Supporting Information

Supramolecular hydrogel infiltrated ceramics composite coating with combined antibacterial and self-lubricating performance

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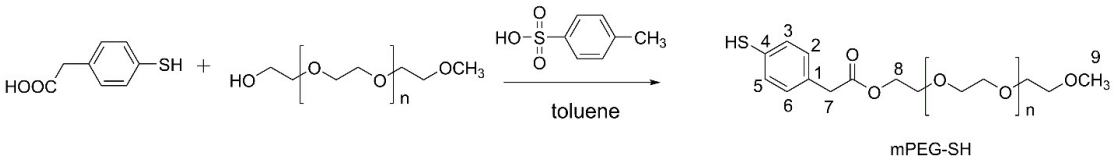
1. General Information

1.1 Chemicals. Monomethoxy polyethylene glycol with a molecular weight of 10000 was purchased from Shanghai Yare Biotech, Inc. 4-Mercaptophenylacetic acid was purchased from Alfa Aesar. α-cyclodextrin (α-CD, purity ≥ 98.0%) were purchased from Aladdin Chemical Co. Ltd. Vancomycin hydrochloride was purchased from MP Biomedicals, LLC. Live/Dead viability assay kit was purchased from Beijing Solarbio Science & Technology Co., Ltd. All other reagents and solvents were of reagent grade or purified according to standard methods before use. Ultrapure water was obtained by a water purification system, which was purchased from Shanghai Laikie Instrument Co., Ltd.

1.2 Materials Characterization. NMR spectra were obtained on a Bruker AVANCE III-400 spectrometers using $CDCl_3$ as the solvent. The morphologies of PEGylated AgNPs were investigated on an FEI-Tecnai G2 Transmission Electron Microscope (TEM). The energy dispersive spectrum (EDS) was also obtained by TEM. The morphologies of AgNPs supramolecular hydrogel were investigated and analyzed on a JSM-5600LV scanning electron microscope (SEM) after the samples were freeze-dried and coated with gold vapor. The X-ray diffraction measurements of hydrogels were performed by a PHILP X'Pert PRO, using Cu Kα (λ = 1.542 Å) irradiation (40 kV, 40 mA) in the range of 2θ=5-80°. Thermogravimetric analyses (TGA) were performed on a STA 449C thermal analysis system with a nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C. The rheological behavior of the hybrid hydrogels was investigated by a HAAKE RS6000 rotational rheometer using a 35 mm

parallel-plate geometry at 20 °C. The gap distance between the two plates was fixed at 1 mm. Oscillating stress was fixed at 1 Pa for all dynamic tests. Fluorescence images on cells and coatings were obtained on an Olympus Fluoview 1000 confocal laser scanning microscope (Olympus, Tokyo, Japan). YSZ coatings were fabricated on titanium alloy substrates using a plasma spraying system, followed by polishing and laser texturing according to the designed pattern. An OLYMPUS optical microscope (OM) and a SEM coupled with an energy dispersive X-ray analyzer were employed to characterize the textured coating surfaces before and after infiltrated with hydrogel. A Micro-XAM-3D non-contact surface profiler (ADE Corporation; Massachusetts, USA) was used to detect wear volume loss, and the morphology of worn surfaces was analyzed by the SEM.



Scheme S1. Synthesis route of mPEG-SH

1.3 Synthesis of methoxy-terminated poly(ethylene glycol)-SH (mPEG-SH). The synthesis route of mPEG-SH w is shown in Scheme S1. In brief, to a solution of monomethoxy polyethylene glycol（mPEG, M_w = 10000，1.0 mmol）in toluene, 4-Mercaptophenylacetic acid (2.0 mmol) was added under nitrogen atmosphere, and the reaction mixture was stirred at 90 °C for 1.0 h. After that, *p*-toluenesulfonic acid dissolved in toluene (5 wt%，0.58 mmol) was added dropwise to the mixture, and the reaction mixture was stirred at 110 °C for another 5.0 h. The solution was evaporated to dryness and purified by dextran gel column to obtain mPEG-SH. $mPEG_{10000}$-SH, ^1H NMR (400MHz, $CDCl_3$) δ: 7.42-7.44 (d, *J*=7.96 Hz, 2, 6-H), 7.20-7.22 (d, *J*=11.24 Hz, 3, 5-H), 4.21-4.24 (t, *J*=4.68 Hz, 4.76 Hz, 8-H), 3.53-3.82 (m, -OCH_2CH_2O- units of PEG chain, 7-H), 3.44 (m, SH), 3.37 (s, 9-H).

1.4 preparation of PEGylated AgNPs. The PEGylated AgNPs were prepared according to ref. 29 with a little modification. In brief, the reaction was carried out under nitrogen atmosphere to prevent oxidation of the reducer and mPEG-SH during formation of the metal NPs. An amount of 32 mL of 7.5 mM $AgNO_3$ ethanol solution was mixed with mPEG-SH powder (0.15 g) and sonicated for 5 min. Ag reduction was achieved by a dropwise addition of 10.4 mL of 90 mM $NaBH_4$ ethanol solution under vigorous stirring. After 2 h reaction time in the dark, the obtained brown suspension was dialyzed against deionized water to remove the excess of mPEG-SH molecules.

1.5 hydrogel degradation. The cuvette contains 1.0 mL of AgNPs hydrogel was immersed in 2.0 mL of PBS (pH 7.4). At predetermined time intervals, the PBS solution was removed by pipette, and the remaining hydrogel was weighed. Then, 2.0 mL of fresh PBS was added into the cuvette. The weight loss (%) of the hydrogel was evaluated by the formula, weight loss (%) = (original mass of hydrogel-remaining mass of hydrogel) / original mass of hydrogel × 100.

To evaluate the gel degradation from composite coating, the fresh prepared composite coating were immersed in 2.3 mL of PBS (pH 7.4). At preset intervals, the PBS solution was removed by pipette, and the composite coating was weighed after wiping off the water from the bottom and side. Then, the sample was re-immersed in 2.3 mL of PBS. The weight loss (%) of the hydrogel from composite coating was calculated using same formula mentioned above.

1.6 AgNPs release. The cuvette contains 1.0 mL of AgNPs hydrogel was immersed in 2.0 mL of PBS (pH 7.4). At preset intervals, 1.0 mL of PBS solution was collected and refilled with 1.0 mL of fresh PBS. The Ag concentration in the solution were determined by atomic absorption spectrophotometry (ContrAA700, Analytik Jena, Germany).

1.7 Antibacterial activity assay. *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were used in our experiments which obtained from the CAS Key Laboratory of Chemistry of Northwestern Plant Resources, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The bacteria were cultured in beef peptone broth for 24 h at 37 °C and then diluted to

a final concentration of approximately 10^7 colony-forming units (CFU) mL^{-1} at an optical density of 600 nm (OD_{600}).

The antibacterial activity of the lyophilized native PPR hydrogel, AgNPs hybrid hydrogel and vancomycin loaded AgNPs hydrogel were tested by the minimum inhibitory concentration (MIC), which was determined using the microtiter broth dilution method. 100 μL of the bacterial dispersions (10^7 CFU mL^{-1}) was added in each well of 96-well plate, followed by the addition of a series of two-fold dilution of each hydrogel samples (100 μL). The plate was incubated at 37 °C for 24 h. the bacteria viability were determined by measuring the OD_{600} using the SpectraMax® Absorbance Reader (Molecular Devices, USA).

The antibacterial activity of the textured YSZ coating, textured YSZ coating incorporated with AgNP hybrid hydrogels and vancomycin loaded AgNPs hydrogel were evaluated by the inhibition zone method. At first, about 50 mL of fresh nutrient agar (1%) was poured into Petri dish and allowed to solidify. The bacterial suspension (1.0 mL, 10^7 CFU mL^{-1}) of *S. aureus* was uniformly coated on the agar surface. The sterilized coatings were inverted on the surface of agar and the dishes were incubated at 37 °C for 24 h. The original and worn (after sliding 1 h on tribometer under same condition with friction and wear tests) composite coating incorporated with vancomycin loaded AgNPs hydrogel was utilized to evaluate the antibacterial effects under same condition. After incubation for 24 h, both samples were took out and the inhibition zone was measured. To evaluate the sustained antibacterial effect of composite coating, the same worn coating was continuously incubated at 37 °C for 7 days. At preset intervals, the dishes were took out and the inhibition zone was measured.

1.8 Biocompatibility evaluation. The HepG2 and L-02 cells were seeded in a 96 well culture plate at a density of 1×10^5 cells mL^{-1}. The cells were cultured in RPMI 1640 medium supplemented with 10% fetal bovine serum at 37 °C in a humidified environment of 5% CO_2 for 4 h. The cells were incubated with various concentrations of native PPR hydrogel and

AgNPs hydrogels (dissolved in cell culture medium) for 24 h, respectively. For YSZ coating, the coating was extracted by 20 mL of culture medium for 24 h, and the cells were incubated with extracted solutions for 24 h. The cell viability was determined by a MTT assay according to the generally procedures and the relative cell viability (%) was expressed as a percentage of that of the control culture.

For Live-Dead assay, the sterilized coatings (textured YSZ coating and composite coating) were placed in a 6-well plate, then L-02 cells were seeded to submerge the coatings and incubated at 37 °C in a humidified environment of 5% CO_2 for one day. The media were removed and a mixture of Live-Dye staining solution was added to each well and incubated at 37 °C in a humidified environment of 5% CO_2 for 30 min. The coating surface was washed with PBS for three times and the image of the stained cells was acquired by confocal laser scanning microscope.

1.9 Friction and wear tests. Tribological characterizations were performed with a ball-on-disk tribometer (CSM, Switerland) at room temperature and in ambient air with a relative humidity of 15-20%. The coating samples were used as lower specimens, and commercially available Al_2O_3 balls (Ø 6mm) were used as upper specimens. The friction and wear tests were conducted at a fixed amplitude of 2.5 mm, a normal load of 5 N, a maximum linear speed of 8 cm/s and sliding distance of 100 m.

2. Supplementary Figures S1-S9

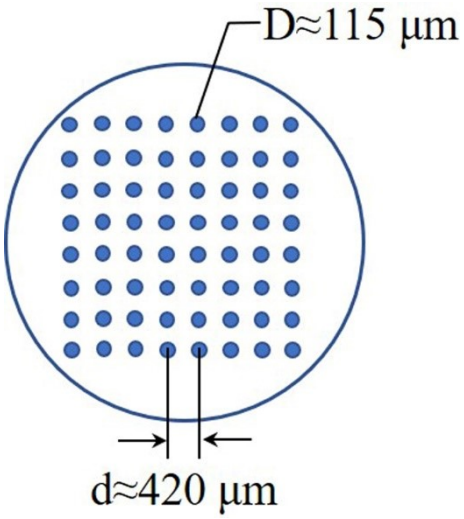


Figure S1. Pattern of laser texture on the YSZ coating surface.

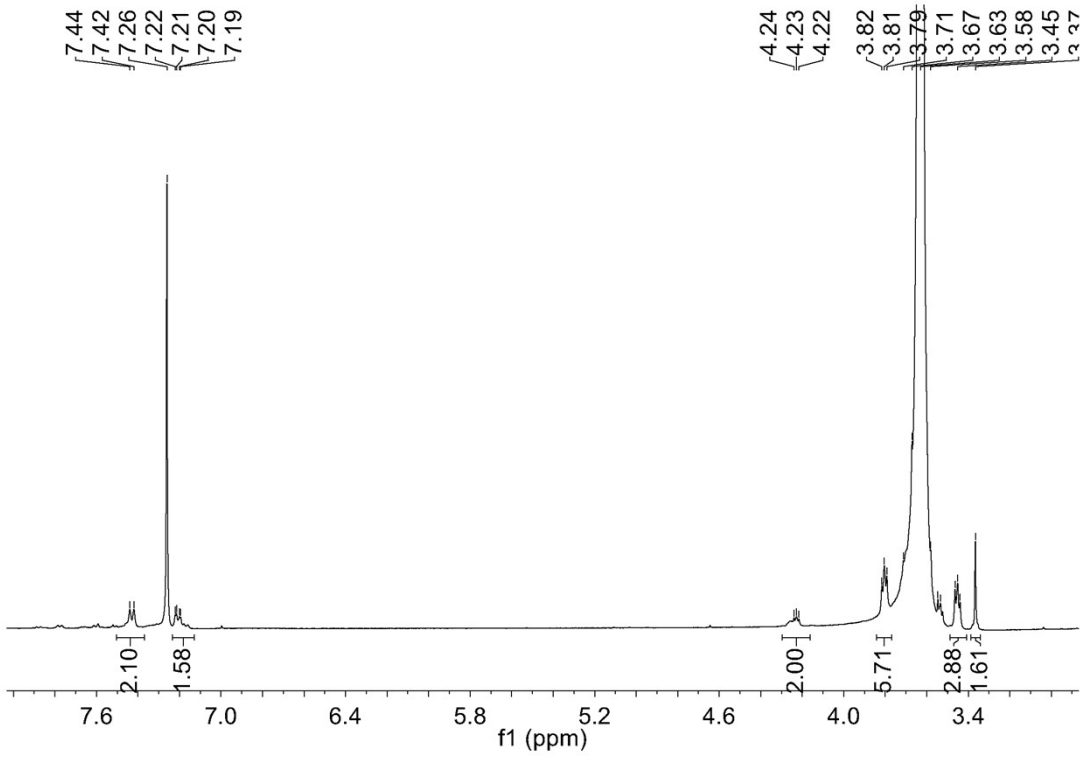


Figure S2. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of mPEG-SH.

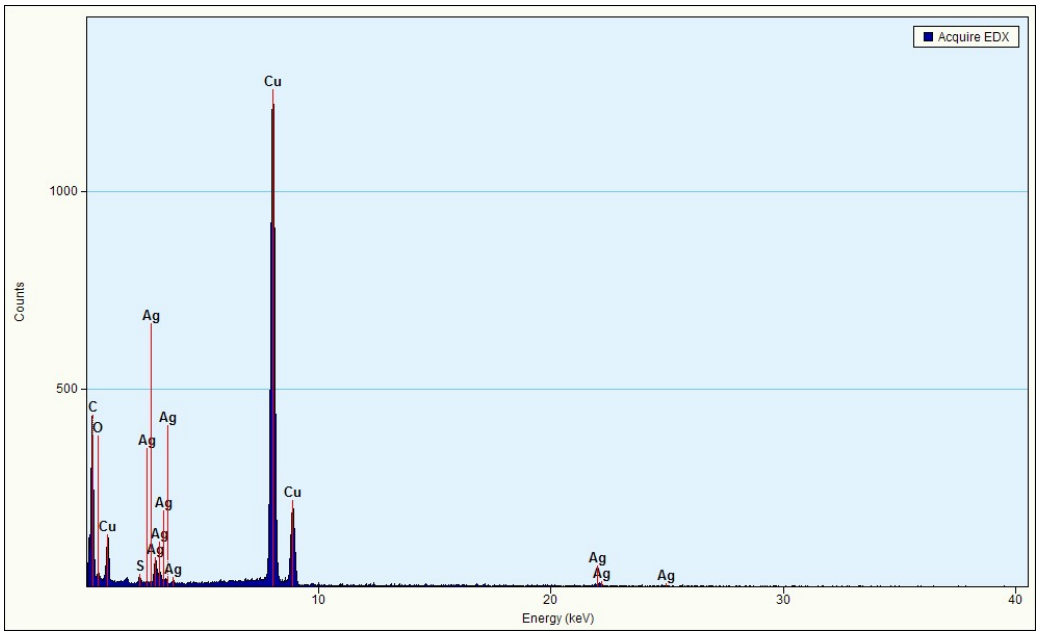


Figure S3. EDS result of PEG-AgNPs.

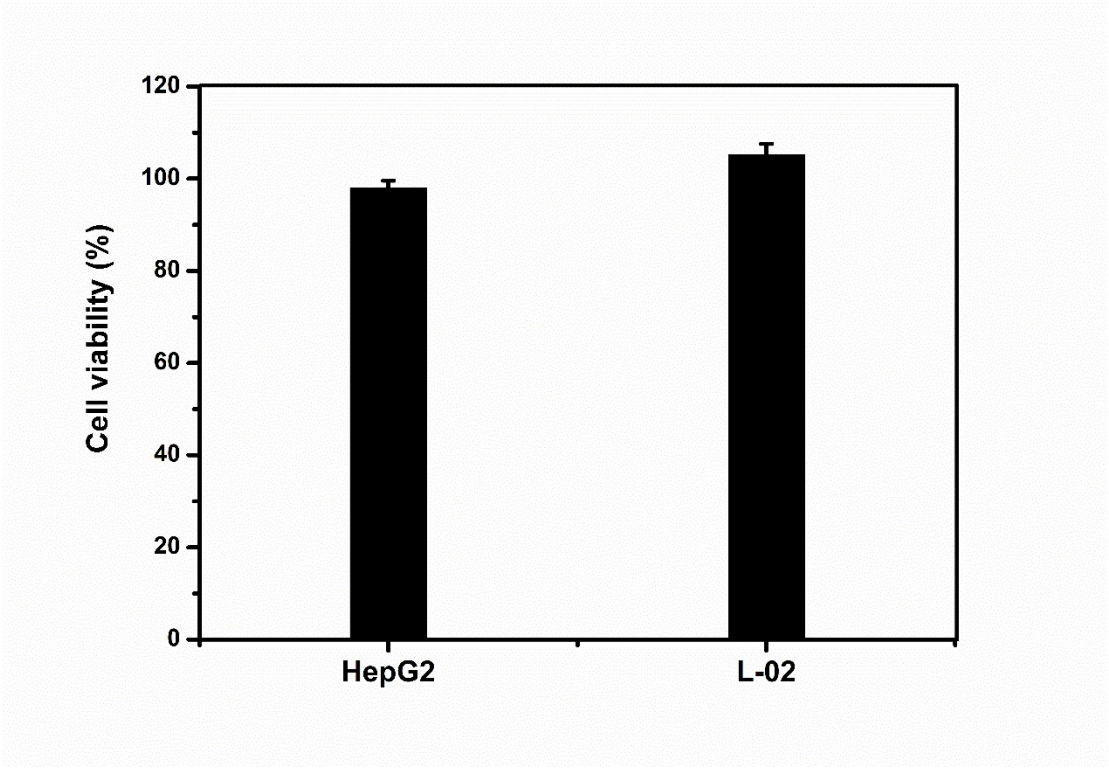


Figure S4. MTT results of YSZ coating extracts against HepG2 and L-02 cells.

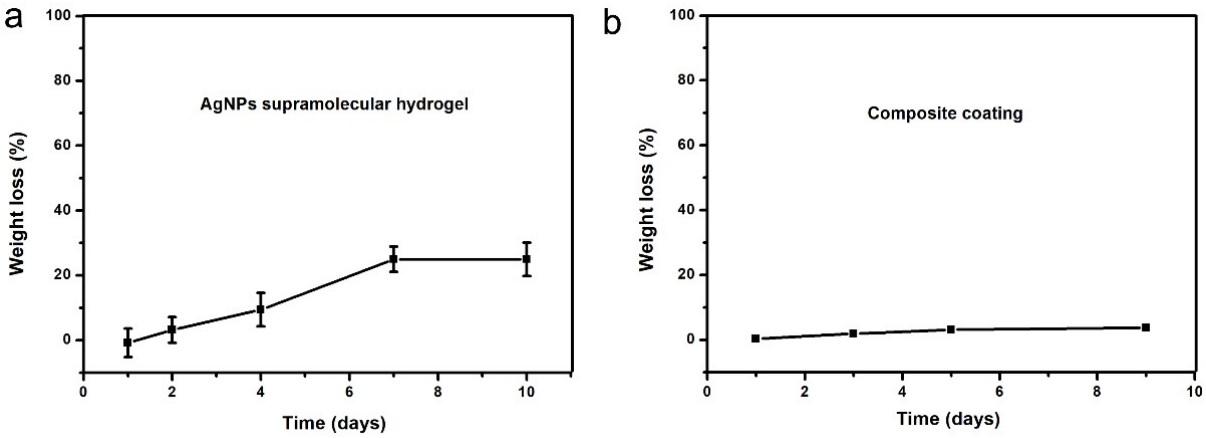


Figure S5. *In vitro* degradation profiles of AgNPs supramolecular hydrogel before (a) and after (b) infiltrated in the textured coating at PBS soltuion (pH 7.4).

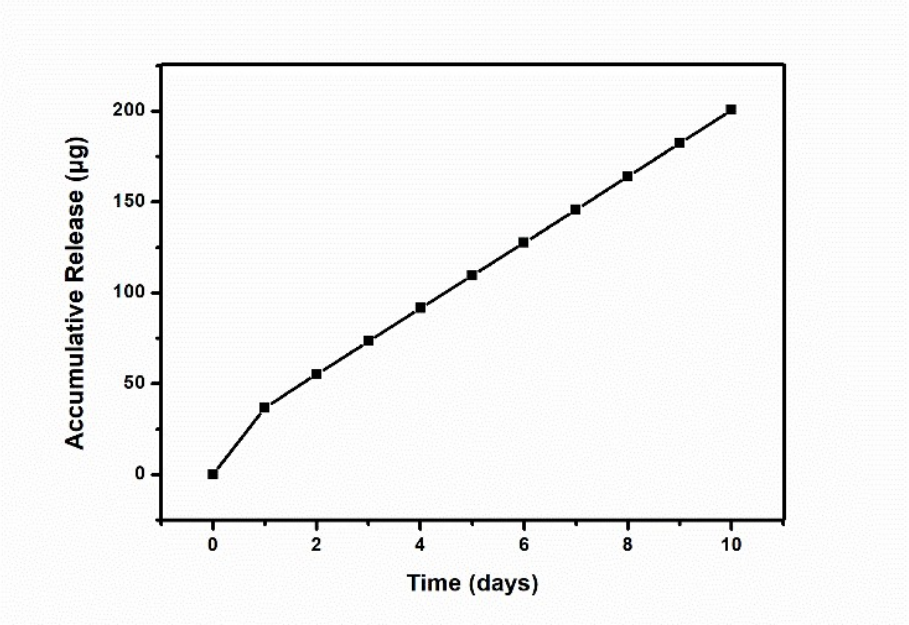


Figure S6. *In vitro* AgNP release profiles of AgNP hydrogel at d PBS soltuion (pH 7.4).

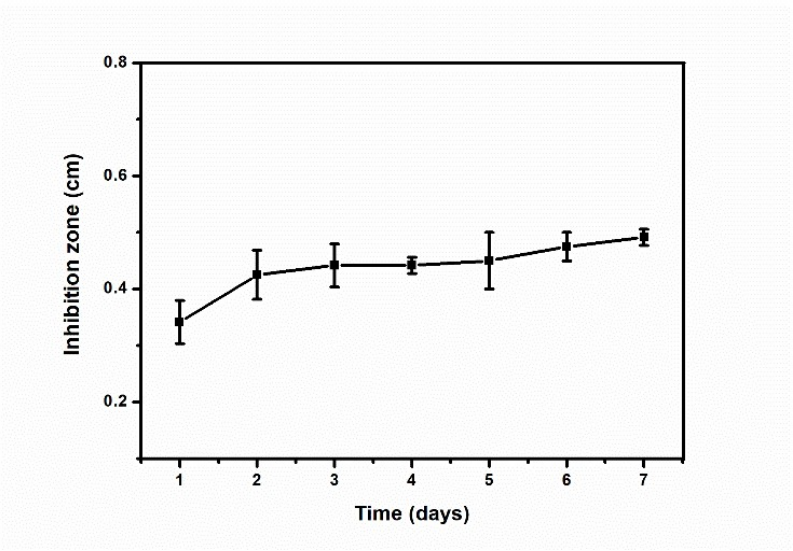


Figure S7. The inbition zone profiles of worn coposite coating against *S. aureus*.

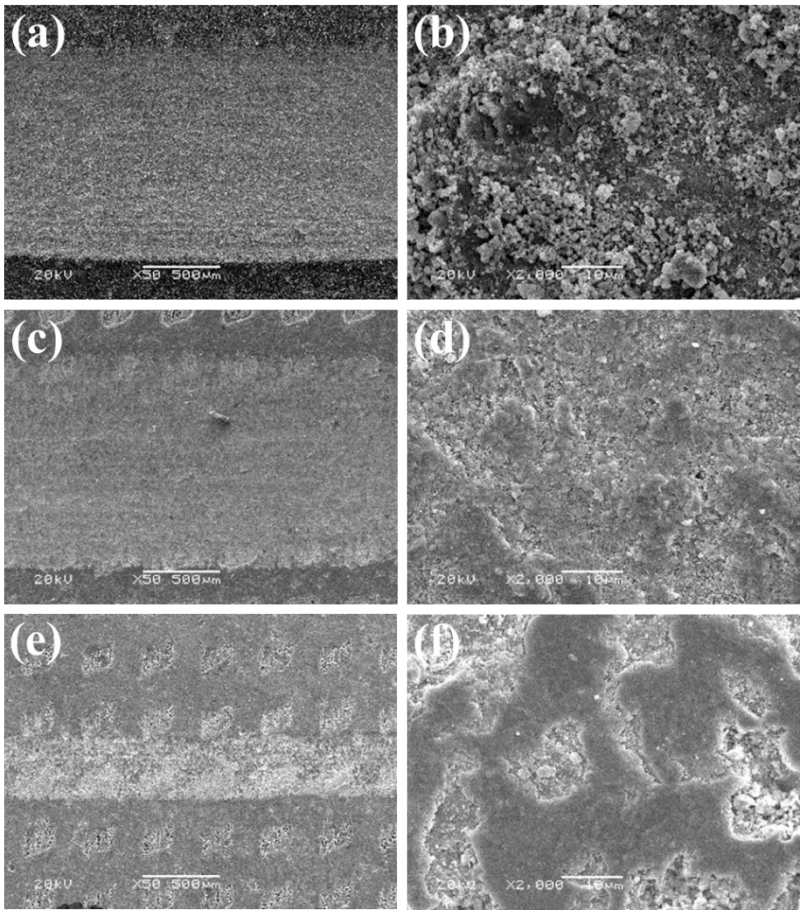


Figure S8. the SEM images of the worn surface of coating samples. (a) blank YSZ coating, (c) textured coating, (e) composite coating, (b), (d) and (f) are magnified view corresponding to (a), (c) and (e), respectively.

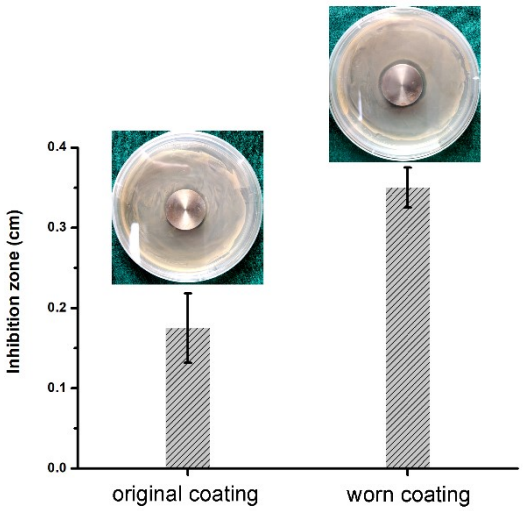


Figure S9. Antibacterial test using inhibition zone method against *S. aureus* after 24 h incubation with drug-loaded composite coating before (original coating) and after (worn coating) performing tribiological test.

3. Supplementary Tables S1-S2

Table S1 Plasma spraying parameters of YSZ coating

Items	Values
Primary gas (Ar) flow rate (L/min)	35
Secondary gas (H_2) flow rate (L/min)	8.5
Current (A)	550
Voltage (V)	65
Powder gas flow rate (L/min)	7
Powder feed rate (%)	10
Gun speed (mm/s)	400
Spray distance (mm)	100
Injector angle (degrees)	90

Table S2 HVOF spraying Parameters of bond coating

Parameters	Value
Oxygen flow (m^3/h)	19.8
Natural gas flow (m^3/h)	13.1
Powder feed rate (g/min)	25
Gun speed (mm/s)	800
Interpass spacing (mm)	2
Spraying distance (cm)	27.5