Supporting Material

Sensitive Electrochemical Sensor Based on Poly(L-glutamic acid)/Graphene Oxide Composite Material for Simultaneous Detection of Heavy Metal Ions

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Experimental Section

Reagents and Materials

(4-aminophenyl)-10,15,20-tris(phenyl)porphyrin(99.0%)   and γ-Benzyl-L-glutamate (99.0%) was purchased from Sigma-Aldrich. Trifluoroacetic acid (TFA, A.R. grade), N,N-dimethylformamide (DMF, A.R. grade),and other solvents were purchased from Shanghai Chemical Reagent and purified by conventional procedures if needed.γ-Benzyl-L-glutamate N-carboxyanhydride (BLG-NCA) was synthesized according to the literature[1].

Synthesis of Polypeptide

The synthetic route of poly (L-glutamic acid) (PGA) is as follows:
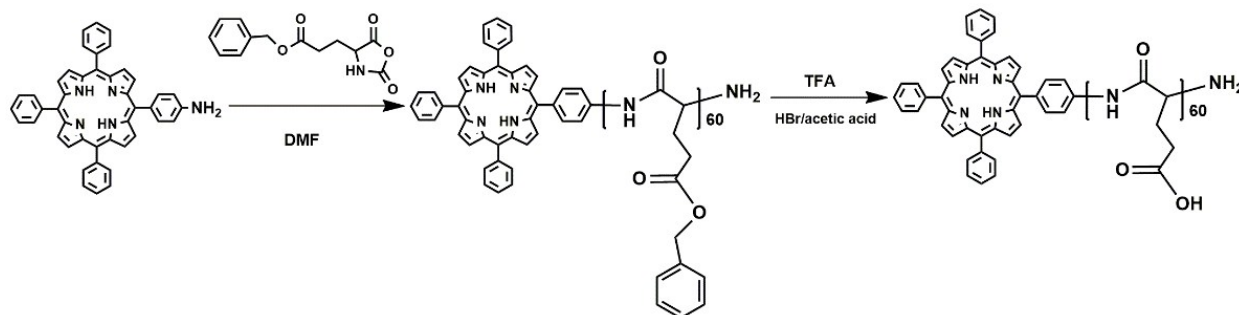
1. Synthesis of Poly (γ-benzyl-glutamate)

Poly (γ-benzyl-glutamate) (PBLG) with a terminal porphyrin group was synthesized by using 5-(4-aminophenyl)-10,15,20-tris(phenyl)porphyrin as an initiator and the

synthetic procedure was adapted from the literature[2].In a typical experiment, BLG-NCA(3.50g, 13.5mmol), 5-(4-aminophenyl)-10,15,20-tris(phenyl)porphyrin (0.17g, 0.27mmol)and anhydrous DMF (40 mL) were added into a dried round-bottom flask with a magnetic bar in a glove box, and then the solution was stirred under pure nitrogen at room temperature for 5 days. After polymerization, the solution was concentrated and then precipitated into an excess amount of methanol, filtered, and dried at room temperature in a vacuum oven overnight.

Yield: 87.2%, M_n (GPC) = 2.25×10^4, M_w/M_n =1.26. ^{1}H NMR(500 MHz, CDCl$_3$+15%TFA), δ(*ppm*): 8.80~8.00 (m, porphyrin), 7.88(br, N**H**CO), 7.31 (br, C$_6$**H**$_5$CH$_2$–), 5.07 (br, C$_6$H$_5$C**H**$_2$–), 4.61(br, –OCC**H**NH–), 2.50~2.42 (m, –OOCC**H**$_2$CH$_2$–), 2.13~1.91 (m, –OOCCH$_2$C**H**$_2$–). (See Fig.1S and Fig. 2S)

2. Synthesis of poly (L-glutamic acid)

Poly (L-glutamic acid) (PGA) was synthesized according to a published procedure[3].In a typical experiment, the above prepared PBLG (1.0g) was dissolved in TFA (1.2 mL) and 33 wt% HBr/acetic acid (4.5 mL), and then stirred for 2 h at room temperature. The polymer was precipitated by using excess anhydrous diethyl ether, filtered, purified three times from acetic acid to anhydrous diethyl ether, and dried at 40°Cunder vacuum for 48 hours.^{1}H NMR (500 MHz, DMSO-d$_6$), δ (*ppm*): 12.10 (br, –COO**H**), 7.95 (s,–CHN**H**CO–), 2.89-2.73 (m, –C**H**$_2$CH$_2$COOH), 2.09 (s, 1H, –C**H**NHCO–).
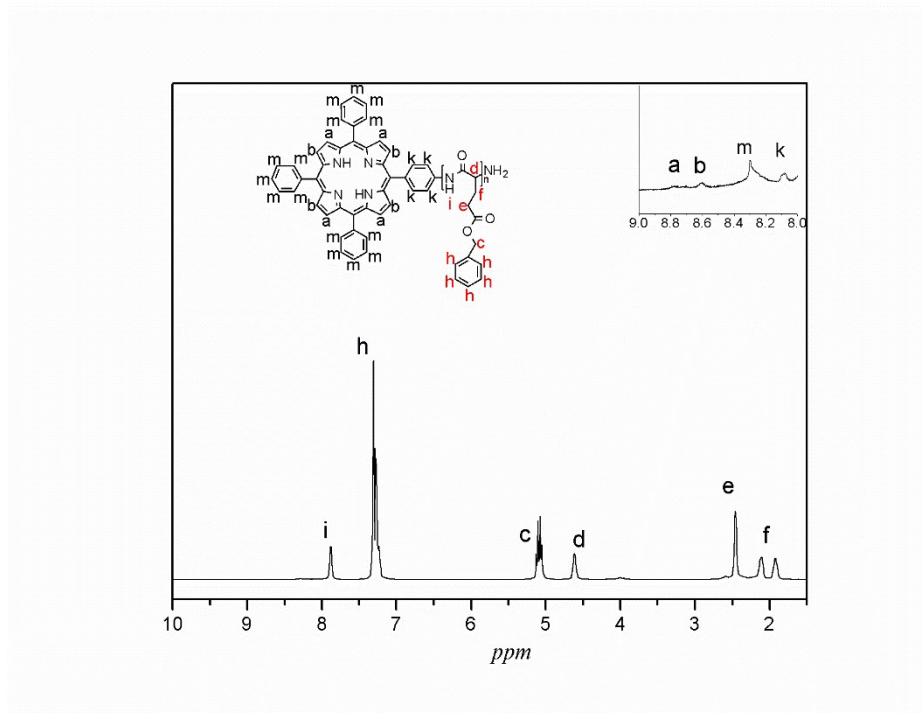
Fig.S1.^{1}H NMR spectrum of poly (γ-benzyl-glutamate).
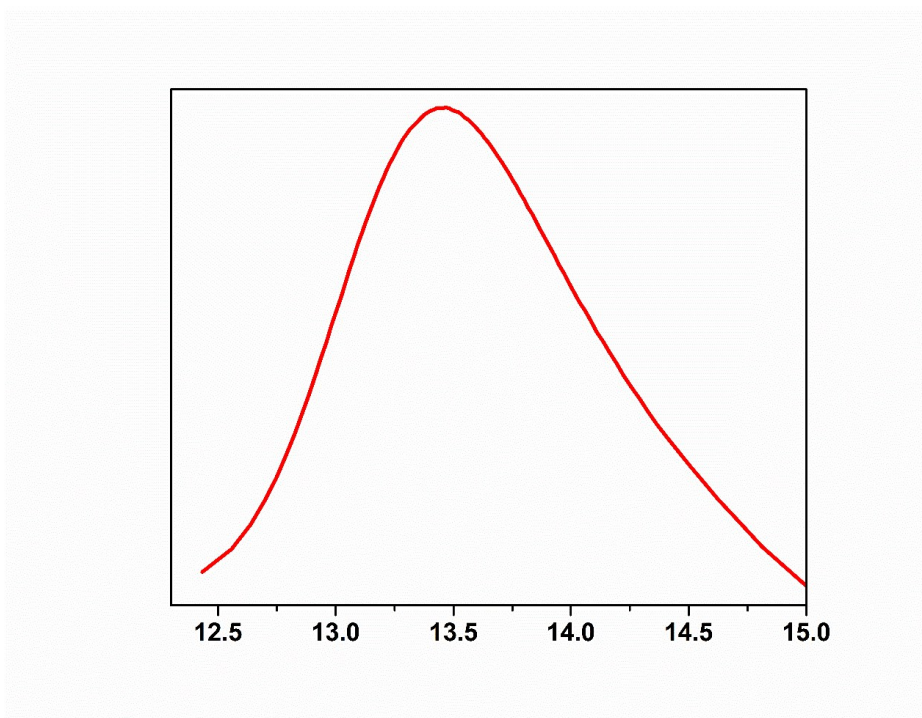

Fig.S2. GPC of poly (γ-benzyl-glutamate).

Reference

[1] E.R. Blout, R.H. Karlson, *J. Am. Chem. Soc.*, **1956**, *78*, 941-946.

[2] X. He, C. Gao, W. Sun, W. Huang, S. Lin, D. Yan, *J. Polym. Sci. Part A: Polym. Chem.,* **2013**,*51*, 1040-1050.

[3] J. Babin, D. Taton, M. Brinkmann, S. Lecommandoux, *Macromolecules*, **2008**,*41,*1384-1392.