


