Supplementary Information for

Extraordinary Enhancement of Porphyrin Photocurrent Utilizing Plasmonic

Silver Arrays

Kosuke Sugawa,*^a Koji Uchida,^a Naoto Takeshima,^a Shota jin,^a Natsumi Tsunenari,^a Yuki

Kida,^a Tsuyoshi Akiyama,^b Joe Otsuki,^a Kouichi Takase^c and Sunao Yamada^d

^a Department of Materials and Applied Chemistry, College of Science Technology, Nihon University,

Chiyoda, Tokyo 101-8308, Japan

^b Department of Materials Science, School of Engineering, The University of Shiga Prefecture, Hikone,

Shiga 522-8533, Japan

^c Department of Physics, College of Science Technology, Nihon University, Chiyoda, Tokyo 101-0062, Japan

^d Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishiku, Fukuoka, 819-0395, Japan

E-mail of corresponding author: sugawa.kosuke@nihon-u.ac.jp

- 1. Detailed fabrication procedure of the AgHS electrodes
- 2. Preparation of porphyrin SAMs onto the AgHS array electrodes
- 3. Quantitation of the number of porphyrin molecules immobilized on the AgHS and AgP electrodes
- 4. Photocurrent action spectra of with and without porphyrin SAMs (Fig. S1)
- 5. Detailed calculation model in FDTD simulation (Fig. S2)

1. Detailed fabrication procedure of the AgHS electrodes

1-1. Preparation of silica colloidal butanol solutions

The colloidal solutions of silica particles with diameters of 190 ± 10 , 290 ± 10 , and 410 ± 15 nm were synthesized according to a modified version of previously reported procedure.^{S1} Typically, NH₃ aq. (28%) (0.41, 2.05, or 6.14 mL, respectively) was added to the mixed solution of absolute ethanol (21.2, 20.6, or 19.6 mL, respectively) and Milli-Q grade water (resistivity: 18.2 M Ω ·cm, 6.76, 5.71, or 2.57 mL, respectively) and the mixture stirred for 10 min at room temperature. Tetraethyl orthosilicate (1.676 mL) was quickly added to the solutions, and the mixtures were stirred for 3 h. The resultant colloidal solutions of silica particles were centrifuged at 9000 rpm for 15 min and then redispersed twice in an equivalent amount of ethanol. They were then centrifuged at 9000 rpm for 15 min and redispersed twice in an equivalent amount of 1-butanol.

1-2. Fabrication of Ag Regularly Arrayed Electrodes.

Firstly, the 2D colloidal crystals consisting of silica particles were fabricated on ITO electrodes. The ITO electrodes $(15 \times 20 \text{ mm}^2)$ were first treated in a mixed solution of NH₃ aq./H₂O₂ aq. (1:1 v/v) at 100 °C for 3 h and then washed thoroughly with Milli-Q water, to produce a hydrophilic surface. A small amount of each colloidal 1-butanol solution of the silica particles was added dropwise to ultrapure water in a Petri dish, resulting in the formation of 2D colloidal crystals of the silica particles on the water surface. After spontaneous transferring of the crystals onto the ITO surfaces by attaching the edge of the electrode vertically to the water surface, the samples were annealed at 500 °C for 1 h to physically strengthen the colloidal crystals.

Next, a mixed solution containing (3-mercaptopropyl)trimethoxysilane (MPTS, 1 mL), Milli-Q water (1 mL), and 2-propanol (40 mL) was refluxed for 1 h at 100 °C. After cooling the solution, the substrate containing the colloidal crystals was immersed into the solution for 30 min, followed by through washing with ethanol and drying in air at 75 °C, to produce thiol groups onto the silica surfaces as a binder between the surface and Ag film. Finally, in order to fabricate the AgHS arrays, Ag with the thickness (95, 145, and 205 nm for 190, 290, and 410 nm in silica diameters, respectively) was thermally deposited under a high vacuum (6.0×10^{-7} Torr) onto the surface of the colloidal crystals. A planar Ag electrode (AgP) was prepared by thermal deposition of Ag (thickness: 100 nm) onto the MPTS-immobilized ITO electrodes.

2. Preparation of porphyrin SAMs onto the AgHS array electrodes

The disulfide derivative of porphyrin was synthesized in our laboratory. The SAMs of the porphyrin on the AgHS electrodes were prepared by immersing them into a toluene solution of porphyrin (0.2 mM) for 24 h to obtain the porphyrin-immobilized plasmonic Ag electrodes.

3. Quantitation of the number of porphyrin molecules immobilized on the AgHS and AgP electrodes^{S2}

The Po/AgHS (or AgP) electrodes were immersed in 6.6 mL of a toluene solution of dodecanethiol (5 M) for one week to dissolve out the surface-immobilized porphyrin into the solution from the electrode surface. After this treatment, the absorption spectra of the toluene solution containing porphyrin were measured and the number of porphyrin molecules on each sample was calculated from the absorbance of the Soret band using the absorption coefficient of 291900 M^{-1} cm⁻¹ at 421 nm.



4. Photocurrent action spectra of with and without porphyrin SAMs

Fig. S1 Photocurrent action spectra with (a) and without (b) porphyrin SAMs. (A) AgP, (B) AgHS(190), (C) AgHS(290), and (D) AgHS(410).

5. Detailed calculation model in FDTD simulation

FDTD calculations were carried out by the FullWAVE program suite (RSoft Design Group, .Inc). The apparent grid size was 1/100 of the unit cell size in the *x*, *y* and *z* directions. An inhomogeneous grid was used for the gap region for reduction of calculation cost. The boundary conditions employed were a two-dimensional periodic boundary in the *x* and *y* directions and a perfectly matched layer (PML) in the *z* direction. The thickness of PML was 25 times as large as the grid size. A thickness of ITO was modeled to be 100 nm. The configuration of each object is illustrated in Fig. S2. The dielectric functions of Ag and ITO were taken from the implemented data in the FullWave program. The dielectric function of SiO₂ and glass was set to be 1.46.



Fig. S2 Calculation model of AgHS electrodes in the FDTD simulation. Top and cross-sectional views of the model of AgHS in which *d* is the diameter of SiO₂ sphere and *t* is the thickness of Ag layer (t = d/2). The surrounding medium is water (n = 1.333). The purple line is the boundary in the calculation.

References

S1. W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci., 1968, 26, 62.
S2. K. Sugawa, T. Akiyama, H. Kawazumi and S. Yamada, Langmuir, 2009, 25, 3887.