Supplementary material (ESI)

# **Electronic Supplementary Information**

# Graphene oxide based heparin-mimicking and hemocompatible polymeric hydrogels for versatile biomedical applications

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## 1. Structure of PEGMA and HEMA

The chemical structures of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and 2-hydroxyethyl methacrylate (HEMA) are shown in Fig. S1. PEGMA and HEMA have the similar structure except that PEGMA owns the repeating unit of ethoxy group, as seen in the figure.



Fig. S1. The chemical structures of PEGMA and HEMA.

#### 2. Preparation and characterization of graphene oxide (GO)

Graphene oxide (GO) was prepared from natural graphite flakes by a modified Hummers method.<sup>1</sup> Briefly, 5 g graphite and 3.75 g NaNO<sub>3</sub> were placed in a flask. Then, 150 mL H<sub>2</sub>SO<sub>4</sub> was added with stirring in an ice-water bath, and then 20 g KMnO<sub>4</sub> was slowly added for over 1 h. The mixture was stirred in an ice water bath for 2 h, followed by a vigorously stirring for 3 days at room temperature. Then, the mixture was diluted with DI water (500 mL) slowly, and the excessive KMnO<sub>4</sub> was decomposed by H<sub>2</sub>O<sub>2</sub> (30 wt.%, 15 mL). The insoluble precipitations were removed by centrifugation. The resulted GO solution was filtered and washed with HCl (10 wt.%, 1 L) and DI water for several times to remove the metal ions. The pristine brown GO solution was dialyzed with DI water for 1 week before use to remove any residual salts and acids.

The prepared GO was further characterized with several methods. Morphological observation was carried out with a transmission electron microscope (TEM) (JEM-1200EX, JEOL, Japan). Two to three drops of the solution (1 mg/ml) were spread on a 3 mm copper grid and dried at ambient temperature to prepare the TEM sample. A Multimode Nanoscope V scanning probe microscopy (SPM) system (Bruker, USA) was used to obtain atomic force microscopy (AFM) images. The samples were prior prepared by dropping and drying on silicon wafers for the AFM analysis. FTIR spectrum was acquired on a FTIR spectrometer (Nicolet 560, USA) between 500 and

4000 cm<sup>-1</sup>, using the KBr disk method. A Q500 Thermogravimetric analyzer (TA instruments, USA) was used to get the thermogravimetric analysis (TGA) curves of the hydrogels under a dry nitrogen atmosphere, the temperature was ranged from 50 °C to 700 °C at a heating rate of 10 °C/min.



**Fig. S2.** (A) TEM images and corresponding SAED patterns of GO. (B) Typical AFM images and cross-section analyses of GO. (C) Chemical structure of GO. (D) FTIR spectrum for the prepared GO. (E) The TGA image for the prepared GO.

# 3. Hydrogel degradation

For the investigation of in vitro degradation of hydrogel, the prepared swollen hydrogels were cut into small pieces with a size about 10 mm × 10 mm with a thickness of 3 mm. Firstly, each initial sample was weighted ( $w_i$ ) and placed into a well of a 24-well plate. Then 2 mL of PBS (pH 7.4) was added into the well of the 24well plate. The in vitro degradation experiment was conducted at 37 °C in a rocking shaker. At designed time intervals, the samples were weighted ( $w_i$ ) after removing the water on the surfaces of the hydrogel with filter paper. The PBS was replaced by fresh PBS once a week. The weight loss percentage W (%) was used to evaluate the degradation of the hydrogels according to Eq. (1).<sup>2</sup>

$$W(\%) = \frac{W_i - W_t}{W_i} \times 100 \tag{1}$$



**Fig. S3.** Degradation profiles of (A) PEGMA derived hydrogels and (B) HEMA derived hydrogels exposed to PBS (pH 7.4) at 37 °C in vitro.

As shown in Fig. S3, all the hydrogels show similar degradation behavior in 29 days. The hydrogels of PEGMA-SSNa and HEMA-SSNa showed improved antidegradation ability compared to the native hydrogels of PEGMA and HEMA. When GO was introduced, the anti-degradation ability of the GO based hydrogels was further improved.

## 4. Compressive test of hydrogel

For the compressive test, the obtained cylindrical hydrogels were tested in equilibrium swelling state. And the mechanical properties were performed on a dynamic mechanical analysis (DMA) Q800 (TA Instruments, USA) in a DMA controlled force mode with compression clamp. The conditions of compressive test were listed as follows: temperature 25 °C; a sample size of 8 mm in diameter and 14 mm length; crosshead speed of 3 N/min until crash.



**Fig. S4.** Typical compressive strain-stress curves of PEGMA, PEGMA-GO, PEGMA-SSNa, PEGMA-SSNa-GO hydrogels.



**Fig. S5.** Mechanical properties of the heparin-mimicking hydrogels and GO based hydrogels. (A) Compressive stress as a function of the strain. (B) Compressive strength of the hydrogels. (C) Compressive modulus calculated from the linear region of the graph in part A. (D) Compressive strain of the hydrogels.

#### 5. Drug loading amount

To confirm the multifunctional ability of the prepared hydrogels, gentamycin sulfate (GS) was chosen as the model drug to test the loading ability of the hydrogels. The experiments were carried out by adding the hydrogels into 5 mg/mL GS aqueous solution to allow the impregnation of the hydrogel with the model drug. After mildly stirring for 48 h at room temperature to equilibrium, the drug loading amount was measured.



Fig. S6. Drug loading amounts of the hydrogels for the model drug (gentamycin sulfate, GS).

# References

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