Supporting Information

Free-standing few-layered graphene oxide films: Selective, steady and lasting permeation of organic molecules with adjustable speeds

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1 Synthesis of AuNps

AuNps was prepared via following process: AuNps were prepared according to reported procedure. Briefly 50 mL water in a 100 mL round-bottom flask was heated to boil and 0.607 ml 20 mM $HAuCl_4$ solution was added. Then, rapid addition of 0.21 mL of sodium citrate (1% by weight) to the boiling solution resulted in a color change from pale yellow to brick-red. After stirring for further 10 min, the heating mantle was then removed. The resultant colloidal solution was characterized using Transmission Electron Microscopy (TEM), which indicated that the prepared gold particles presented a size of around 100 nm.

2. AFM morphological observation of GO sheets and GO-PAH bilayer on silicon sheets.

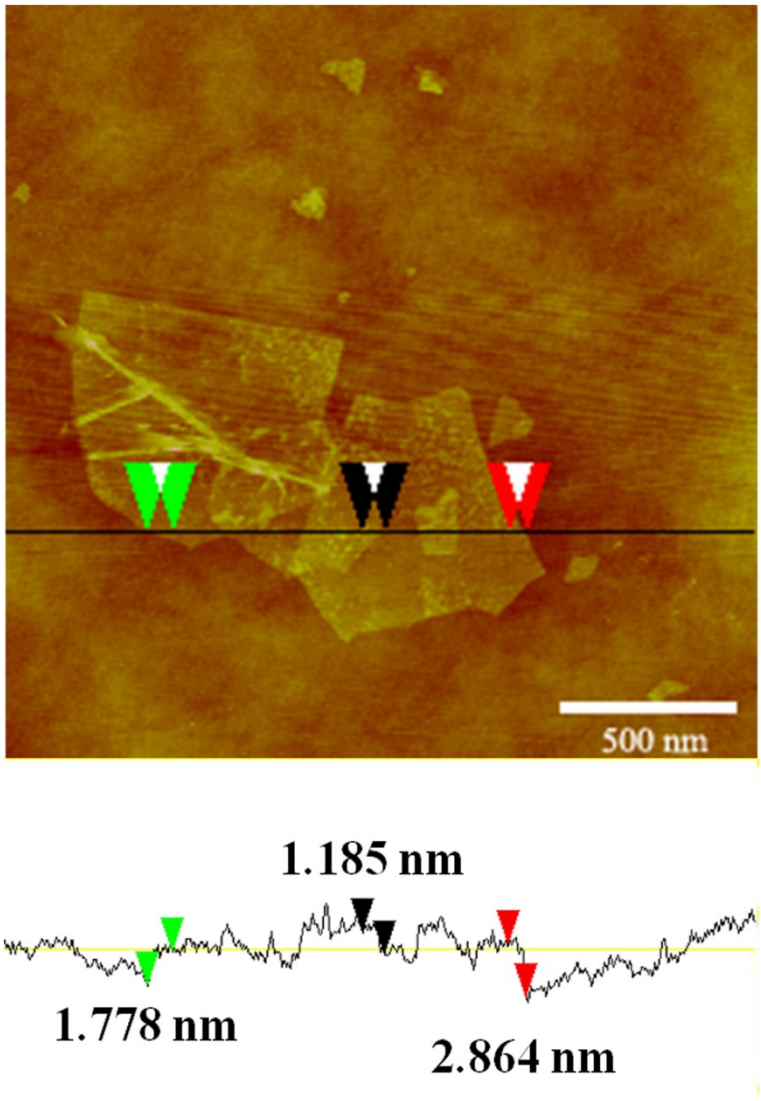

Fig. S1 (a,b) The AFM images of the lateral dimension and the thickness of the commercial GO.

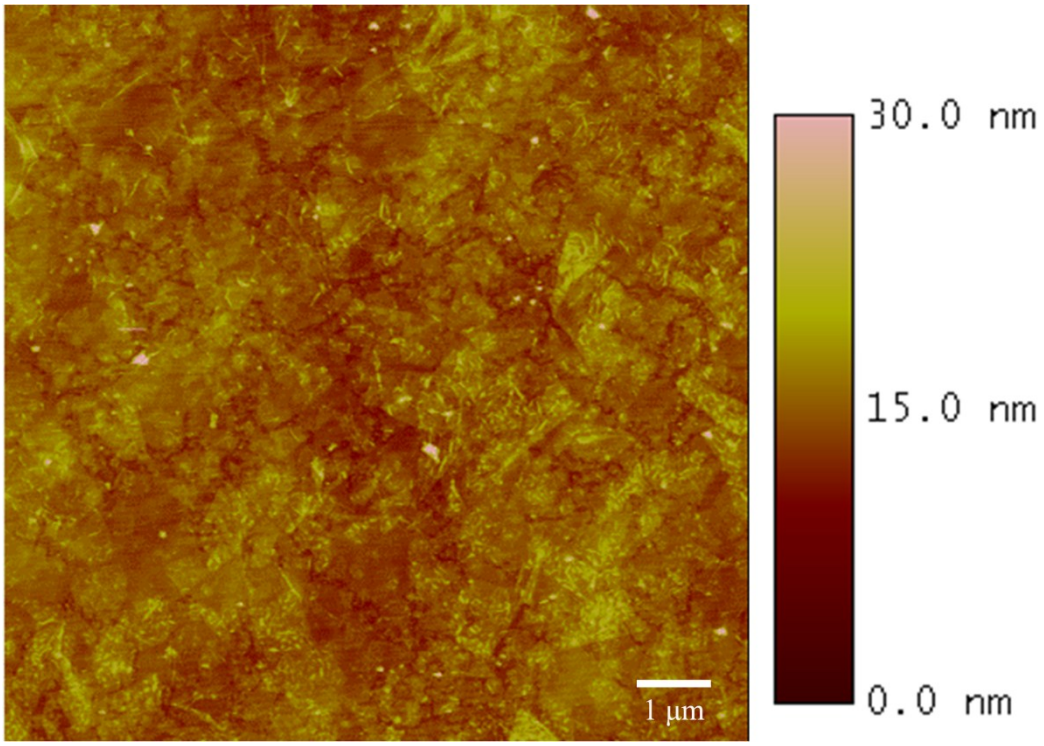

Fig .S2 The AFM images of the (PAH/GO)1 bilayer .

3. The calculation of DAS loading density

We calculated the maximum loading amount of DAS by standard curve method as described in detail in our previous work.[1] Briefly, $(PAH/GO)_{7.5}$ PAH multilayers were immersed into DAS solution (5 mg mL^{-1} , pH=3.8) for about 4 hours. Then the as-prepared substrate was immersed into 10 mL aqueous solution of NaOH (pH=10) for 30 min, in order to release the DAS thoroughly. The obtained solution was further characterized by UV-visible spectrum and the absorption value was about 0.15865 (shown in Fig. S2), which indicates the concentration of DAS in this solution was 2.1712×10^{-3} mg mL^{-1} by the standard curve method. Considering that the volume of the solution is 10 mL, we can calculate that the total amount of DAS in the $(PAH/PAA)_7$PAH multilayers to be 21.712 μg. The surface area of the substrate is 5.2

cm^2, the total number of PAH layer on both side of the substrate is 16. Therefore, the maximum loading amount of DAS was calculated to be about 0.2538 μg/cm^2/layer.

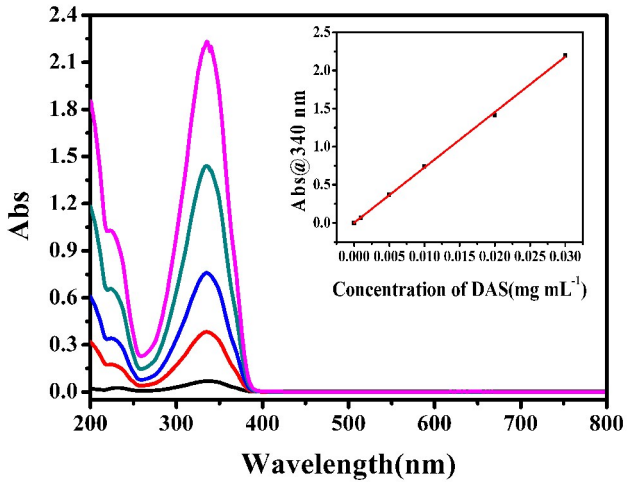

Fig S3. UV-visible spectra of DAS at different concentrations and inset: standard curve of DAS.

4. Chemical structure of molecules used in permeation experiments.

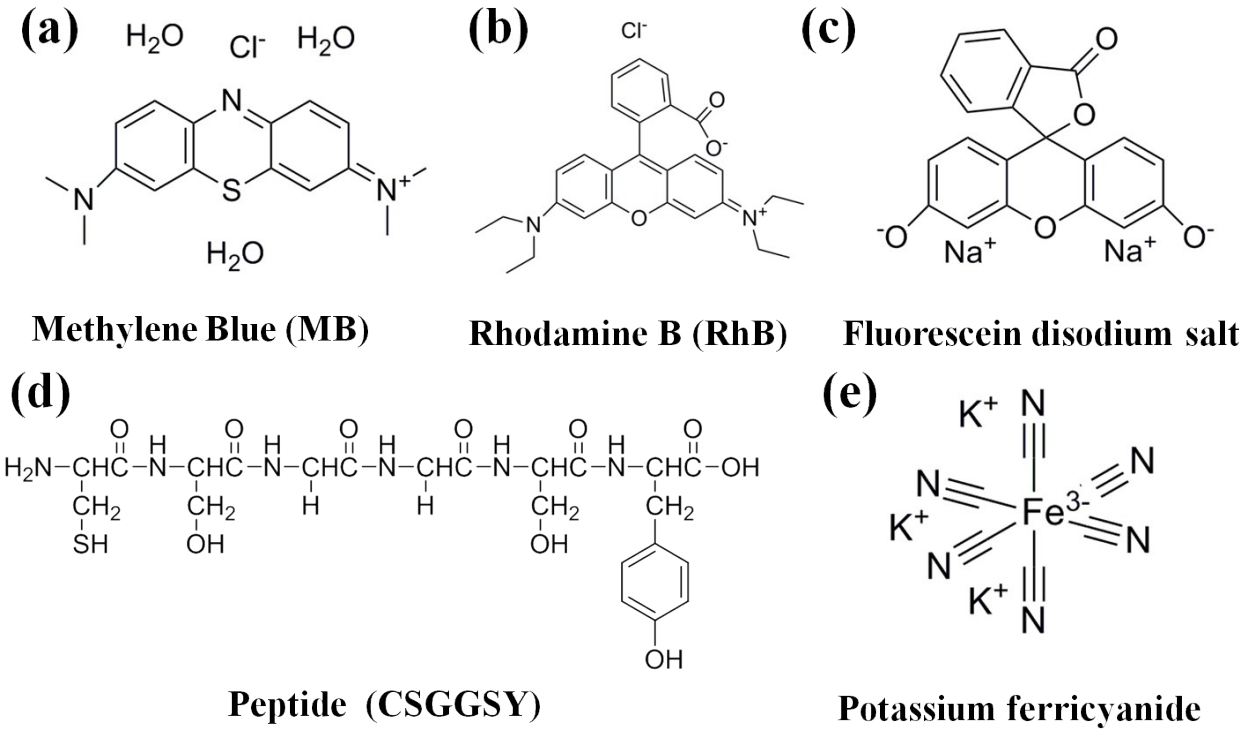

Fig S4. The chemical structures of the molecules used for in the permeation experiments.

5. Delayed release performance of five different films showed high fidelity.

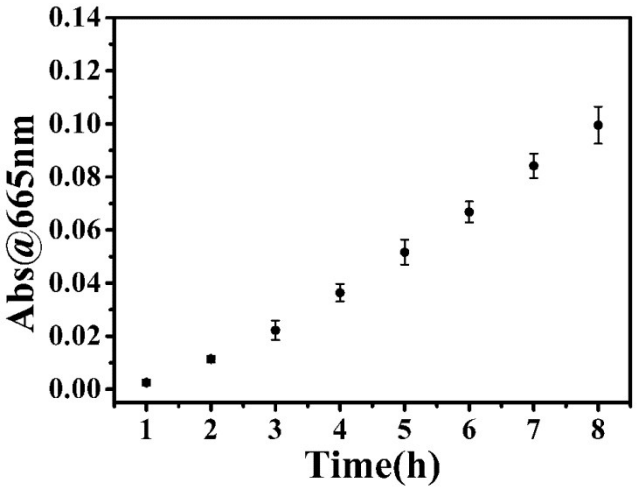

Fig S5. The delayed release of Methylene Blue trihydrate (MB) through $(PAH/GO)_{10}PAH$ multilayers. We conducted five sets of parallel test and calculated the standard deviation per hour.

6. UV-vis of the lasting penetration of methylene blue(MB) for 9 days using the $(PAH/GO)_{10}$ film.

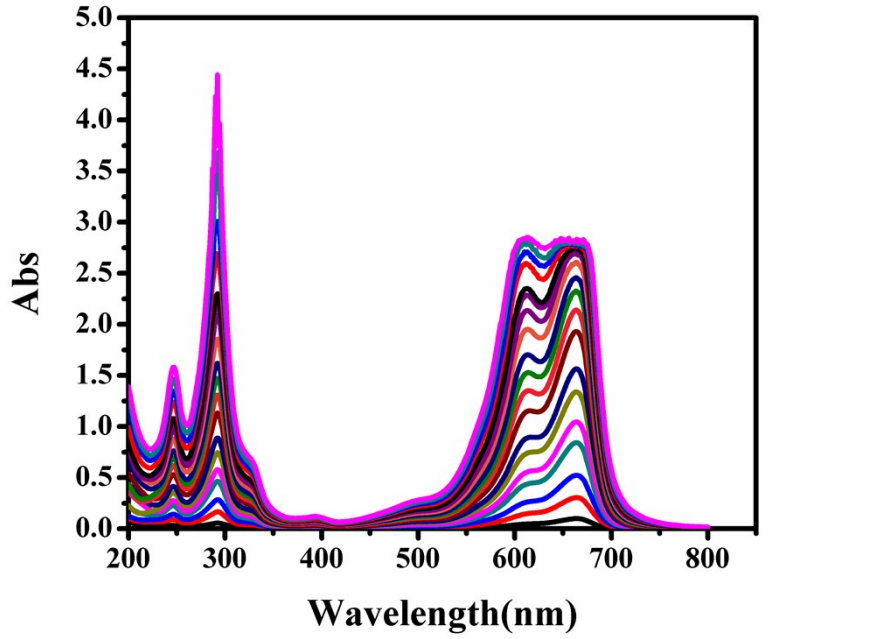

Fig S6. UV-vis spectra of the lasting penetration of methylene blue(MB) using $(PAH/GO)_{10}$ film.

7. TEM images of prepared AuNPs.

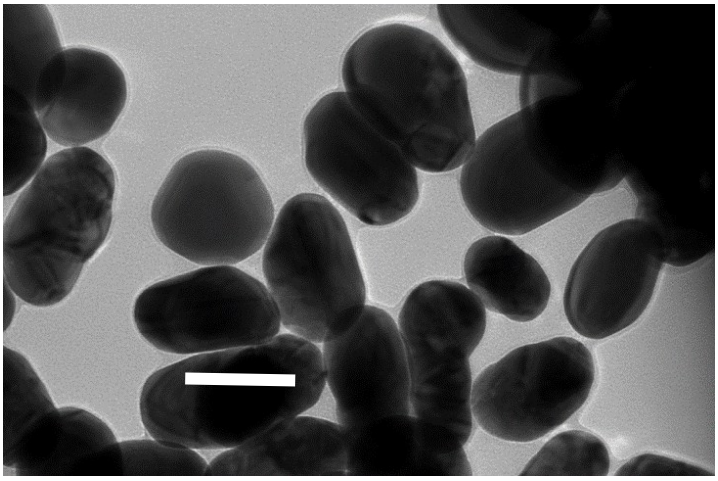

Fig S7. TEM images of AuNPs. The scale bar denotes 100 nm.

8. Electrochemical studies of the GO multilayers.

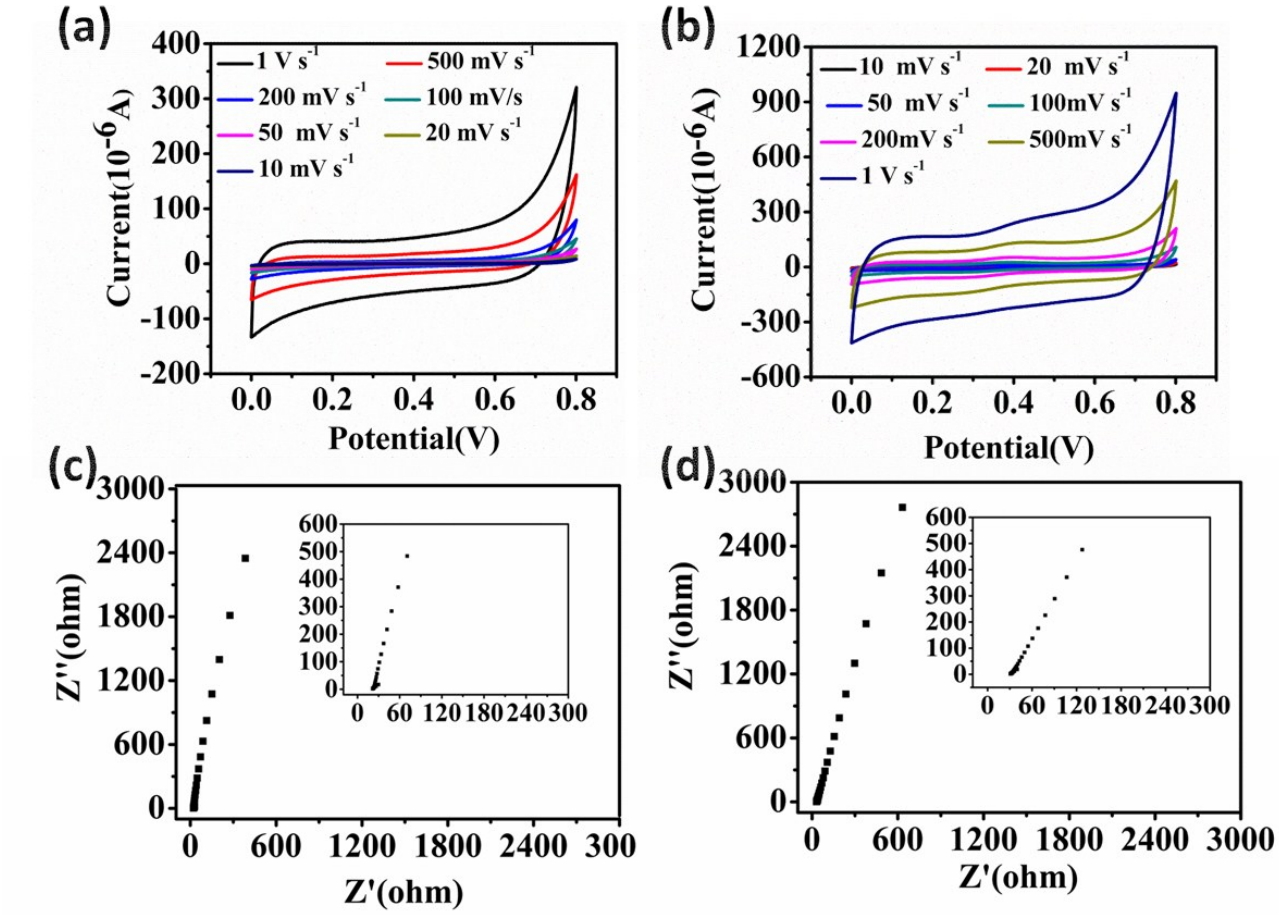

Fig S8. CV curves of the multilayered films with 10.5 (a) and 15.5 (b) bilayers under different scanning rates. Nyquist plot for the multilayer film with 10.5 (c) and 15.5 (d) bilayers in the frequency range from 1 MHz to 0.1 Hz at an ac amplitude of 10 mV.

9. Determination of the Amount of Graphene Oxide

The amount of graphene oxide in the multilayered films was determined by using UV-vis spectroscopy based on Lambert-Beer Law. We assumed that the extinction coefficients of GO are the same as in aqueouse dispersion. By measuring the absorbance at 230 nm for a series of the GO dispersions, the working curve was obtained and given in the following figure.

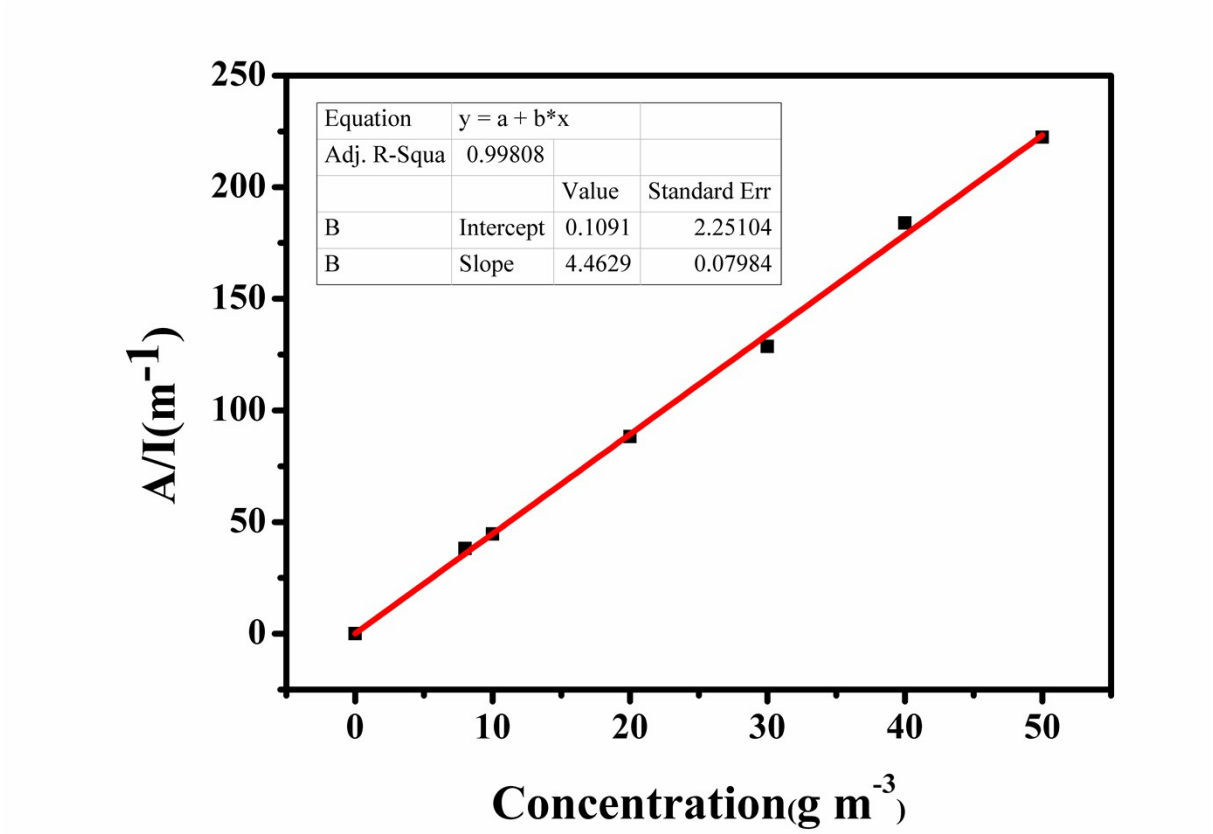

Fig S9. The relationship between the reduced absorbance and concentration of GO in the figure, A and I refers to the UV-vis absorbance at 230 nm and thickness of the sample cell, respectively. The abscissa corresponds to the concentration of GO in the dispersion. According to Lambert-Beer Law, the graphene oxide assembled was calculated by the equation,

$$m = c \cdot S \cdot b = \frac{AS}{4.4629} = 22.56$$

where S is the size of the film, b is film thickness and A is the absorbance of a piece of the 7.5-bilayere film at 230 nm.[2]

Refs:

1. X. Zhang, C. Jiang, M. Cheng, Y. Zhou, X. Zhu, J. Nie, Y. Zhang, Q. An and F. Shi, *Langmuir*, 2012, **28**, 7096-7100.
2. Z. Xiong, T. Gu and X. Wang, *Langmuir*, 2014, **30**, 522-532.