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Supporting Information

Dual-Functional Composite Coating with Flame-retardant and Antibacterial Properties for Flexible Polyurethane Foams

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1. Materials and methods

1.1. Materials

Flexible polyurethane foam with a density of 30 kg/m^3 was purchased from Yongjia Sponge Processing Plant. Chitosan (CS, 95% deacetylation, 100-200 mPa.s), poly(acrylic acid) (PAA, average Mw~100000, 25 wt.% in H_2O), and branched poly(ethyleneimine) (BPEI, Mw~25000), were purchased from 3AMaterials®. Dopamine hydrochloride (DA), ammonium persulphate (APS), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), and potassium chloride (KCl) were purchased from Meryer (Shanghai) Biochemical Technology Co., Ltd. The tungstophosphate precursor salt, $[B\text{-}PW_9O_{34}]^{9-}$, was prepared according to the literature.[1]

1.2. Synthesis of PDA@CS nanoclusters

The synthesis of PDA@CS nanoclusters started with a study performed to screen for suitable synthesis conditions that prevent agglomeration of PDA and gelation of the reactant mixture. Parameters investigated include the concentration and pH of sodium acetate buffer, the mass ratio of DA to APS, and the reaction time. Details are provided in the Supporting Information. The optimal synthesis procedure is as follows: CS solution was prepared at a concentration of 2 mg/mL in 0.5 M sodium acetate buffer at pH 5.0. At t=0, a weighted amount of DA and APS was added to the CS solution to reach concentrations of 2 mg/mL DA and 2.4 mg/mL APS (molar ratio of DA to APS is 1:1). The solution was stirred at 700 rpm at room temperature for 24 h to yield the PDA@CS nanoclusters. Then, the solution of the PDA@CS nanoclusters was dialyzed against deionized water at room temperature for one day using a dialysis membrane with a molecular weight cut-off of 10 kDa. The solid PDA@CS was collected by filtration (filter paper, 0.22 μm), washed with deionized water, and air-dried at room temperature.

1.3. Synthesis of the POM, $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2] \cdot 20H_2O$

$K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2] \cdot 20H_2O$ was prepared as described in the literature:[1] Solid $Co(NO_3)_2 \cdot 6H_2O$ (0.41 g, 1.4 mmol) was dissolved in 15 mL of water. To this light pink solution was added 2.0 g of solid $[B\text{-}PW_9O_{34}]^{9-}$ (0.8 mmol), and the solution was heated under vigorous stirring until a homogeneous purple to burgundy solution resulted. 5 g of solid KCl was added, resulting in the precipitation of a blue-purple solid. After the mixture was cooled to room temperature, the precipitate was collected and redissolved in 10 mL of hot water to allow for recrystallization overnight at 5 °C. A crystalline blue-purple solid was collected and vacuum-dried at 80 °C for 2 h. Yield: 1.24 g (64.6 % based on Co). The FTIR spectrum confirmed the successful synthesis of the target POM (Fig. S1).

1.4. LbL assembly of PDA@CS-POM coating

The PDA@CS-POM coating was assembled on silicon wafer or flexible PU foam by alternating dips into solutions of cationic PDA@CS and anionic POM. The PDA@CS solution, used immediately after the dialysis, and the POM solution, prepared at 3 wt.% unless otherwise specified, were initially dipped for 5 min each. Subsequent dips lasted 1 min each. After every immersion, the substrate was rinsed with deionized water and dried. Each cycle of dipping corresponded to one bilayer of the coating. Upon achieving the desired number of bilayers, the coated substrates were dried in an oven at 80 ^{o}C. For the reference CS-POM coating, a similar deposition process was employed with modifications to the cationic solution and the addition of a primer layer before assembly. Specifically, the cationic solution is 2 mg/mL of CS in 0.5 M sodium acetate buffer at pH 5.0, and a primer layer was applied by immersing the substrate in 1 wt.% BPEI (for silicon wafer) or 1 wt.% PAA (for PU foam) for 5 min. The substates coated with PDA@CS-POM and CS-POM coatings are denoted as PCP-xBL and CP-xBL, respectively, where x represents the number of bilayers.

1.5. Characterization

UV-vis spectroscopy was performed using a Techcomp UV 2600 spectrophotometer. Fourier-transform infrared spectroscopy (FTIR) was recorded on a Bruker Tensor II spectrometer. The hydrodynamic diameter and zeta potential of the clusters were measured by dynamic light scattering (DLS, Nicomp Z3000 NanoZLS). Surface chemistry of the coatings was analyzed by X-ray photoelectron spectroscopy (XPS, PHI VersaProbe III). Film thickness on the silicon wafers was measured using an ellipsometer (Gaertner L116 S). The microstructures of the samples were observed using scanning electron microscopy (SEM, Hitachi SU8020) at an acceleration voltage of 20 kV. The water contact angle measurements were made by a contact angle goniometer (DataPhysics Instruments, OCA 50). Compression mechanical properties of the foams were measured using an electronic universal testing machine (DXLL-5000), with a sample size of 10 mm^3 and a strain rate of 1 mm/min. Thermogravimetric analyses (TGA, Netzsch STA 449 F5) were carried out from room temperature to 900 ^{o}C with a heating rate of 10 ^{o}C/min under a nitrogen atmosphere. The limiting oxygen index (LOI) values of the foams were measured with an oxygen index analyzer (Fire Testing Technology) according to ASTM D2863 with a sample size of 150 mm × 10 mm × 10 mm. Cone calorimetry (Fire Testing Technology) was conducted to analyze the combustion behavior of the foams according to ISO 5660-1 with a sample size of 100 mm × 100 mm × 25 mm at a heat flux of 35 kW/m^2. The graphitization degree of the samples was identified by Raman spectroscopy (Renishaw inVia) with an argon laser of 514 nm in a wavelength range from 500 to 2000 cm^{-1}. Thermogravimetry coupled with Infrared spectroscopy (TG-IR, NETZSCH X70) was performed with a heating rate of 10 ^{o}C/min from room temperature to 800 ^{o}C under a nitrogen atmosphere. The antibacterial activity was evaluated by soaking a sample sized 5×10×10 mm^3 in 5 mL of 10^5 CFU/mL *E. coli* suspension at 37 ^{o}C. At different incubation times (1 and 4 h), 100 μL of the bacterial suspension was withdrawn and coated on a LB agar plate, followed by incubation at 37 ^{o}C for 12 h. The same procedure was employed to assess the antibacterial activity against *S. aureus*.

2. Supplemental results

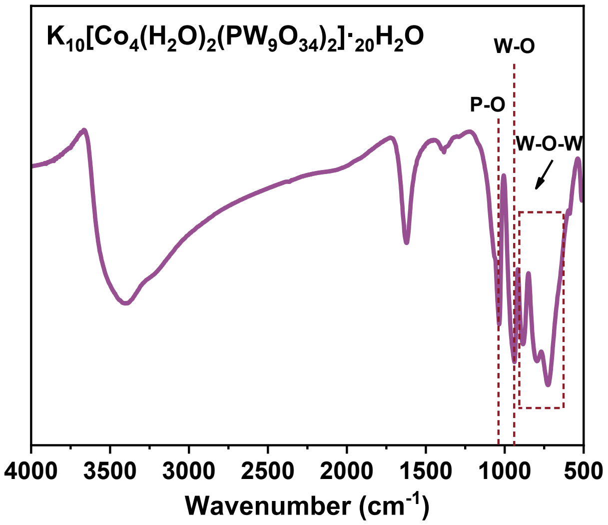


Fig. S1 FTIR spectrum of $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$.

Fig. S2-S4 shows the effects of the PH and concentration of sodium acetate buffer, the ratio of DA to APS, and the agitation time on synthesis of PDA@CS nanoclusters. The sodium acetate buffer with a low pH (< 6) and high concentration (≥ 0.5 M) was favored to facilitate the protonation of CS and prevent the precipitation of the PDA@CS particles. However, conversely, the formation of PDA is favored at a high pH and low concentration of the buffer, as indicated by the UV-vis spectra of the supernatants from the DA/CS/APS mixtures after 24 h agitation (Fig. S2). A similar trend was found in the effects of the molar ratio of DA to APS. Decreasing the ratio of DA to APS promoted the formation of PDA, while also increasing the tendency toward undesired gelation of the reactant mixture (Fig. S3). Based on these results, a trade-off was made to determine the optimal conditions, as described in the materials and methods section, for the synthesis of the stable PDA@CS nanoclusters for subsequent LbL assembly.

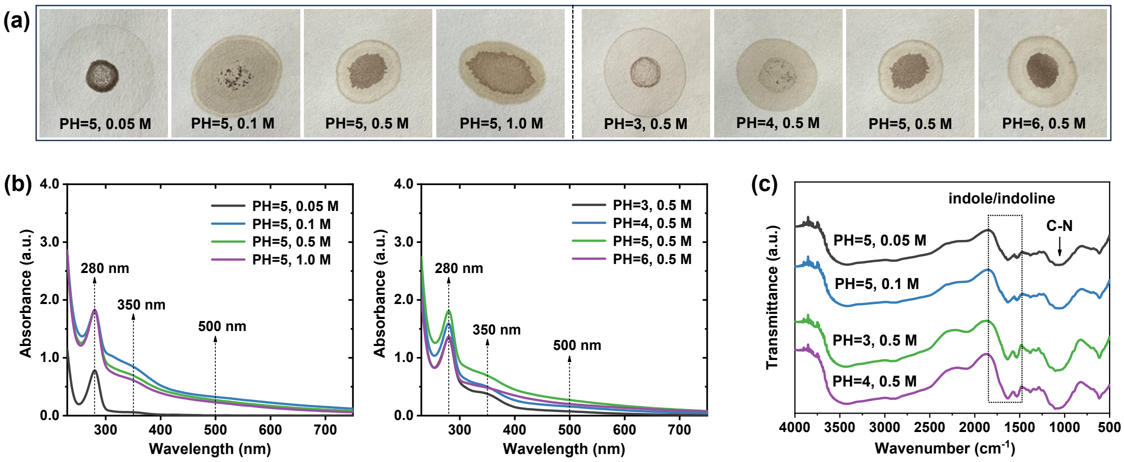


Fig. S2 Effects of PH and concentration of sodium acetate buffer on synthesis of PDA@CS nanoclusters. (a) Images of the dried droplets taken from the mixture of CS/DA/APS in different buffers after 24 h agitation. (b) UV-vis spectra of the supernatants and (c) FT-IR spectra of the precipitations of the CS/DA/APS mixtures after 24 h agitation.

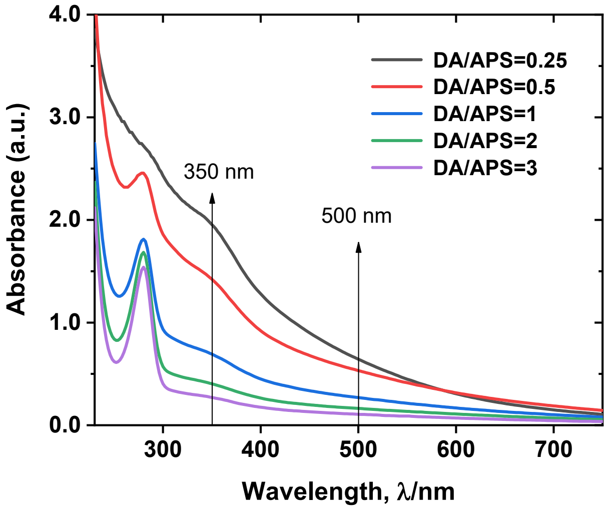


Fig. S3 Effects of the ratio of DA to APS on the UV-vis spectra of the CS/DA/APS mixtures after 24 h agitation. Decreasing the ratio of DA to APS promoted the formation of PDA, while also increasing the tendency toward undesired gelation of the reactant mixture.

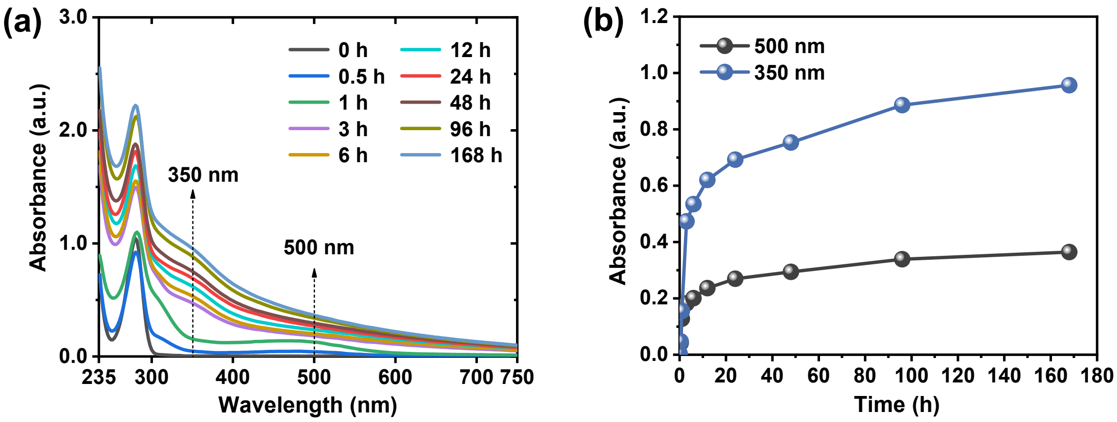


Fig. S4 Changes of the CS/DA/APS mixture after different agitation times: (a) UV-vis spectrum and (b) absorption intensity at 350 and 550 nm.

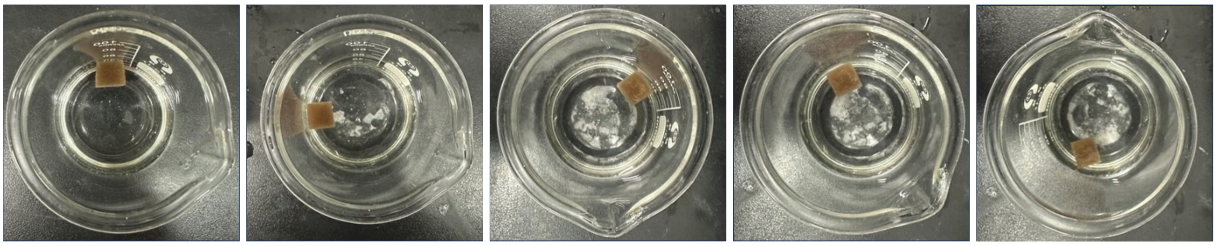
Table S1 Data from thermogravimetric analyses of the neat PU foam and the coated foams under a nitrogen atmosphere.

Samples	$T_{5\%}$ (°C)	T_{max1} (°C)	R_{max1} (wt.%/°C)	T_{max2} (°C)	R_{max2} (wt.%/°C)	Residual weight (wt.%)
PU foam	255.5	283.5	0.63	372.3	1.35	8.7
PCP-5BL	254.6	288.3	0.56	373.2	1.44	13.0
PCP-10BL	266.2	300.8	0.46	378.8	1.17	18.9
PCP-20BL	264.0	295.6	0.41	374.5	0.93	26.1

Table S2 Data from cyclic compression-recovery tests on the neat PU foam and the foam PCP-10BL.

Samples	$\sigma_{6\%}$[a] (kPa)	1st cycle at 60% strain			20th cycle at 60% strain		
		σ (kPa)	Hysteresis loss[b] (%)	$\varepsilon_{def.}$[c] (%)	σ (kPa)	Hysteresis loss (%)	$\varepsilon_{def.}$ (%)
PU foam	4.78	8.95	60.5	5.4	8.94	41.1	6.1
PCP-10BL	7.64	8.96	67.4	6.5	9.20	42.2	6.2

[a] $\sigma_{6\%}$ represents the stress at a strain of 6% during the compression test conducted up to 90% strain; [b] Hysteresis loss is defined as the ratio of energy losses to the energy expended on deformation; [c] $\varepsilon_{def.}$ denotes the permanent plastic deformation observed after the compression-recovery test.



0 min **10 min** **30 min** **1 h** **2 h**

Fig. S5 Stability of the PU foam coated with 10 bilayers of PDA@CS-POM coating (PCP-10BL) under different durations of water bath sonication.

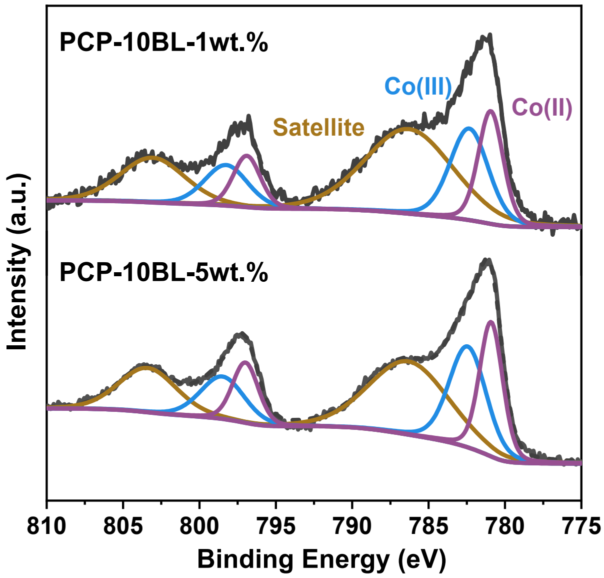


Fig. S6 High-resolution Co 2p spectra of the foam PCP-10BL-1wt.% and PCP-10BL-5wt.% after cone calorimetry.

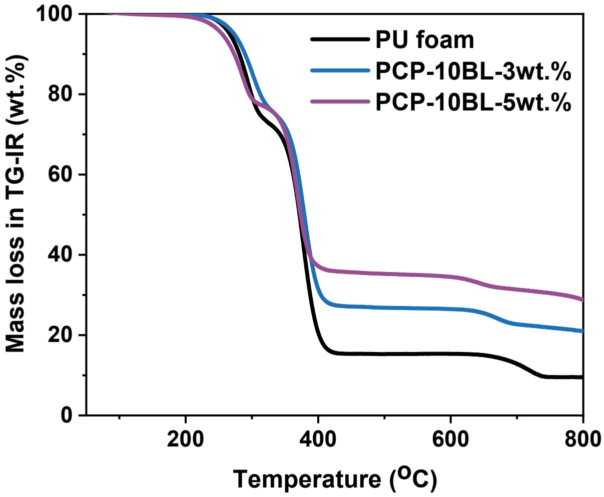
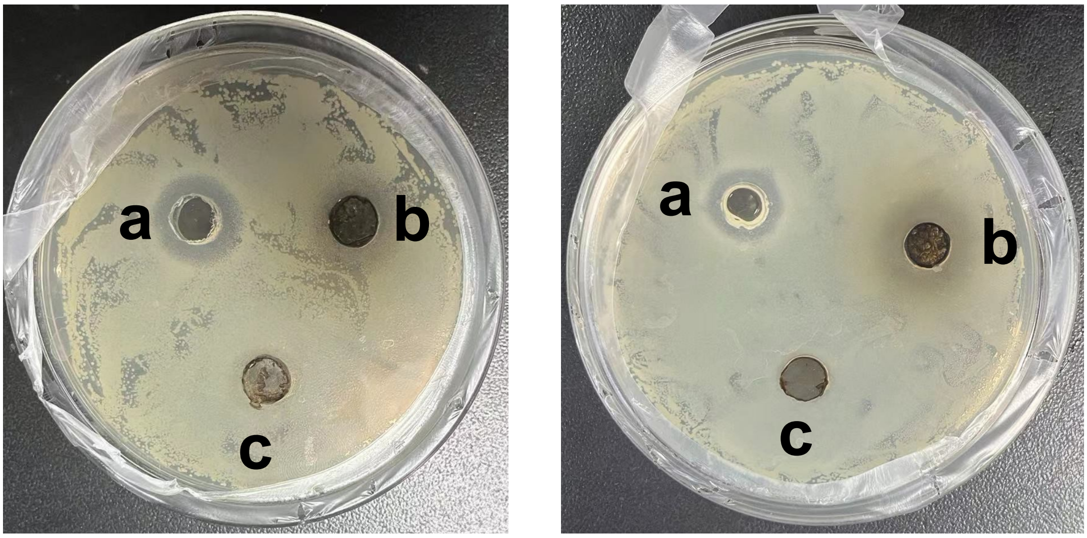


Fig. S7 Mass loss of the neat PU foam and the PCP coated foams in TG-IR.



E. coli ***S. aureus***

Fig. S8 Zone of inhibition of (a) the POM and the PDA@CS (b) before and (c) after dialysis against *E. coli* and *S. aureus*.

3. Reference

1 Finke, R. G.; Droege, M. W.; Domaille, P. J. Trivacant Heteropolytungstate Derivatives. 3. Rational Syntheses, Characterization, Two-Dimensional Tungsten-183 NMR, and Properties of Tungstometallophosphates $P_2W_{18}M_4(H_2O)_2O_{68}^{10-}$ and $P_4W_{30}M_4(H_2O)_2O_{112}^{16-}$ (M = Cobalt, Copper, Zinc). *Inorg. Chem.* **1987**, *26*, 3886–3896.