Supporting Information

Proteolytic Disassembly of Peptide-mediated Graphene Oxide Assemblies for Turn-on Fluorescence Sensing of Proteases

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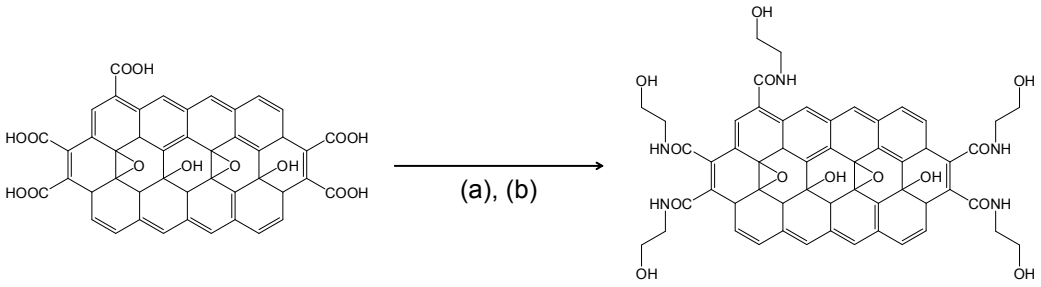
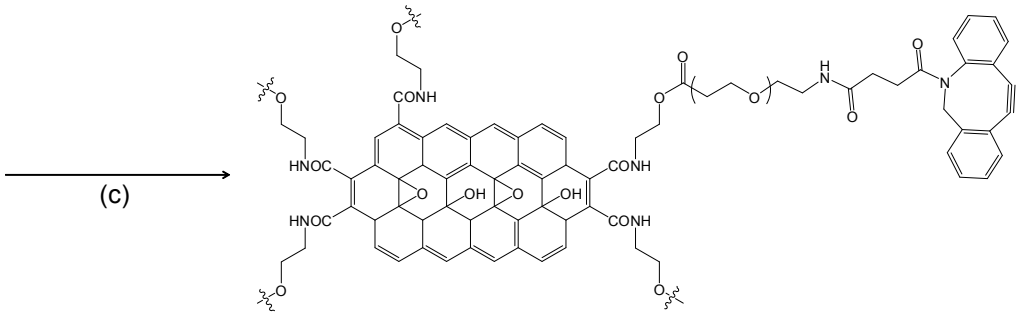
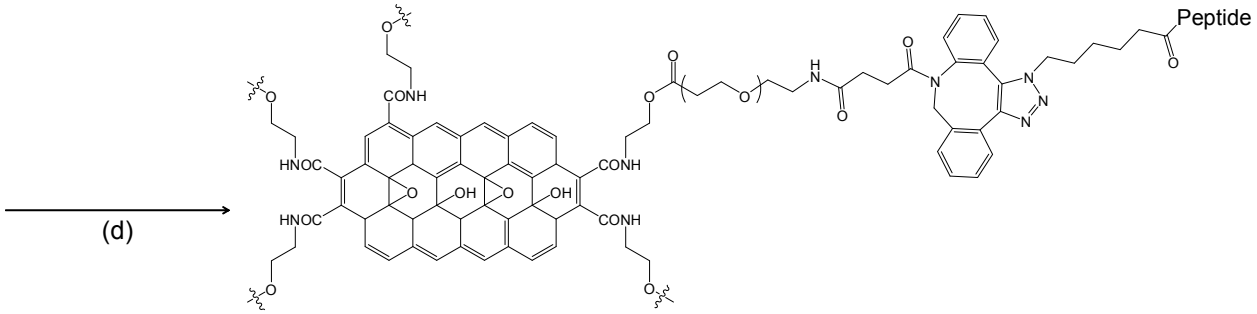


GO
(4 mmol carboxylic acid/g)

Hydroxyl terminated GO (GO-OH)

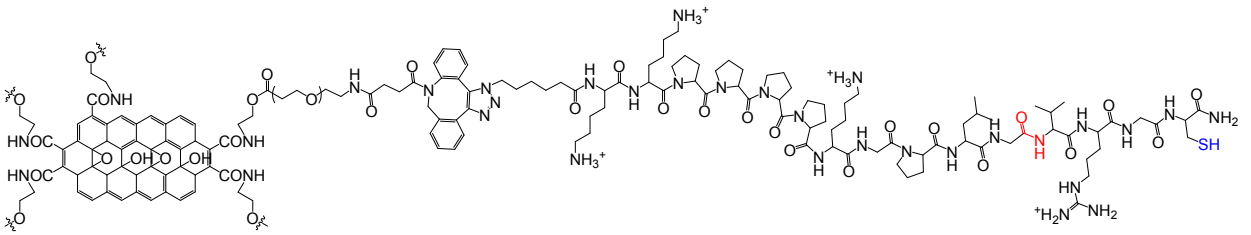


Dibenzocyclooctyne terminated GO (GO-DBCO)

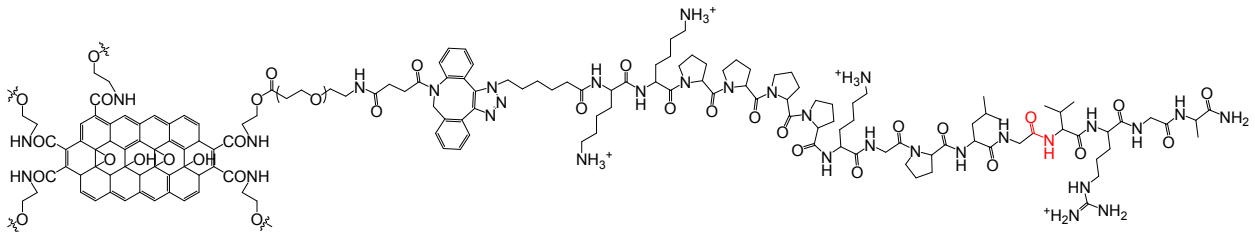


GO-Peptide

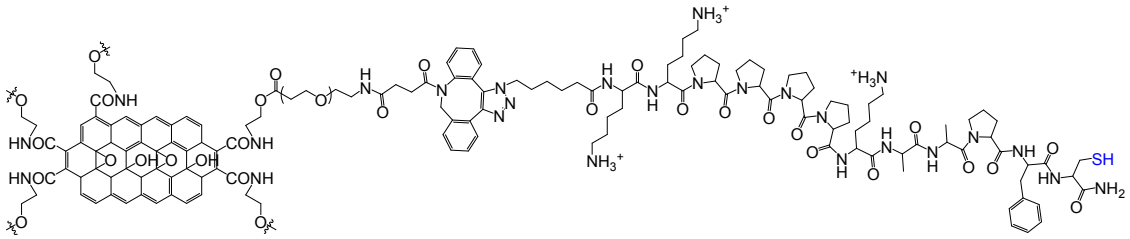
Scheme S1. Synthesis of GO–peptide hybrids (GO-P): (a) EDC (20 equiv) and NHS (20 equiv) in 50 mM PBS (pH 6.0) for 0.5 h; (b) ethanolamine (40 equiv) for 3 h; (c) preactivated DBCO-PEG-acid (2 equiv) and DMAP (0.1 equiv) in DMF for 6 h; (d) N_3-peptide (1 equiv) in PBS (50 mM, pH 7.0) for 2 h.



a) GO-P1

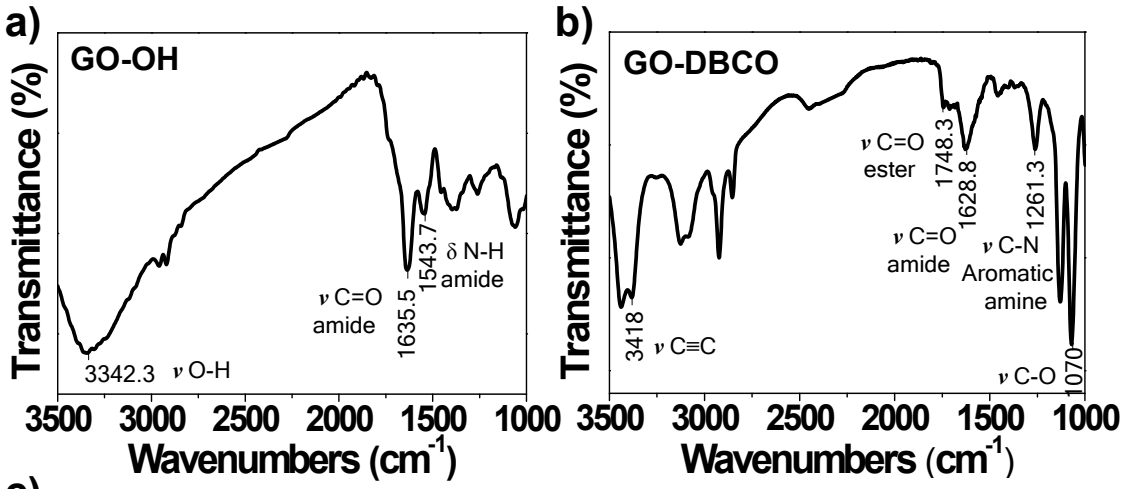


b) GO-P2



c) GO-P3

Figure S1. Chemical structures of GO-P hybrids. (a) GO-P1 for specific optical detection of MMP-2, containing two functional sites: MMP-2–cleavable substrate (cleavage site, red) and disulfide bridging site (blue). (b, c) negative control sensors: (b) GO-P2 containing MMP-2–cleavable site without a thiol group, (c) GO-P3 containing non-specific peptide sequence for MMP-2 with a thiol group.



c)

	C (wt %)	H (wt %)	N (wt %)
GO	56	2.3	0.3
GO-OH	51	2.8	3.4
GO-DBCO	50	1.1	1.8
GO-P1	45	7.9	5.5

Figure S2. Characterization of functionalized GO. FT-IR (KBr) spectra of (a) GO-OH, and (b) GO-DBCO. (c) Elemental analysis of GO, GO-OH, GO-DBCO, and GO-P1.

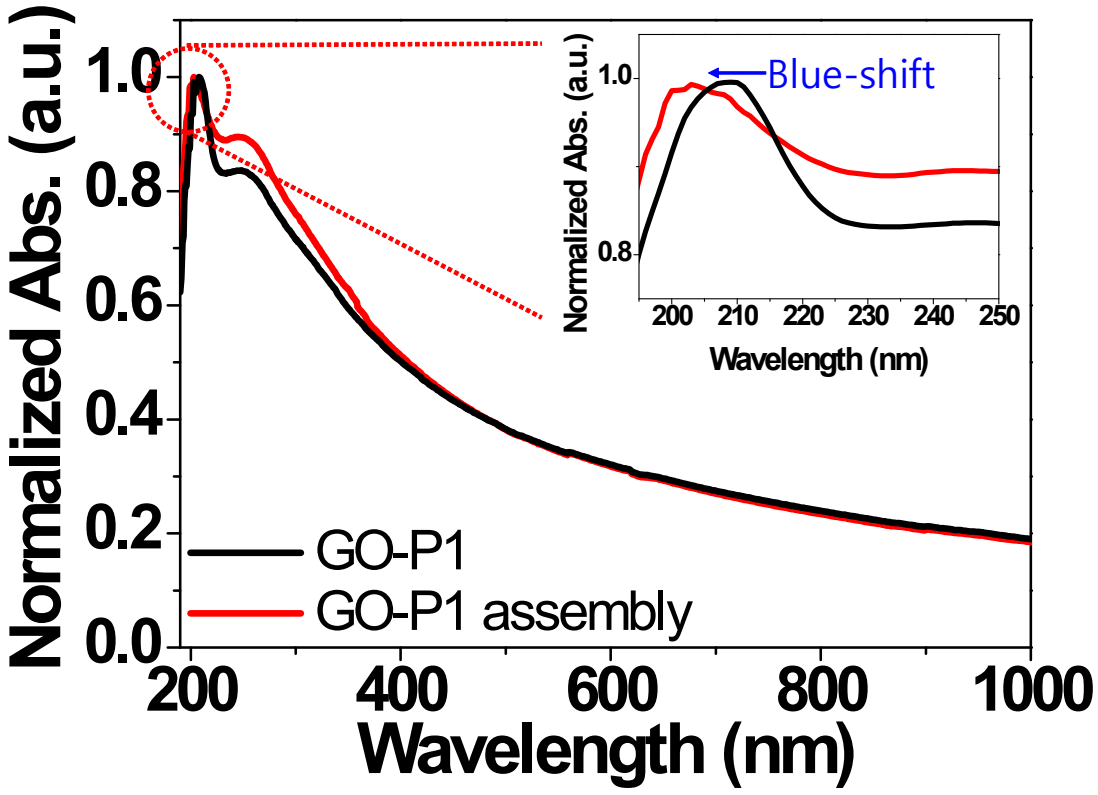


Figure S3. UV/Vis absorption spectra of GO-P1 (black line, 0.1 mg/mL), and GO-P1 assembly (red line, 0.1 mg/mL), showing absorption maxima at 210 and 203 nm, respectively.

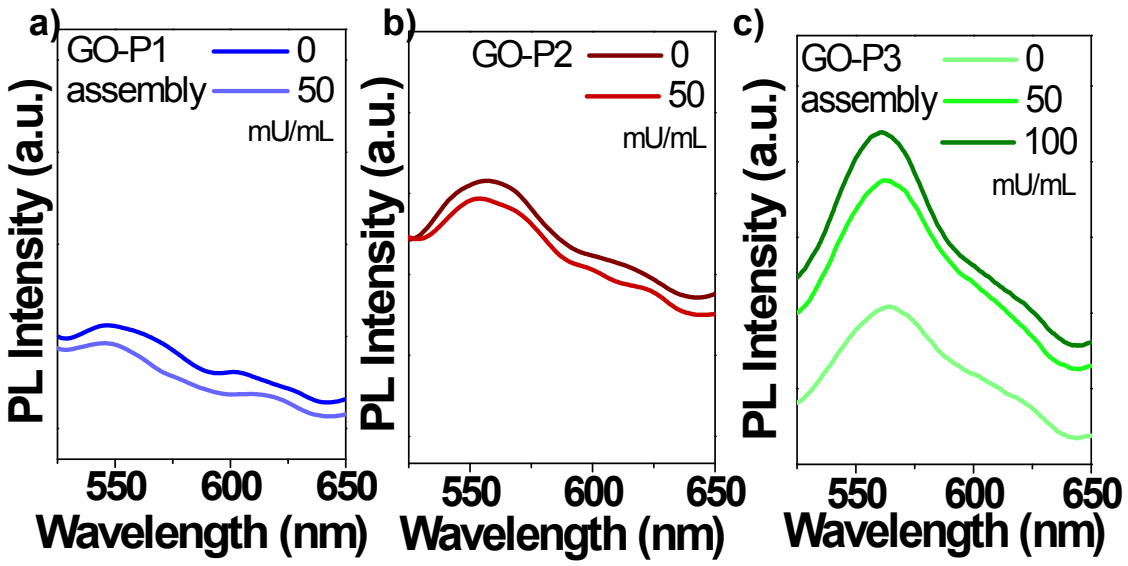


Figure S4. Fluorescence responses of (a) GO-P1 assembly, (b) GO-P2, and (c) GO-P3 assembly in the presence of chymotrypsin. Fluorescence recovery was observed only for the GO-P3 assembly containing the chymotrypsin substrate peptide. All spectra were obtained under excitation at 400 nm.

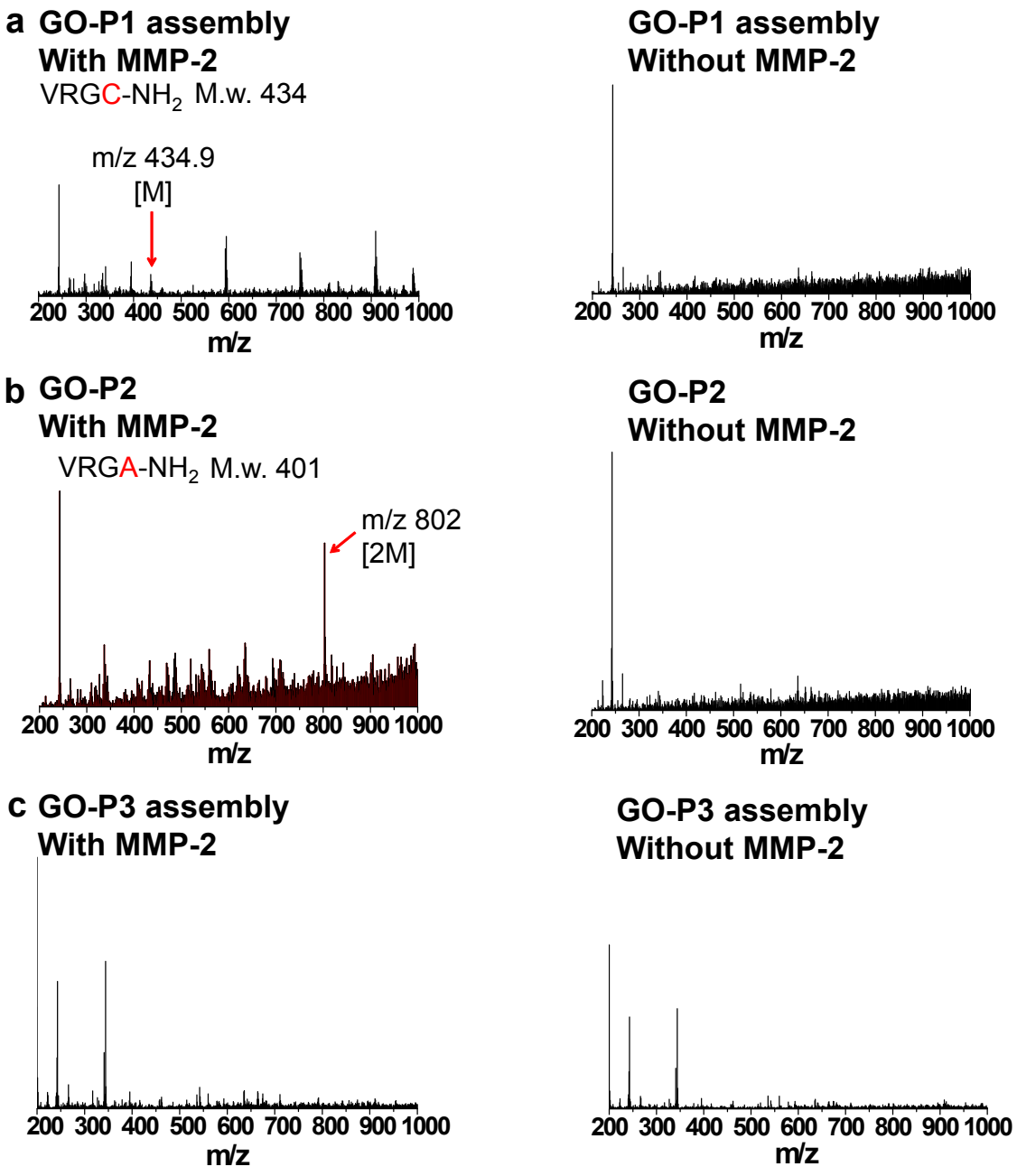


Figure S5. Mass spectroscopic analysis of proteolytic cleavage of the peptide substrates on several GO-Peptide sensor by MMP-2. MS spectrum of (a) GO-P1 assembly, (b) GO-P2, and (c) GO-P3 assembly with (left panels) or without (right panels) MMP-2, MMP-2 was treated for 2 h at 37 ˚C. The sequences cleaved from the GO-P1 assembly and from GO-P2 by MMP-2 were VRGC-NH_2 and VRGA-NH_2, respectively.