# Supporting information for

# Droplet array on local redox cycling-based electrochemical (LRC-EC) chip device

Kosuke Ino<sup>1</sup>, Takehito Goto<sup>1</sup>, Yusuke Kanno<sup>1</sup>, Kumi Y. Inoue<sup>1</sup>, Yasufumi Takahashi<sup>2</sup>, Hitoshi Shiku<sup>1</sup>, Tomokazu Matsue<sup>1,2</sup>

<sup>1</sup> Graduate School of Environmental Studies, Tohoku University, Japan.
<sup>2</sup> WPI-Advanced Institute for Materials Research, Tohoku University, Japan.

Corresponding authors: Kosuke Ino (ino.kosuke@bioinfo.che.tohoku.ac.jp) Tomokazu Matsue (matsue@bioinfo.che.tohoku.ac.jp)

Keywords: Electrode array Droplet array Electrochemical detection Redox cycling Chip device



#### Figure S1

Detection scheme for electrochemical imaging. The potentials of all of electrodes except the first column electrodes are set to 0.00 V, and the potential of the first column electrode is set to 0.50 V. Reduction currents from the row electrodes are then sequentially acquired [1-3]. The arrows indicate the detection points. When redox compounds are contained in the droplets, redox cycling of FcCH<sub>2</sub>OH/FcCH<sub>2</sub>OH<sup>+</sup> is established at the detection points. After acquisition of the currents on the first column electrode, the potential of the first column electrode is stepped back from 0.50 to 0.00 V, and the potential of the second column electrode is stepped from 0.00 to 0.50 V. The scanning process is then sequentially performed on the other column electrodes to complete electrochemical imaging. The three working electrodes of the multichannel potentiostat (WE1, WE2, and WE3) are used during detection [1-3]. The potential of the row and column electrodes are controlled by changing the connection of the row and column electrodes to WE1, WE2, and WE3 through the switch matrix [1-3]. The Pt pseudo-reference/counter electrodes are connected with RE/CE of the potentiostat. To measure PAP, the potentials are set to -0.40 and 0.20 V instead of 0.00 and 0.50 V.



## Figure S2

Electrochemical detection of ALP activity in HeLa cells within droplets. (A) Scheme for ALP detection using PAPP. PAPP is catalytically hydrolyzed by ALP to yield PAP. Redox cycling of PAP/QI is established by application of 0.20 and -0.40 V at the generator and collector electrodes, respectively. (B) Electrochemical detection of ALP activity in HeLa cells within droplets is achieved when PAP accumulates in the droplets after ALP reacts in the HeLa cells, and the redox cycling-based currents from the collector electrodes are acquired.



#### Figure S3

Evaluation of the LRC-EC chip device. (A) Cyclic voltammograms for  $FcCH_2OH$  droplet (0, 0.1, 0.25, 0.50, and 1.0 mM) from the generator (G) and collector (C) electrodes in dual mode. (B) Dependence of the collector currents at 0.50 V on the  $FcCH_2OH$  concentration (0, 0.10, 0.25, 0.50, and 1.0 mM).

### References

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