Supporting Information

Real-time monitoring of electroreduction and labelling of disulfide-bonded peptides and proteins by mass spectrometry

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TABLE OF CONTENTS

Fig. S1. Experimental photography. 3

Fig. S2. CID spectra of *m/z* 308. 4

Fig. S3. Schematic overview**.**. 5

Fig. S4. Labeling of GSH by dopamine and phenol. 6

Fig. S5. GSSG reduction and phenol labeling. 7

Fig. S6. Sequence of *β*-lactoglobulin A. 8

Fig. S7. LOD of GSH. 9

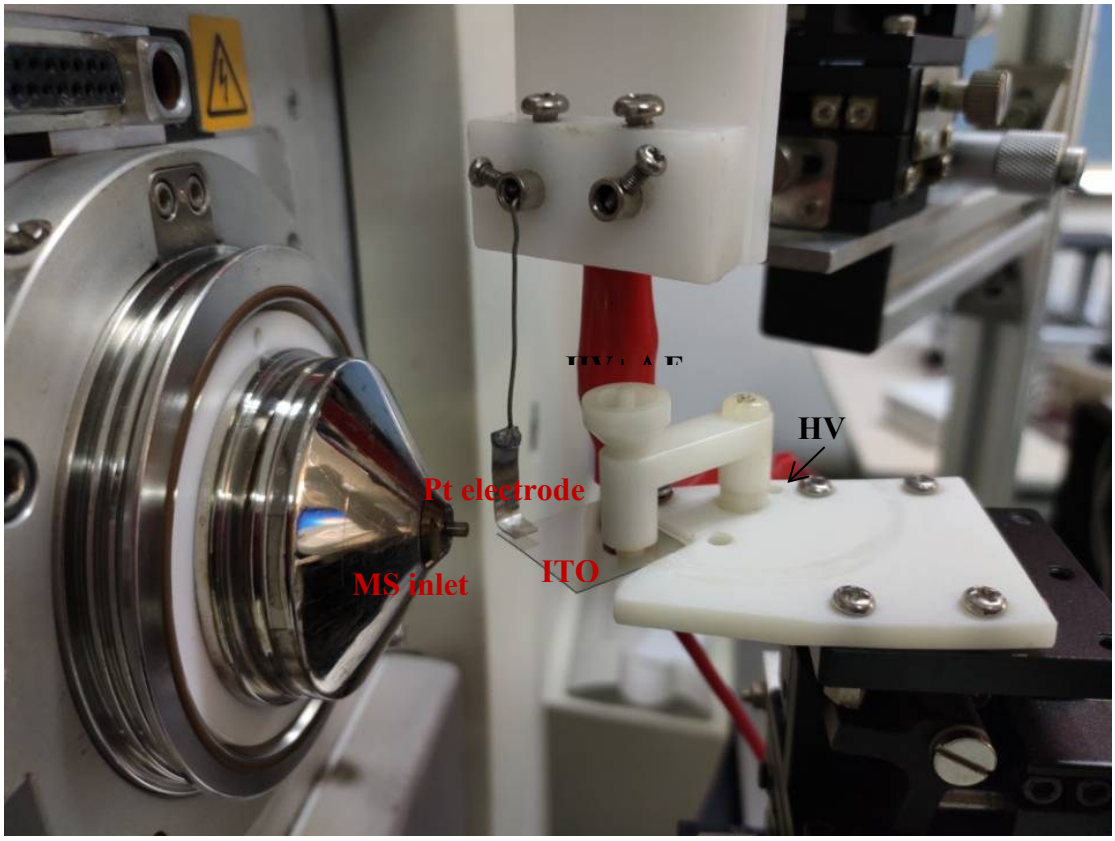

Fig. S1 Experiment photography.

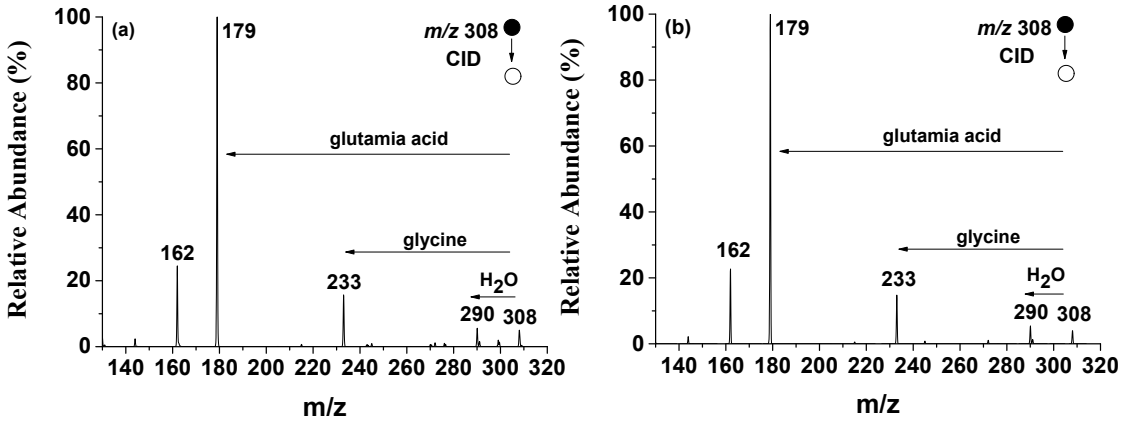

Fig. S2 (a) CID spectrum of m/z 308 [GSH+H]+ generated by the reduction of GSSG using ITO-based-EC-DSI-MS apparatus. (b) CID spectrum of m/z 308 [GSH+H]+ generated by DSI of authentic GSH sample solution. Note that the two CID spectra are identical.

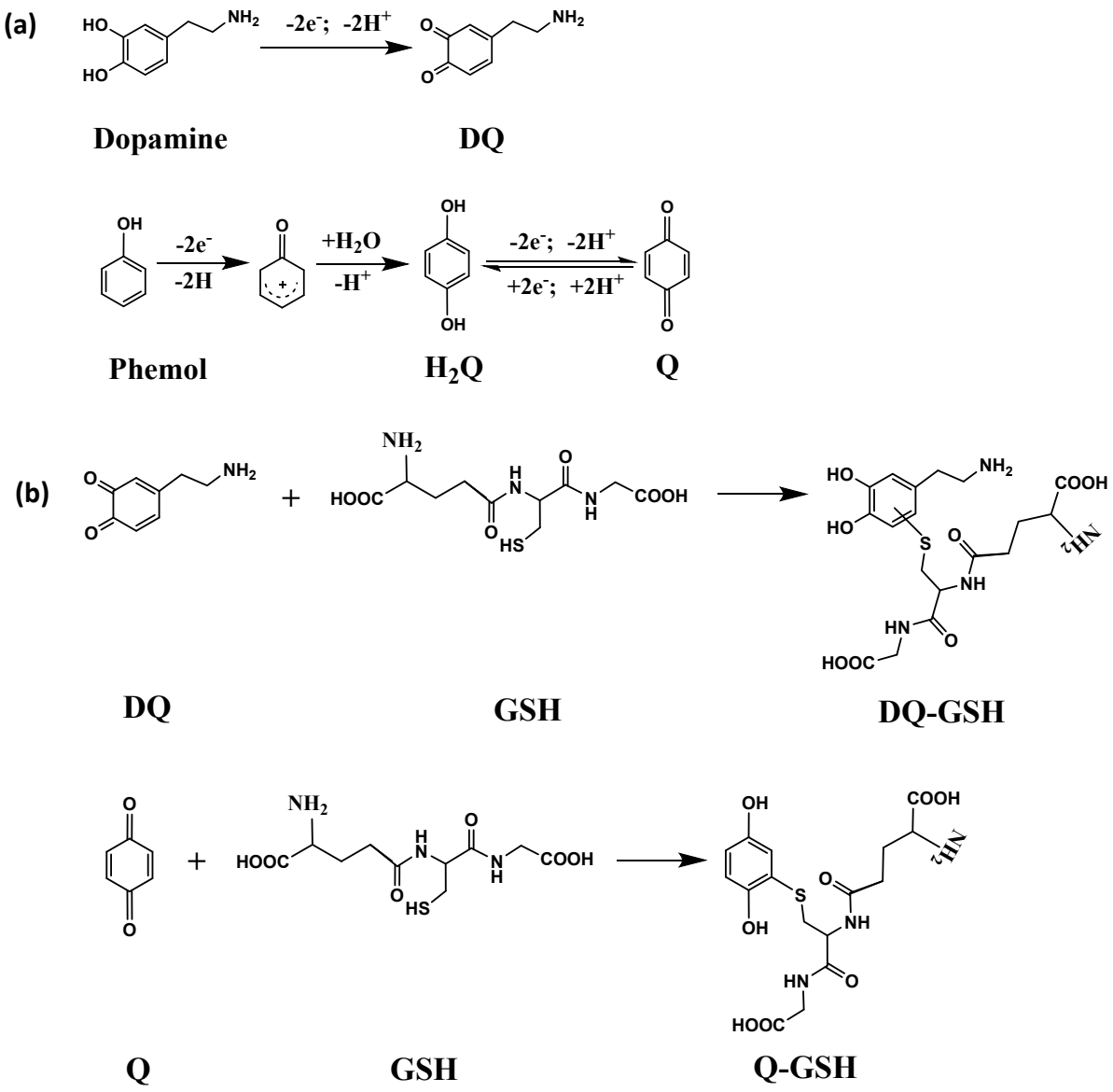

Fig. S3 Schematic overview on (a) oxidation pathway of dopamine and phenol, which results in the formation of reactive benzoquinone intermediates, (b) Michael-type addition of dopamine orthoquinone and benzoquinone with glutathione resulting in the corresponding adducts.

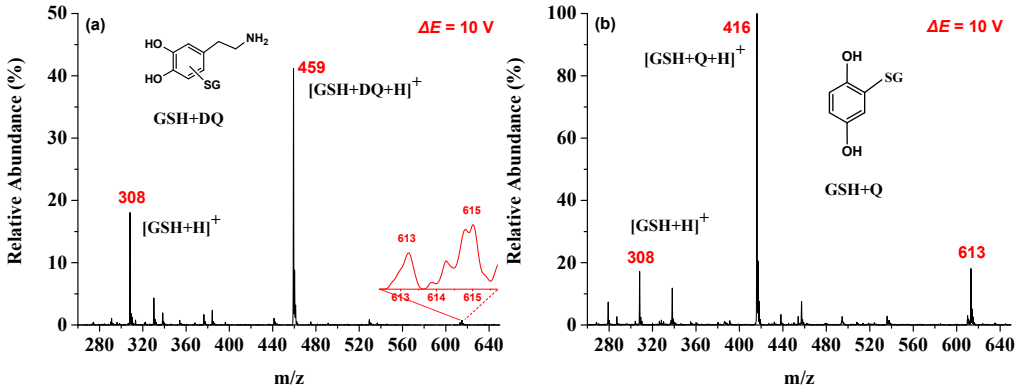

Fig. S4 Thiol labeling reaction mass spectrum. (a) Dopamine hydrochloride was labeled with GSH in positive ion mode with a potential of 10.0V. (b) Phenol was labeled with GSH in positive ion mode with a potential of 10.0V.

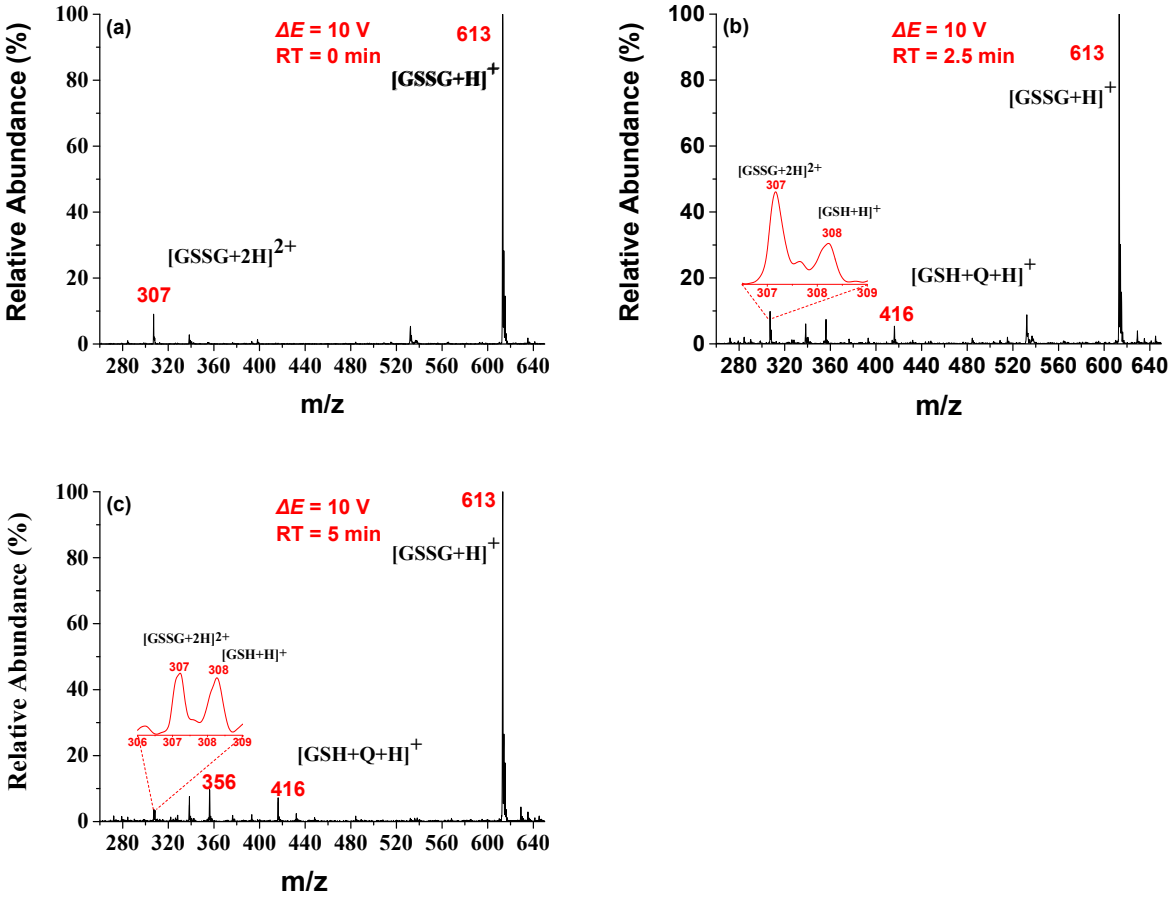

Fig. S5 Real-time mass spectra for electroreduction of GSSG and labeling with phenol. The applied potential across the two electrodes was 10.0 V. The above mass spectra are (a) 0 min, (b) 2.5 min, (c) 5 min.

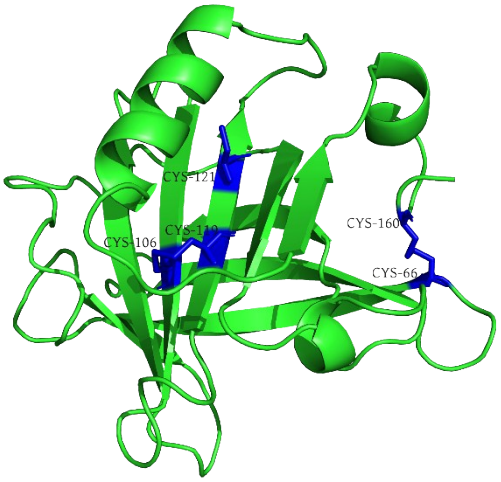

Fig. S6 Tertiary structure of *β*-lactoglobulin A with cysteine thiol highlighted. The *β*-lactoglobulin A molecular configuration of the cartoon structure, the disulfide bonds and the free thiol are represented in sticks and are shown in blue.

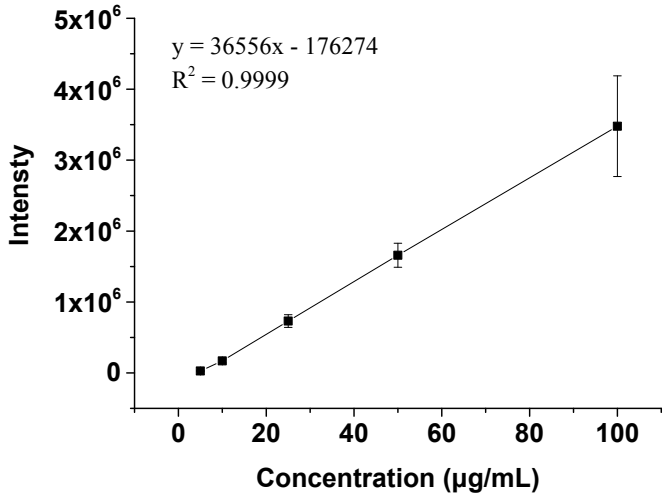

Fig. S7 LOD of GSH. y = 36556x – 176274, R^2 = 0.9999, LOD=0.398.