Supporting information

Functional reduced graphene oxide–based membranes with selective ions transport channels for zwitterionic separation based on pH gradient

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Experimental section

Reagents

Sulfuric acid (98.0%), potassium permanganate (99.5%), hydrochloric acid (36%), nitric acid (68%), sodium dihydrogen phosphate (99.0%), disodium hydrogen phosphate (99.0%), Potassium peroxydisulfate (99.5%), hydroquinol (98.0%) and phosphorus oxide (99.0%) were purchased from Chengdu Kelong Chemical Reagent Company). Hydrogen peroxide (30%) was purchased from ChongQing Maoye Chemical Reagent Co., Ltd. Fluorescein isothiocyanate (95.0%) was purchased from Sigma–Aldrich Co. LLC), Eosin Y was purchased from Aladdin Industrial Corporation.

Preparation of graphene oxide (GO)

Firstly, flake graphite powders were subjected to pre–oxidize. Graphite powders (4.0 g) were dispersed in H_2SO_4 (98%, 16 mL) then $K_2S_2O_8$ (3.3642 g) and P_2O_5 (3.3608 g) powders were added into the mixture consecutively. The mixture was allowed to react at 80°C for 4.5 h. The products were diluted and washed with amount of deionized water by filtration and obtained after overnight drying in the oven at 80°C. Secondly, the pre–oxidized products were re–oxidized by concentrated H_2SO_4 and $KMnO_4$.

Namely, the dried products were added into the beaker with H_2SO_4 (98%, 92 mL) while keeping the temperature at 0°C. Then $KMnO_4$ (24.0240 g) was slowly added into the mixture with magnetic stirring, overnight. The mixture was kept at 35°C for 2 h. Then, deionized water (200 mL) was poured into the aforementioned beaker and went on reacting for 2 h at 35°C. After that, deionized water (600 mL) and H_2O_2 (30 mL) were added, consecutively, and the mixture turned into yellow. The final product was washed with 1 mol L^{-1} HCl to remove the remaining impurities. Finally, the products underwent dialysis for several weeks. The graphene oxide solution was exfoliated into GO sheets by ultrasonic in water for 2 h. The resulting brown dispersion (1 mg mL^{-1}) was centrifuged to remove unexfoliated GO and stored at room temperature for further use.

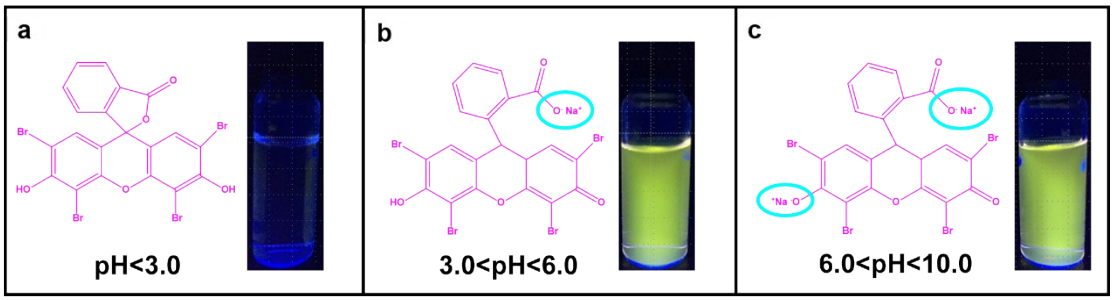


Fig. S1 The photograph of Eosin Y solution under UV light (a: pH<3.0; b: 3.0<pH<6.0; c: 6.0<pH<10.0) and the main formation of Eosin Y under different pH conditions.

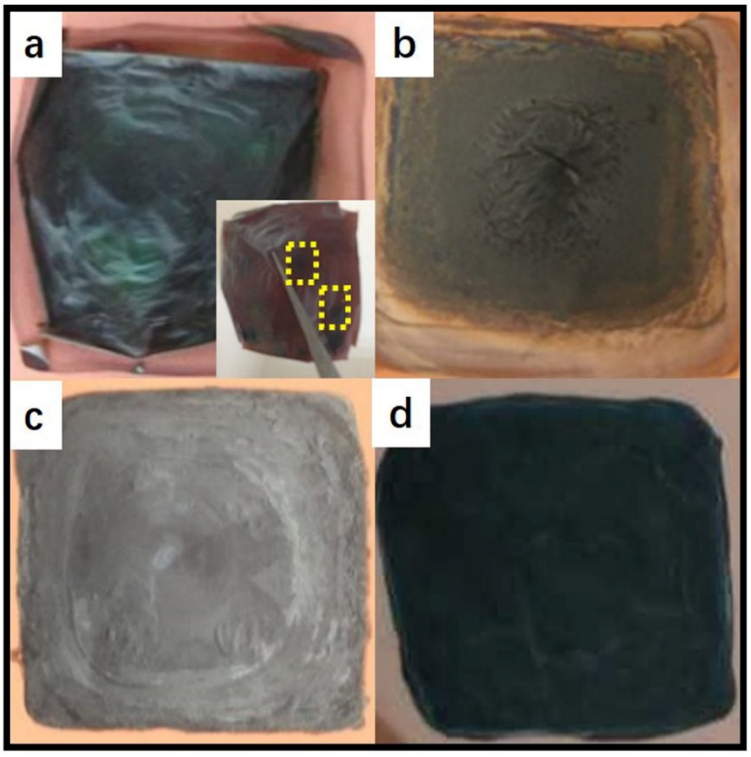


Fig. S2 Photographs of different membranes on Cu foil. (a) GO@EY, (b) GO, (c) GO@HQ, and (d) FGM.

The test of the molar fluxes:

The molar fluxes were tested as follows: a series of graphene–based membranes were prepared with different GO@HQ/EY ratio, ranging from 20:1 to 20:4, which were named as FFGM1, FFGM2 and FFGM3. Isoleucine (Ile) and Glutamic acid (Glu) were applied as the research objects to evaluate the molar fluxes of these membranes. These membranes were equipped on the custom–built glass reservoirs with a steel holder. 20 mL pH 3.22 buffer with 1 mmol L^{-1} of Ile and Glu was used as the feed solution, and 20 mL pH 6.02 buffer was applied as the receiver solution. The feed vessel was connected with anode, and the receiver vessel was connected with cathode. In the feed solution, Ile is positively charged and Glu is neutrally charged. Therefore, Ile will transport into receiver vessel, which connects with the cathode, and Glu will stay in the feed vessel in the electric field. Receiver samples were collected at a certain time interval (2 h), and capillary electrophoresis was used to accurate sample concentration.

The molar fluxes (J) and selectivity (S) of FFGM1, FFGM2 and FFGM3 were calculated by the following equations (1) and (2), respectively.[1, 2]

$$J = \frac{M}{A \times t} \quad (1)$$

$$S = \frac{C_{A,receive}}{C_{A,feed}} \times \frac{C_{B,feed}}{C_{B,receive}} \quad (2)$$

Where A is the effective area, t is the operation time, M is the molar mass of the target amino acid, $C_{receiver}$ and C_{feed} are the concentration in receiverr and feed vessels.

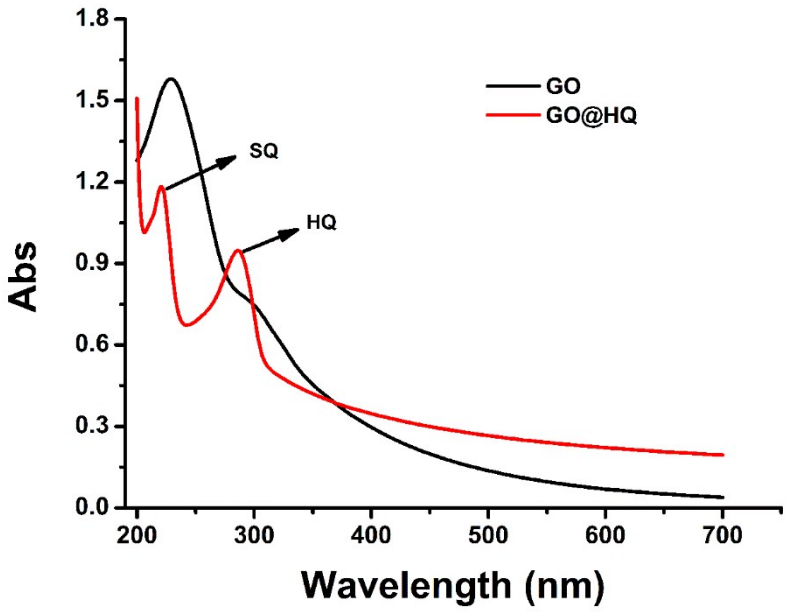
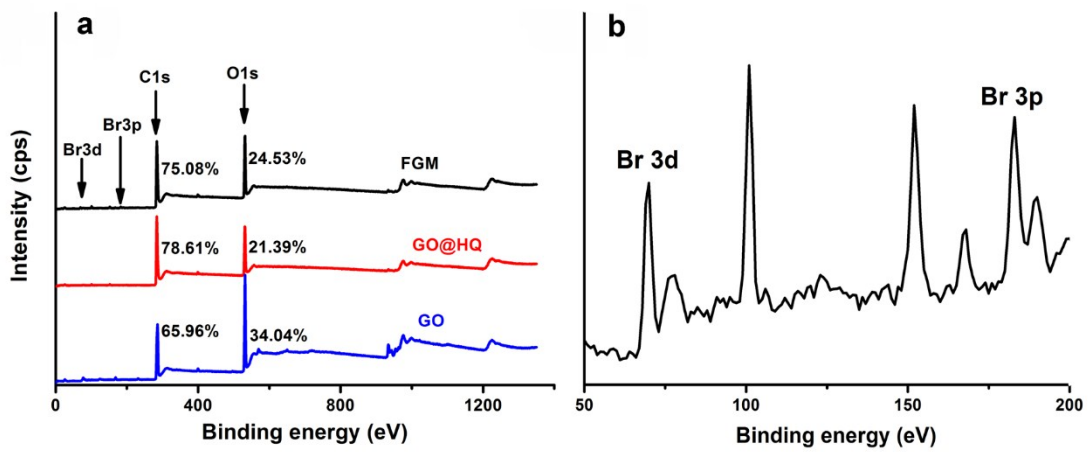


Fig. S3 UV–vis spectra of GO and GO@HQ.



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72 **Fig. S4** XPS spectra of the composite membranes. a is the survey spectra of GO,

73 GO@HQ and FFGM. b represents the Br3d and Br3p spectra.

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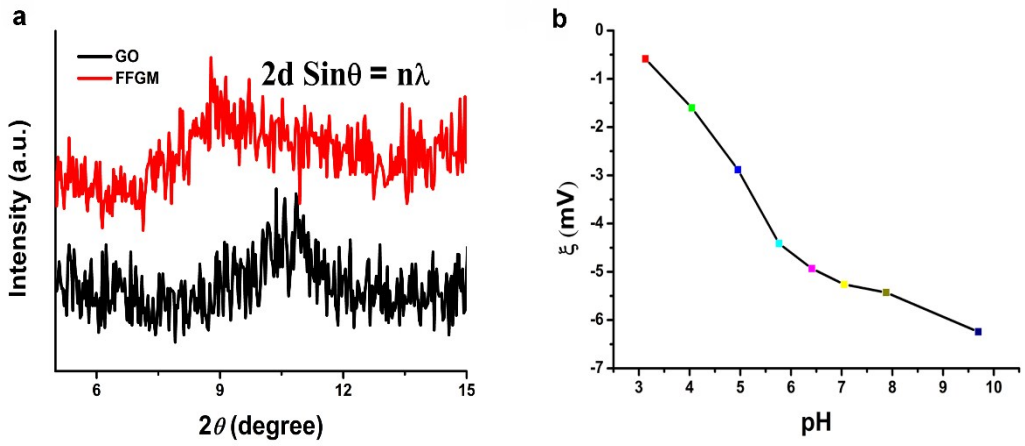

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76 **Fig. S5** XRD spectra of GO and FFGM (a) and the zeta potential of FFGM under

77 different pH (b).

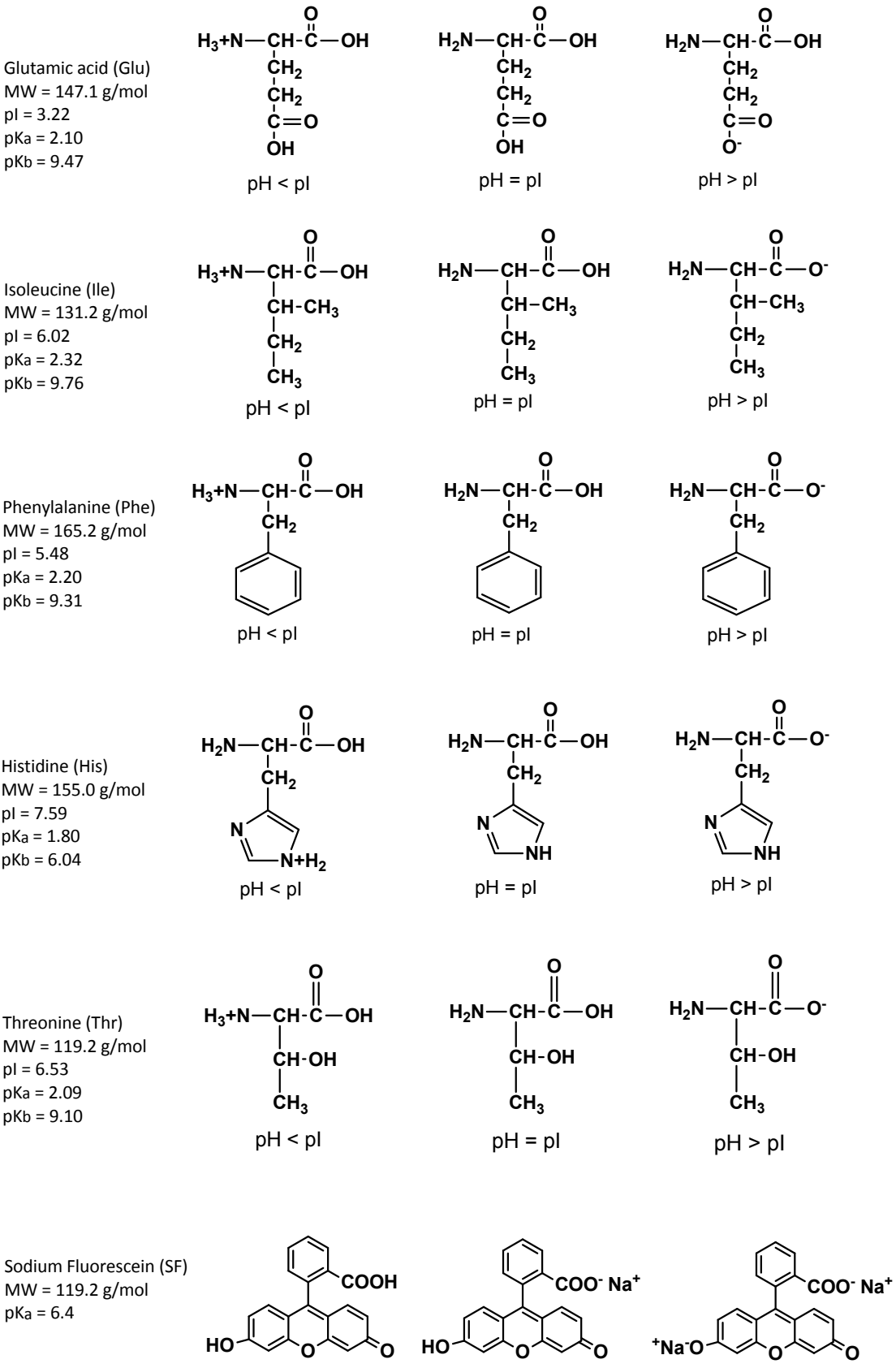
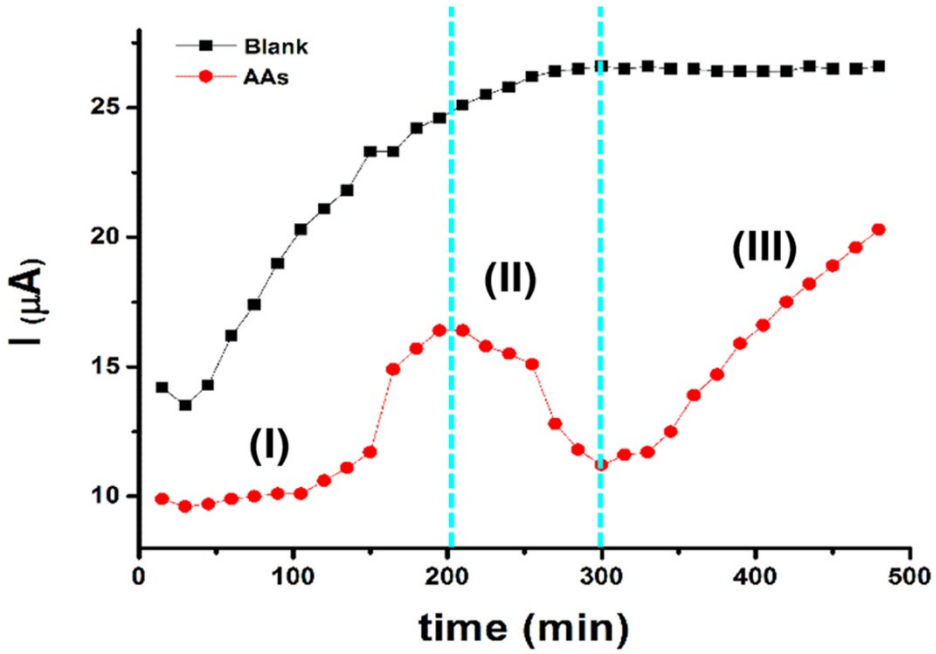


Fig. S6 Structures of amino acids (AAs) and sodium fluorescein (SF).



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83 **Fig. S7** Current–time curve of blank system and amino acids system with FFGM.

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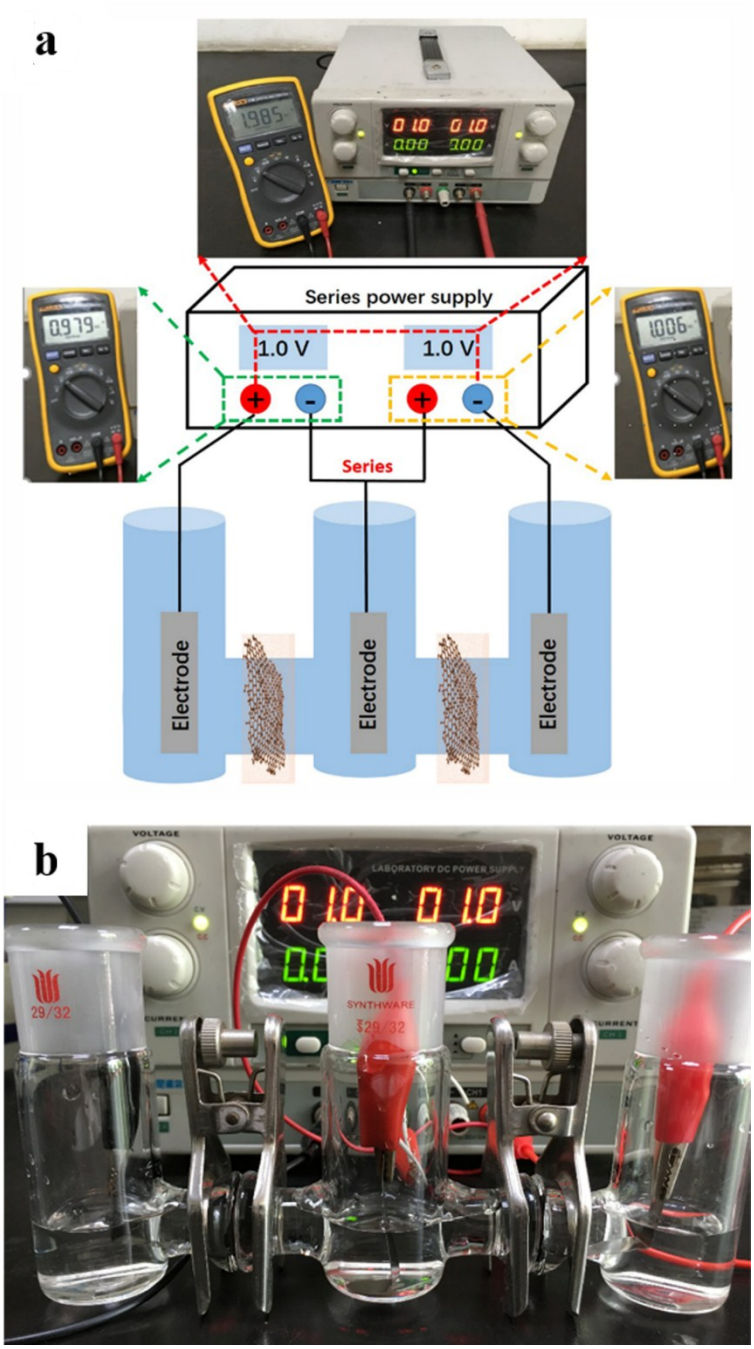

Fig. S8 The schematic diagram and physical map of the series power supply (SPS). (a) the schematic diagram of SPS, (b) the physical map of SPS.

As shown in Fig. S8a, a SPS with ± 1.0 V output voltage was divided into three parts, as shown in green, yellow and red dashed box of Fig. S8a. Fig. S8b is the physical map of the separation device and SPS.

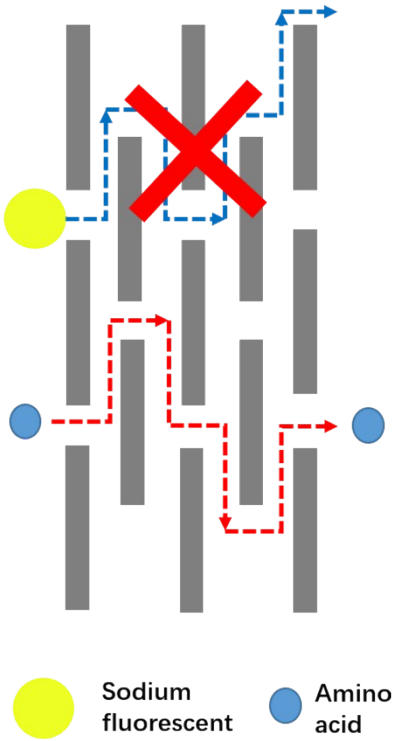

Fig. S9 Schematic view for possible permeation route: amino acid transports through the nanochannels of FFGM (red imaginary line) and sodium fluorescent is restricted due to its large radius to the nanochannels of FFGM.

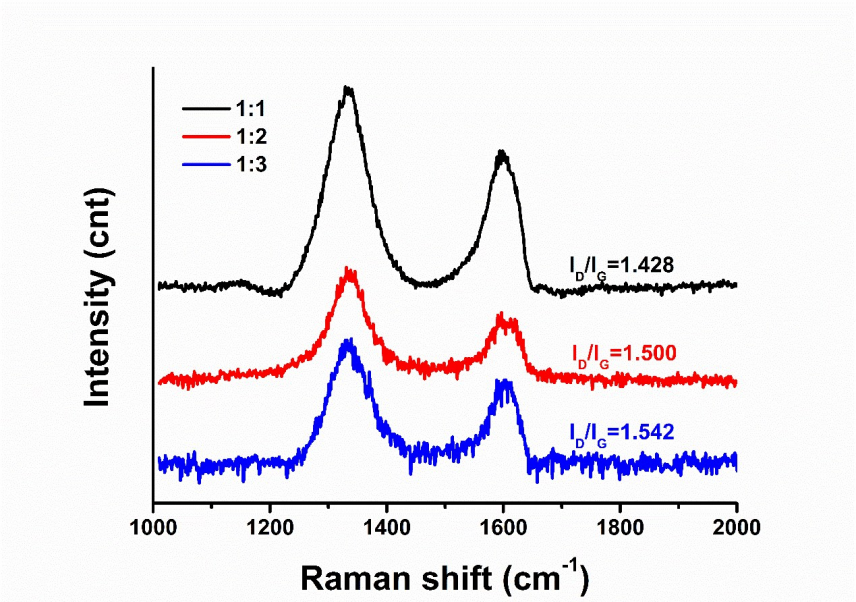

Fig. S10 Raman spectra of FFGM with different reduction degree.

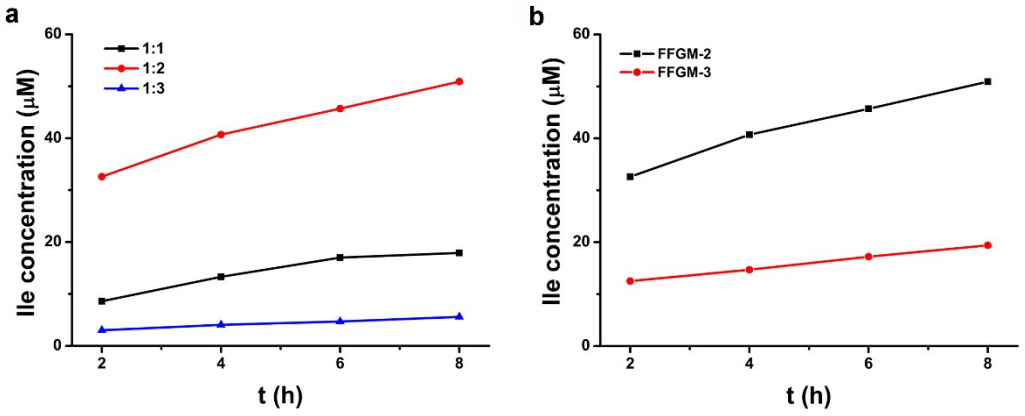

Fig. S11 Concentration of Ile in receiverr vessel via the FFGM with different reduction degree (a) and different thickness (b).

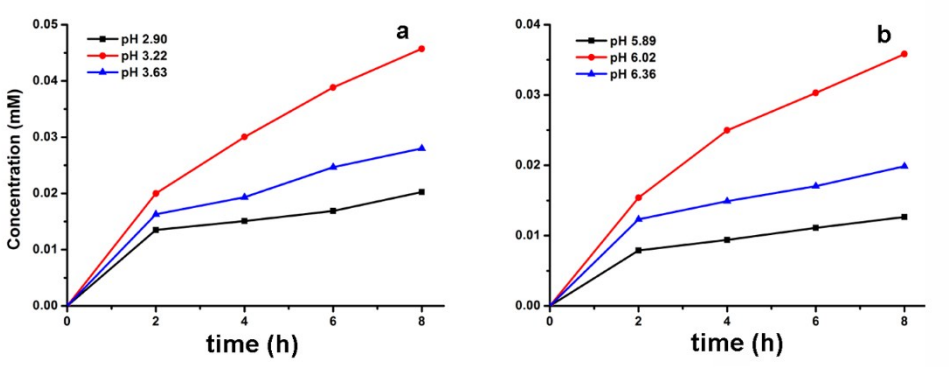

Fig. S12 Separation results of different conditions: a and b represent the concentration of Glu and Ile in different pH receiverr solution, respectively.

The effect of different pH buffer on the separation performance.

In ternary amino acids mixture system, the different pH buffers were used as receiverr solutions. Ile, Phe and Glu were took as the research objects. Firstly, pH 5.48 and 6.02 buffer were fixed as (a) and (b') vessels solution (as shown in Fig. 4B), respectively. pH 2.90, 3.22 and 3.63 buffers were used as (b) vessel solution. As shown in Fig. S12a, in pH 3.22 receiverr solution, the concentration of Glu is much higher than the other two pH. This is because of the different charge behavior of Glu in different pH solutions. When $pH=pI_{Glu,}$ Glu was electroneutral and stayed in the anode solution. When $pH \neq pI_{Glu}$, Glu took positive or negative charge and migrated to the opposite electrodes. Secondly, pH 5.48 and 3.22 buffers were fixed as (a) and (b)

vessels solution, and pH 5.89, 6.02 and 6.36 buffers were used as the (b') vessel solution. As shown in Fig. S12b, obviously, it has the same trend with Glu, when pH=pI_{Ile}, the concentration of Ile was the highest.

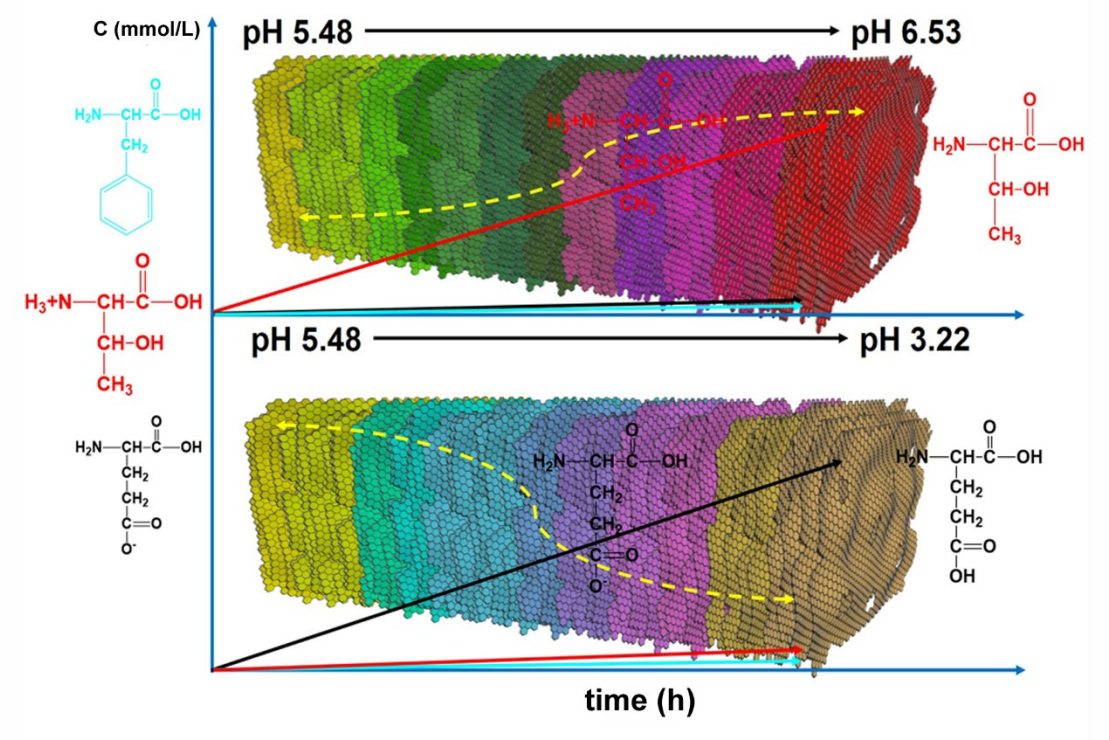

Fig. S13 Separation process of Glu, Thr and Phe through FFGM (the yellow dashed line represents the inner pH gradient in FFGM, the red, blue and black line represent the concentration tendency of Thr, Phe and Glu in receiverr vessel, respectively).

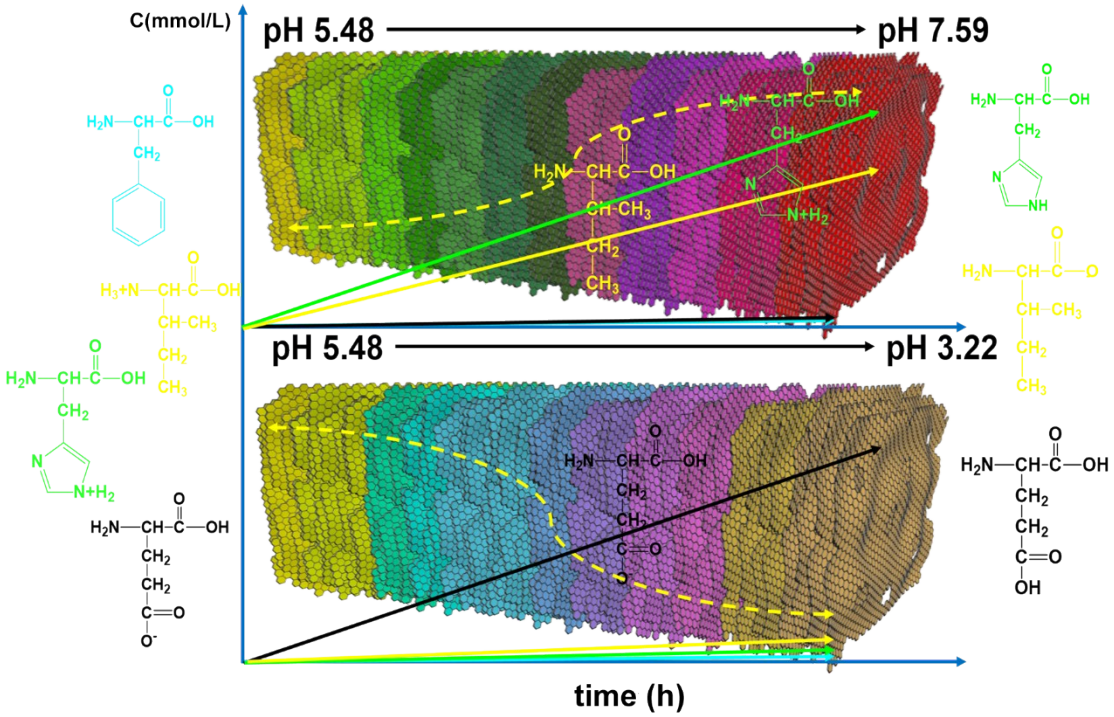

Fig. S14 Separation process of Glu, Ile, His and Phe through FFGM (the yellow dashed line represents the inner pH gradient in FFGM, the yellow, green, blue and black line represent the concentration tendency of Ile, His, Phe and Glu in receiverr vessel, respectively).

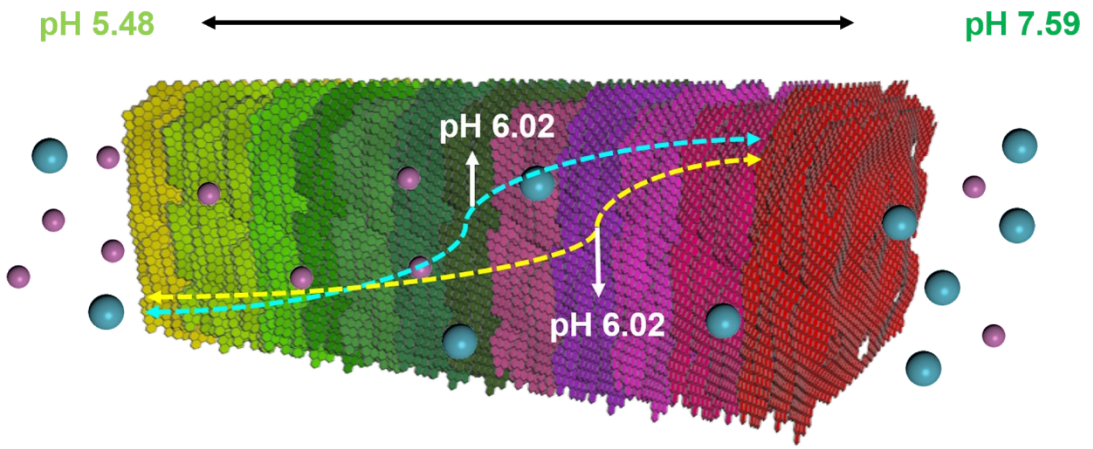

Fig. S15 The pH gradient migrates in the FFGM over time.

Reference

1 S. Zinadini, A. A. Zinatizadeh, M. Rahimi, V. Vatanpour, H. Zangeneh, *J. Membr. Sci.*, 2014, **453**, 292.

2 S. U. Hong, M. L. Bruening, *J. Membr. Sci.*, 2006, **280**, 1.