Supporting Information

Cell-inspired Biointerfaces Constructed by Patterned Smart Hydrogels for Immunoassay in Whole Blood

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1. Preparation of PEG modified SEBS Substrate and Patterned SEBS-*g*-PEG-*g*-NaAc Samples

The virgin SEBS substrates were immersed into an ethanol solution of BP (1.5 wt%) for 30 min and then dried in vacuum under dark condition for 1 h at 25 °C. The substrates were put on a quartz plate and coated with an aqueous solution containing PEGMA (15 vol%), followed by covering with another quartz plate. The sandwich system was subsequently exposed to UV light (high-pressure mercury lamp, 400 W, main wavelength 380 nm) for 8 min (**Figure S1a**). All the grafted substrates were thoroughly rinsed with water and ethanol for 24 h and then dried in a vacuum oven for 24 h at room temperature. The so-obtained PEG-grafted film was referred as SEBS-*g*-PEG samples.

Copper grids with 100 meshes served as photomasks and SEBS-*g*-PEG samples incorporating copper grids were prepared in a cleanroom environment. 10 wt % aqueous solution of sodium acrylate was prepared. NaAc-grafted film was obtained according to the above procedure. The so-obtained sample was referred as SEBS-*g*-PEG-*g*-NaAc samples (**Figure S1b**). Similarly, the aqueous solution (8 ml) of NaAc (0.054 g, 0.5 mmol) and PEGDA (2 ml) were prepared. And NaAc/PEGDA-grfated film was obtained according to the above procedure, which was referred as SEBS-*g*-PEG-*g*-NaAc/PEGDA.

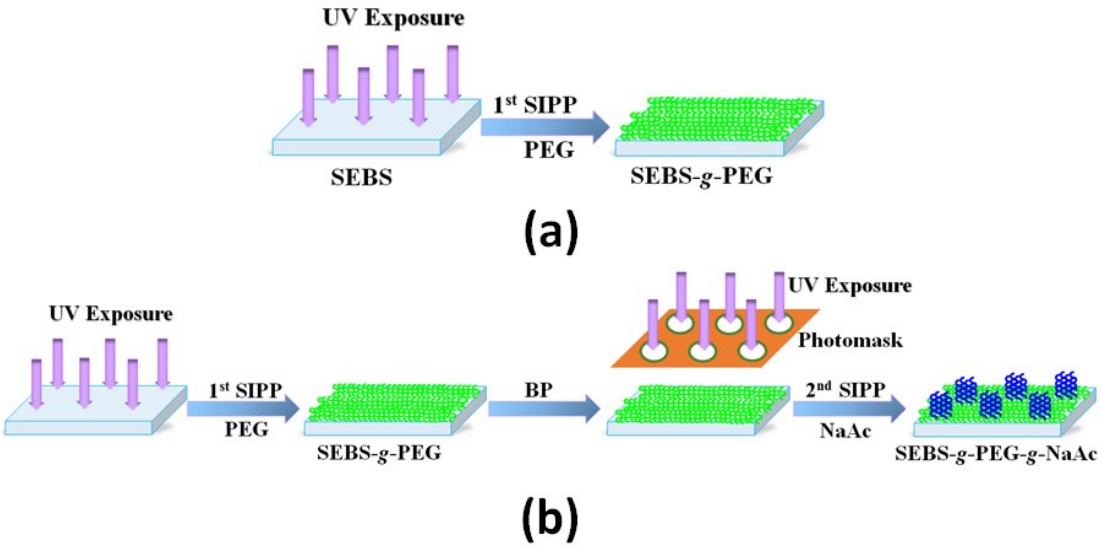

Figure S1. Schematic diagram of the preparation of (a) SEBS-*g*-PEG; (b) SEBS-*g*-PEG-*g*- NaAc samples

2. Thickness of PEG Layer

The model surfaces with the patterned polymer chains made it possible for AFM to measure the layer thickness accurately. [1]

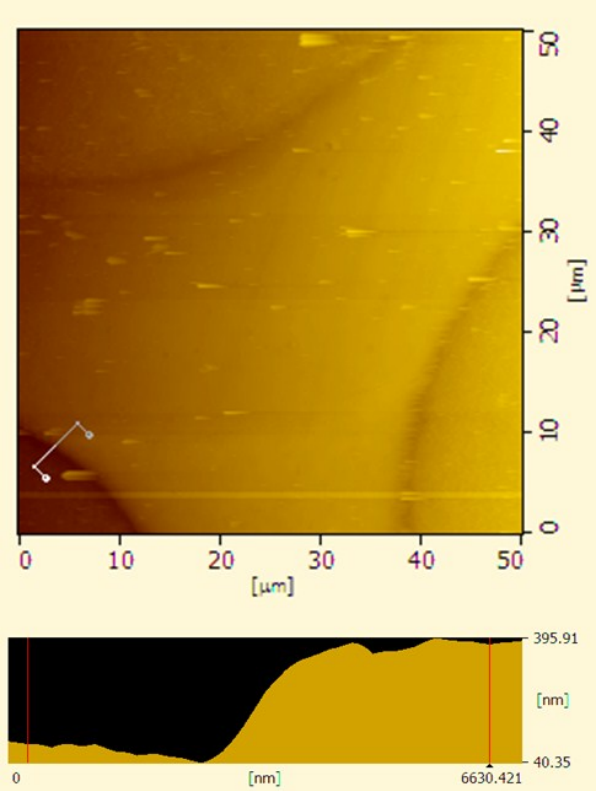

Figure S2. AFM image of thickness of PEG layer

Copper grids were served as photomasks and tightly covered on the surface of SEBS substrates. The coated SEBS samples were immersed in the ethanol solution of BP (1.5 wt%) for 30 min and dried in vacuum under dark cleanroom environment for 1 h at 25 °C. Then, the BP-preadsorbed samples were put on a slide glass and coated with the PEGMA solution (10 wt%), followed by covering with another quartz plate (0.8 mm thick). The sandwiched system was then exposed to UV illumination (high-pressure mercury lamp, 400 W, main wavelength 380 nm) at a distance of 15 cm for 6 min at ambient temperature (22 °C). After UV exposure, all films were washed drastically with deionized water and ethanol for 24 h to remove unreacted initiators and monomers. Finally, all films were dried in vacuum oven for at least 24 h at 37 °C. The dried samples were used for AFM measurements

(**Figure S2**). Figure S2 presented the AFM images and their corresponding line profiles of the patterned SEBS-*g*-PEG surfaces. The AFM image showed the thickness of PEG brushes was about 284 nm.

3. XPS Results

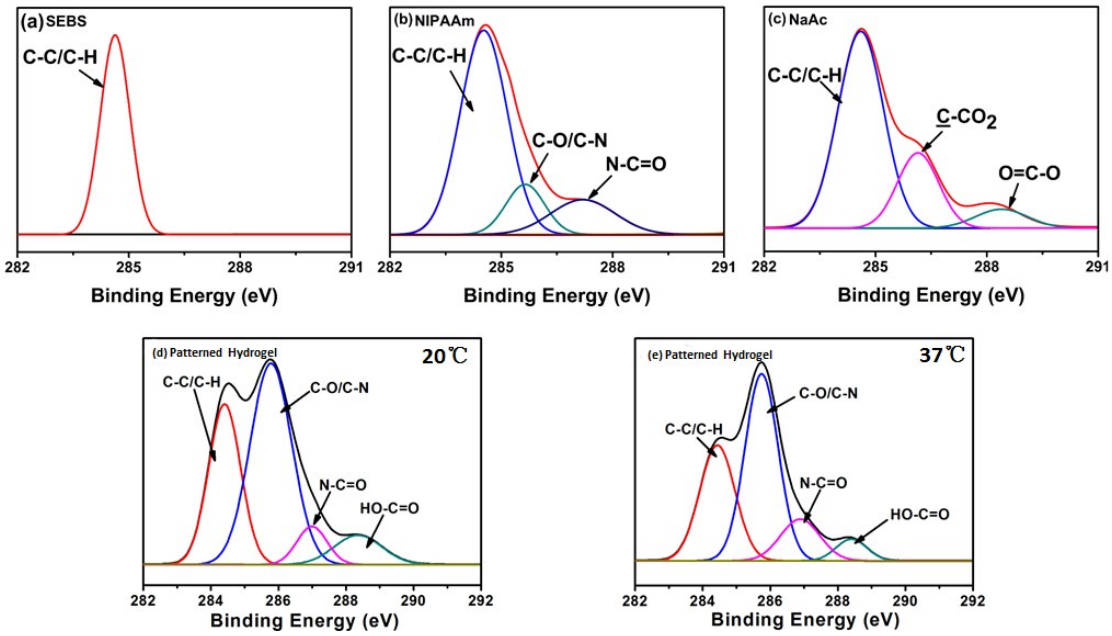

Figure S3. C1s core-level spectra of (a) SEBS, (b) NIPAAm, (c) NaAc, (d) Patterned hydrogel (20 °C), (e) Patterned hydrogel (37 °C).

The high-resolution spectra corresponding to C1s were shown in **Figure S3** to distinguish different types of functional groups on the surfaces. In comparison with the single peak in C1s spectrum of the virgin SEBS sample (**Figure S3a**), the C1s spectrum of NIPAAm-modified film showed three peaks at 284.6, 286.5 and 287.6 eV, which are attributed to the C-H, C-O(C-N), and N-C=O species, respectively. [2] These results provided direct evidence of successful grafting of NIPAAm brushes onto SEBS surface via SIPP (**Figure S3b**). Compared with SEBS film, the intensity of peaks at 285.7 eV (C-CO2) and 288.5 eV (O–C=O) indicated that NaAc was grafted successfully (**Figure S3c**). The four-peak components with binding energies at about 284.6, 285.5, 287.6 and 288.5 eV are attributed to the C-C/C-H, C-O/C-N, N-C=O and HOC=O species, respectively. The results confirmed successful preparing hydrogel onto SEBS surface (**Figure S3d and 3e**). In addition, Figure S3d and 3e indicated different peak areas of hydrogel at 20°C and 37°C, respectively. The

concentration of N-C=O and HOC=O at 20°C and 37°C was listed in **Table S1**. Table S1 showed the concentration of N-C=O increased from 20 °C to 37 °C, confirming the phase-transition of PNIPAAm hydrogels. [3]

Table S1 Peak area of hydrogels from XPS results

Ratio to total C peak area	20 °C	37 °C
[N-C=O]/[C]	0.11	0.35
[HO-C=O]/[C]	0.13	0.12

4. Cell Adhesion on the Patterned Surfaces in Whole Blood

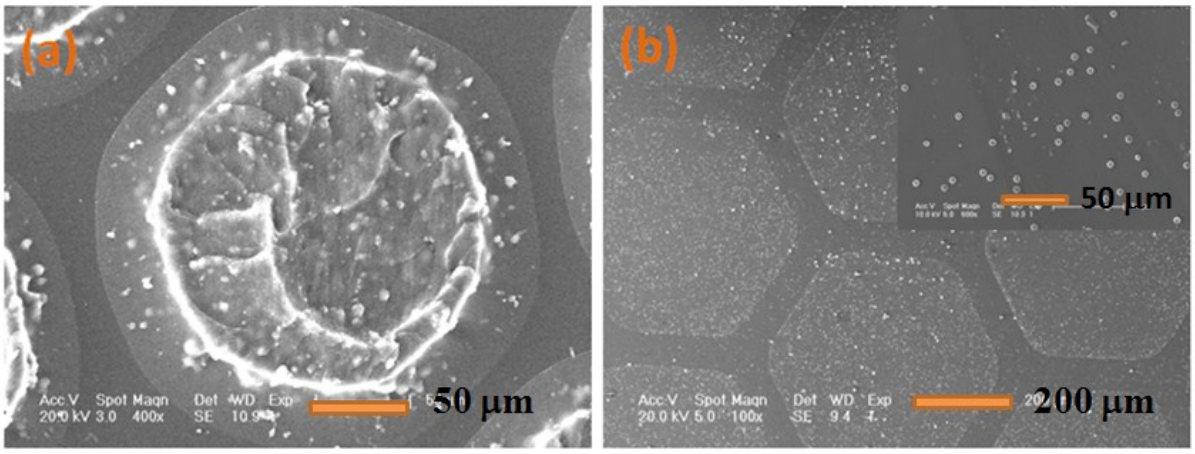

Figure S4. SEM images of captured blood cells on (a) the biointerfaces of patterned hydrogel and (b) patterned SEBS-*g*-PEG-*g*-NaAc (antibody immobilized) surface.

The cell adhesion on the biointerfaces of patterned hydrogels and patterned SEBS-*g*-PEG-*g*-NaAc (antibody immobilized) in the blood were performed. After incubation with whole blood for 60 min at 37 °C under static conditions, the non-adhered blood cells were removed by gently rinsing with PBS. Subsequently, captured blood cells were fixed using 2.5 vol% glutaraldehyde in PBS for 10 h at 4 °C, followed by frozen dry and observation with SEM. SEM images showed that some platelets and RBCs adhered on the surface of (antibody immobilized) SEBS-*g*-PEG-*g*-NaAc

(**Figure S4b**). In contrast, almost no blood cells were captured on the antibody-immobolized biointerfaces constructed by patterned hydrogels (**Figure S4a**), demonstrating that the cell-inspired biointerfaces resist blood cells adhesion.

5. Antigen Recognition in Whole Blood, Plasma and PBS Buffer Solution

The fresh blood from healthy white rabbits was diluted with PBS into 10% whole blood. Then, the 10% whole blood, blood plasma and PBS buffer solutions containing antigen (FITC-Rabbit IgG) concentrations of 2%, 3% and 5% were pre-configured, respectively. The patterned antibody-immobilized samples were gently washed with PBS solution, then incubated with pre-configured antigen solution at 20 °C for 12 h in the dark, respectively. Antigen recognition in PBS solutions was performed at 37°C according to the above procedure. After rinsing with PBS solution and drying in a nitrogen flow, the samples were then tested by fluorescence scanning (**Figure S5**). The fluorescence intensity at the same operation parameters were used to estimate the amount of recognized antigens. [4]

As shown in the Figure S5a-5c, fluorescence intensity increased with the antigen concentrations from 2%, 3% to 5% in whole blood, plasma and PBS buffer solutions, respectively. At the same antigen concentrations, the fluorescence intensities of recognized antigen at 20°C were stronger than the signal at 37°C (**Figure S5c** Vs **S5d**), indicating detection signal can be further manipulated by temperature control.

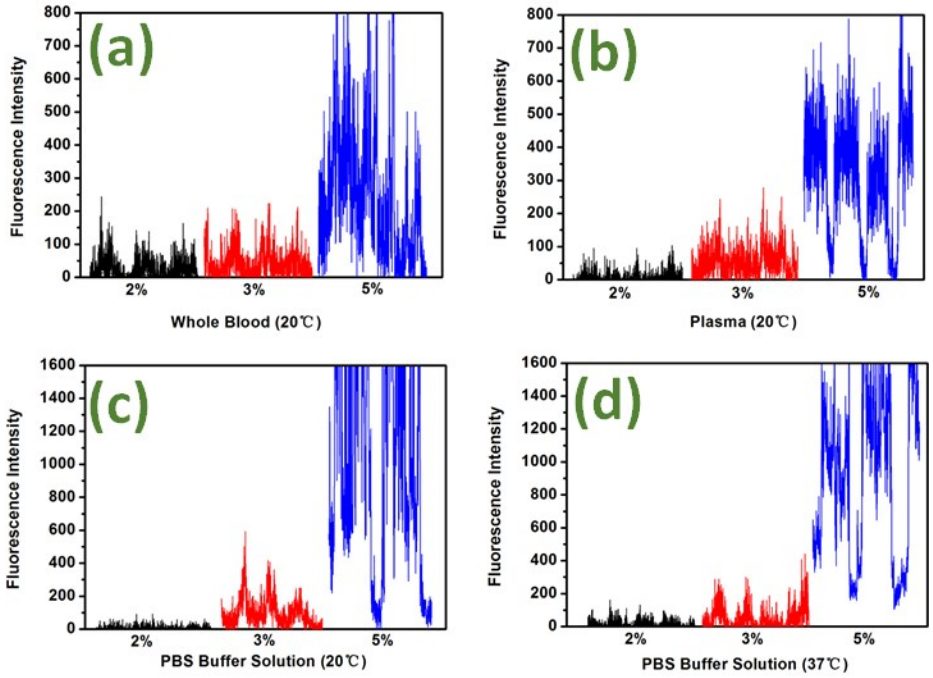

Figure S5. The fluorescence intensity for antigen recognition on the patterned antibody-immobilized samples in different solutions at 20 °C (a, b, c) and 37 °C (d), respectively.

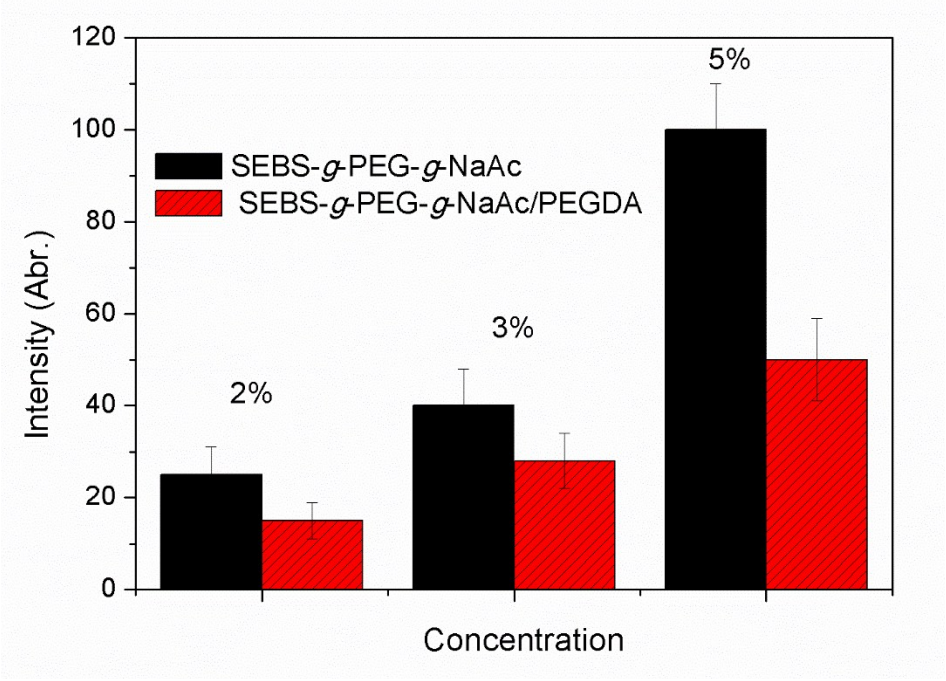

Figure S6. The average fluorescence intensity for antigen recognition on samples of SEBS-*g*-PEG-*g*-NaAc and SEBS-*g*-PEG-*g*-NaAc/PEGDA in whole blood at 20 °C.

The antigen recognition on samples of SEBS-*g*-PEG-*g*-NaAc and SEBS-*g*-PEG-*g*-

NaAc/PEGDA were performed in whole blood at 20 °C. As shown in the Figure S6, fluorescence intensity of SEBS-*g*-PEG-*g*-NaAc was much stronger than that of SEBS-*g*-PEG-*g*-NaAc, indicating SEBS-*g*-PEG-*g*-NaAc was more sensitive than SEBS-*g*-PEG-*g*-NaAc/PEGDA for immunoassay in the whole blood .

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