Supporting Information

A Self-powered Delivery Substrate Boosts Active Enzyme Delivery in Response to Human Movements

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This supporting information file includes:

Section S1. The FTIR-ATR spectra of the GO, TFB and rGO-TFB.

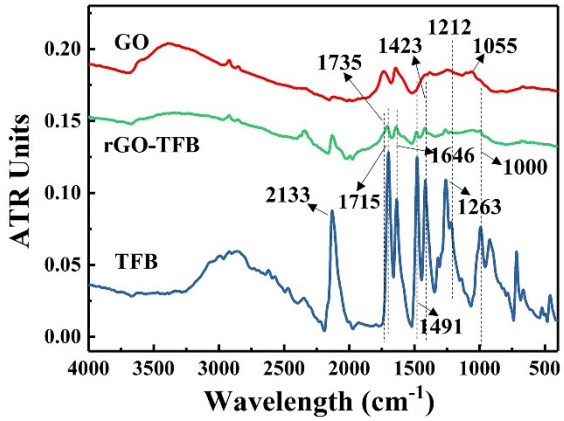

Figure S1. The FTIR-ATR spectra of the GO, TFB and rGO-TFB.

Section S2. The contact angles before and after plasma treatment.

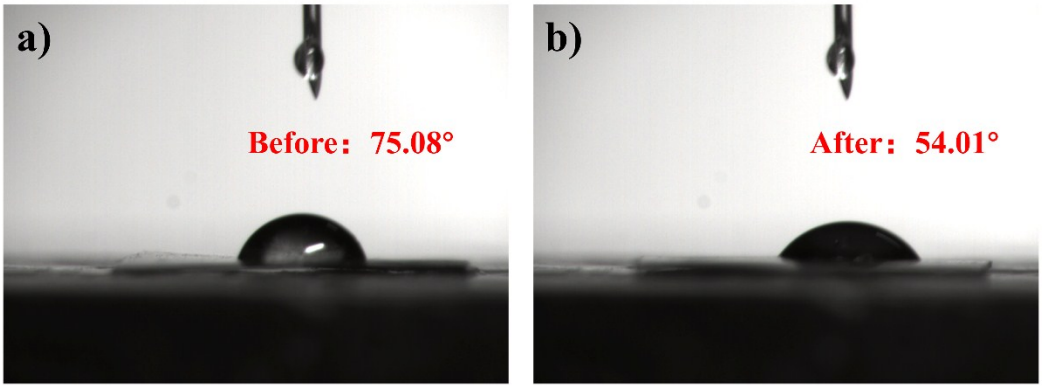

Figure S2. The contact angles a) before and b) after plasma treatment.

Section S3. The TEM images and the adsorption-desorption curve of mesoporous silica.

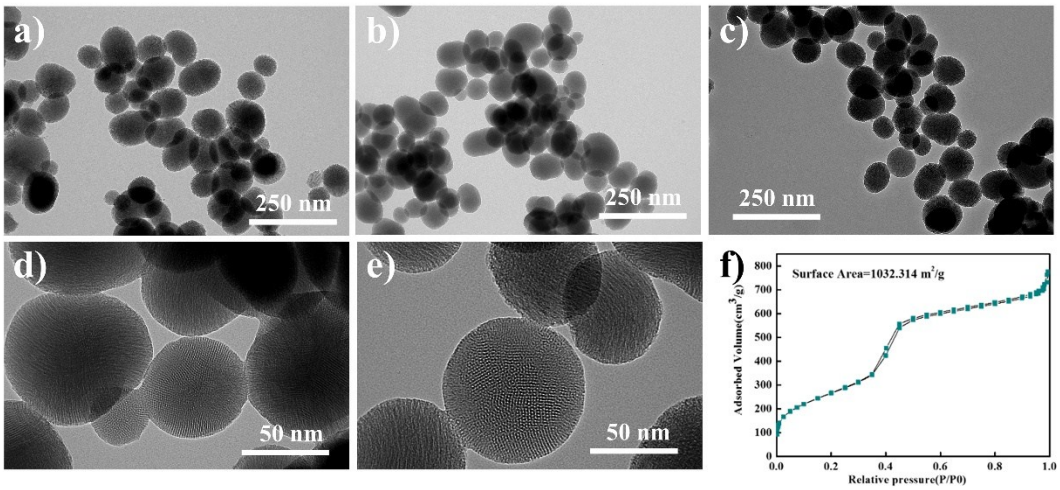

Figure S3. a-e) The TEM images of mesoporous silica at different magnifications, f) The adsorption-desorption curve of the mesoporous silica.

Section S4. The SEM images and AFM image of multilayers at different magnifications.

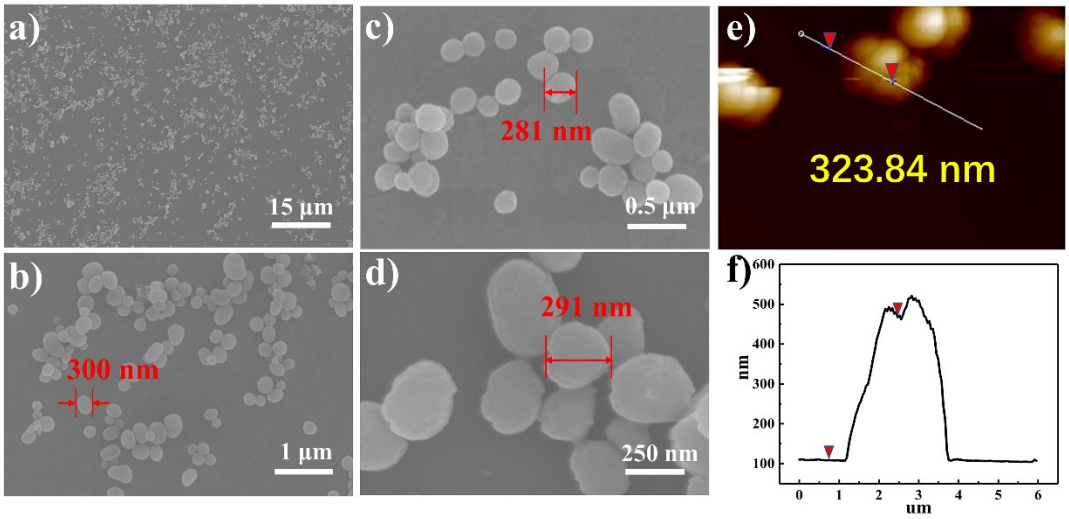

Figure S4. a-d) The SEM images of multilayers at different magnifications based on the quartz sheets. e-f) The AFM image of multilayers.

Section S5. The adsorb-release process of the MB in $(PAH/PAA)_n$ and $(PAH/MS)_n$ multilayers.

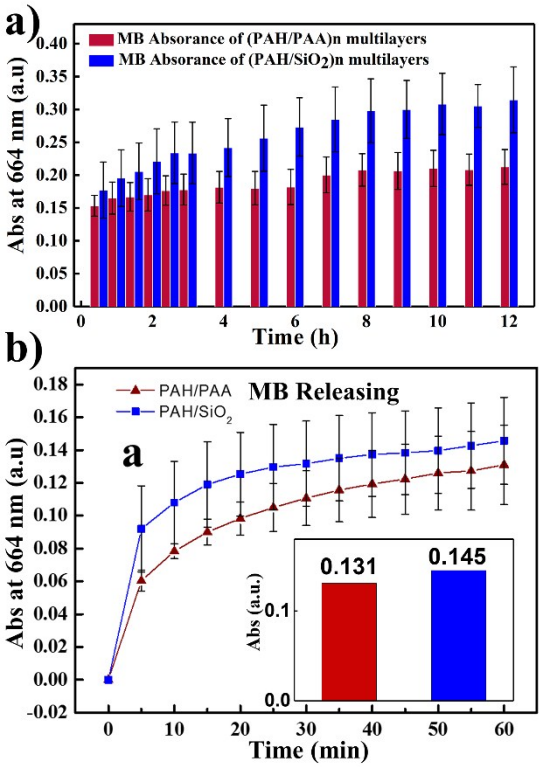

Figure S5. The adsorb-release process of the MB in $(PAH/PAA)_n$ and $(PAH/MS)_n$ multilayers.

Section S6. The SEM images of multilayers at different magnifications based on the composite film.

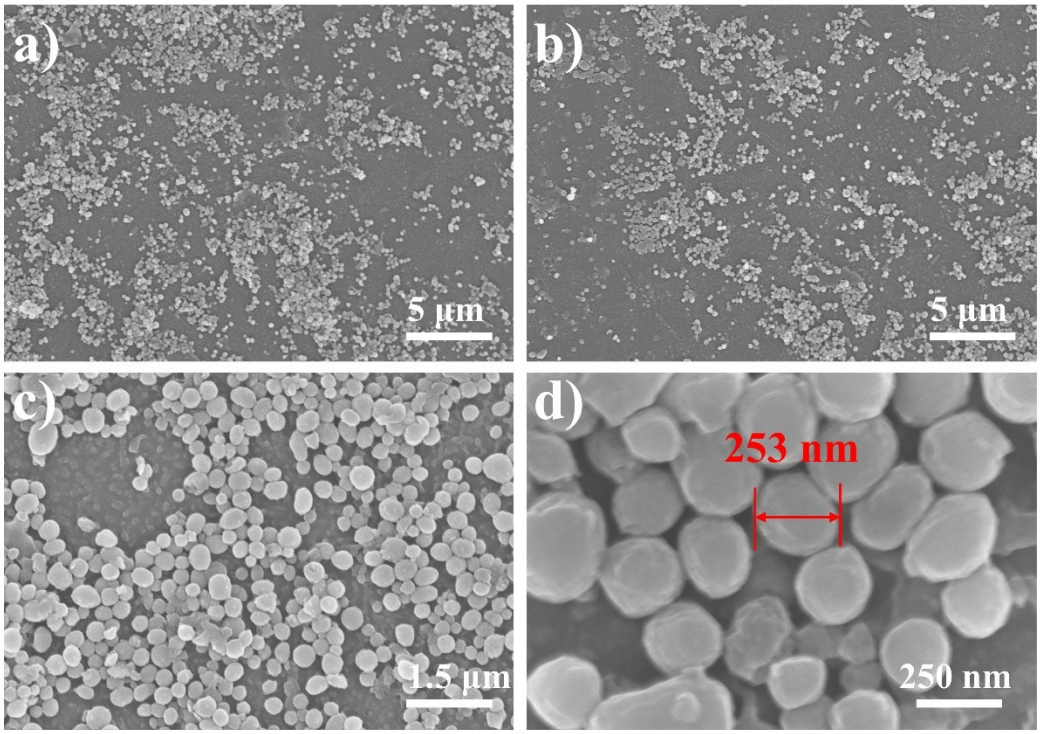

Figure S6. The SEM images of multilayers at different magnifications based on the composite film.

Section S7. The Fluorescent images of HaCaT cells.

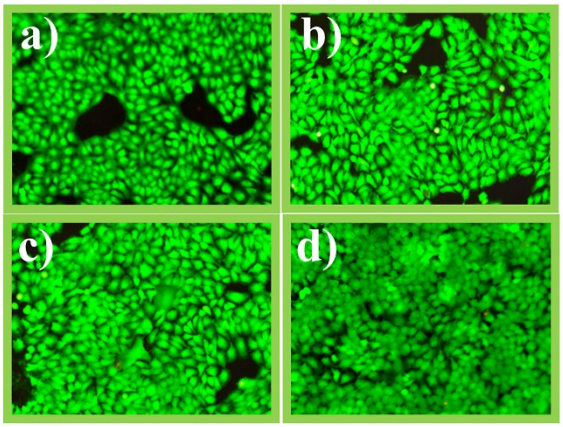

Figure S7. The Fluorescent images of HaCaT cells cultured on a) the bottom of a 24-well plate and b) the LbL composite film for 24 h, c) immediately after repeatedly finger-tapping on the composite film (to generate piezoelectricity) for 5 min, d) 2 hours culturing after the piezoelectricity applications.

Section S8. Experimental Section.

Materials: PVDF-HFP (density 1.78g*cm^{-3},5%–20% molar of hexafluoropropene) was purchased from Sigma–Aldrich. Natural flake graphite (300 mesh) was purchased from the Shuangxing graphite processing plant, China. Methyl pentafluorobenzoate (≥99%) and sodium azide (NaN_3, ≥99.5%) were purchased from Sigma-Aldrich. Potassium persulfate (KPS, ≥99.5%), phosphorus pentoxide (PPO, ≥98%), potassium permanganate ($KMnO_4$, ≥99.5%), sulfuric acid (H_2SO_4, 95%–98%), hydrochloric acid (HCl, 36%–38%), perhydrol (H_2O_2, 30%), N,N-dimethyl formamide (DMF, ≥99.5%), acetone(≥99.5%), methanol (≥99.5%), and chloroform (≥99.0%) were obtained from local commercial sources and used as received. Cetyltrimethylammonium bromide surfactant ($CH_3(CH_2)_{15}N(CH_3)_3Br$ (CTAB)), poly(allylamine hydrochloride) (PAH, Mw=15000) were obtained from Sigma Aldrich. 4,4′-Diazostilbene-2,2-disulfonic acid disodium salt (DAS) was obtained from Tokyo Chemical Industry, Japan. A polypeptide (RhB-SGSGRGD) was synthesized and purified (90.59% pure) by GL Biochem (Shanghai) Ltd, China. The human permanent biochemical epidermal cells (HaCaT) and the human lung fibroblasts cells (HLFC) was obtained from the Chinese Academy of Medical Sciences. Fetal bovine serum (FBS) was purchased from Sangon Biotech Co. (Shanghai). Calcium- and magnesium-free phosphate buffered saline (PBS), Minimum Essential Medium (MEM Eagles with Earle's Balanced Salts) (MEM-EBSS), trypsin and dulbecco's modified eagle medium (DMEM) were obtained from Thermo Fisher Scientific Inc. (USA). Paraformaldehyde and dimethyl sulfoxide (DMSO) were obtained from Beijing Chemical Plant (Beijing, China).

Preparation of TFB : The TFB was prepared as reported. Ester Methyl 4-Azidotetrafl ourobenzoate: A mixture of 0.30 g of NaN_3 and 0.88 g of methyl pentafluorobenzoate in acetone (8 mL) and water (3 mL) was refluxed for 8 h. The mixture was cooled, diluted with water (10 mL), and then extracted by ether (30 mL). The extract was dried ($MgSO_4$) and evaporated to leave of pale-yellow liquid which solidified at standing. A solution of 0.586 g of methyl pentafluorobenzoate with 20% aqueous NaOH (0.8 mL) in MeOH (10 mL) and water (1 mL) was stirred at 25 °C for 8 h. The solution was acidified by HCl in an ice bath to pH<1 and extracted by $CHCl_3$

(3×10 mL). The extract was dried ($MgSO_4$) and evaporated to leave TFB as a colorless solid.

Preparation of rGO-TFB: An additional graphite oxidation procedure was used and the preoxidized graphite was prepared by KPS and PPO in concentrated H_2SO_4. Then, this preoxidized graphite was subjected to oxidation by Hummers' method to prepare to GO [2]. Next, 0.05 g GO and 0.25 g TFB were mixed and heated for 40 min, and subsequently the mixture of rGO-TFB were washed by ethanol to remove extra TFB. Finally, the rGO-TFB was obtained and dried at 40 °C.

Cell Culture: HaCaT cells were cultured in MEM-EBSS with 15% FBS added antibiotic-antimycotic solution containing 100 U mL^{-1} penicillin and 100 U mL^{-1} streptomycin sulfate. The culture conditions were a humidified atmosphere of 5% CO_2 and 95% air at 37 ºC.