Supporting Information

High Density Single-layer Coating of Gold Nanoparticles onto Multiple Substrates by Using an Intrinsically Disordered Protein of α-Synuclein for Nano Applications

*Ghibom Bhak,[a,‡] Junghee Lee,[a,‡] Chang-Hyun Kim,[b] Dong Young Chung,[a,c] Jin Hyoun Kang,[d] Soojung Oh,[e] Jungsup Lee,[a] Jin Soo Kang,[a,c] Ji Mun Yoo, [a,c] Jee Eun Yang,[a] Kun Yil Rhoo,[f] Sunghak Park,[g] Somin Lee,[f] Ki Tae Nam,[g] Noo Li Jeon,[e,h] Jyongsik Jang,[a] Byung Hee Hong,[d] Yung-Eun Sung,[a,c] Myung-Han Yoon,[b] and Seung R. Paik[a,]**

[a] School of Chemical and Biological Engineering, Institute of Chemical Processes, College of Engineering, Seoul National University, Seoul 151-744, Korea

[b] School of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea

[c] Center for Nanoparticle Research, Institute for Basic Science, Seoul 151-747, Korea

[d] Department of Chemistry, Seoul National University, Seoul 151-744, Korea

[e] School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-744, Korea

[f] Interdisciplinary Program for Bioengineering, Seoul National University, Seoul 151-744, Korea

[g] Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

[h] Institute of Advanced Machinery and Design, Seoul National University, Seoul 151-744,

Korea

‡ The first two authors equally contributed to this work.

*E-mail: srpaik@snu.ac.kr (S.R.P.).

EXPERIMENTAL DETAILS

Purification of α-synuclein (αS)

Wild-type human αS protein was prepared according to the procedure reported previously.[1] Briefly, human αS gene cloned in pRK172 vector was transformed into *Escherichia coli* BL21 (DE3) for the αS over-expression. The heat-treated cell lysate was subjected to successive fractionations using DEAE-Sephacel anion-exchange, Sephacryl S-200 size-exclusion, and S-Sepharose cation-exchange chromatography. The purified αS was dialyzed against total 6 L of fresh 20 mM MES at pH 6.5 with two changes overnight, and stored in aliquots at a concentration of 1 mg/ml at -80ºC.

Preparation of Substrate

n-Si (Siltron Inc., Korea), GaAs (University Wafer, Boston, MA), fluorine-doped tin oxide (FTO, Pilkington, Toledo), SiO_2 (Global Wafers Co., Ltd., China), mica, graphite (NGS Naturgraphit GmbH, Germany), glass (Corning, Corning, NY), quartz (Perkin Elmer, Waltham, MA), Au (Phasis, Switzerland), polyethylene terephthalate (PET) were cleaned ultrasonically in deionized water (DW) or isopropanol (IPA), and purged with nitrogen gas. Polystyrene (Sigma-Aldrich, M.W. = 38k, 4 wt % in xylene), polycarbonate (Sigma-Aldrich, M.W. = 64k, 5 wt % in chloroform), poly(methyl methacrylate) (Microchem, M.W. = 950k, 5 wt % in anisole) were spin-coated on cleaned Si/SiO_2 wafer at 4,000 rpm for 30 s. Each polymer was annealed over its glass temperature (T_g) for 30 s. Polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning, Midland, MI) was prepared by mixing pre-polymer and curing agent at 10:1 and subsequent incubation of the mixture at 80^{o}C for 30 min. The cured PDMS was cleaned in DW with ultra-sonication. Al_2O_3 and TiO_2 were prepared by atomic layer

deposition (ALD) on O_2-plasma cleaned SiO_2 wafer and washed ultrasonically in IPA. Fluorinated wafer was prepared by the reaction between 1H,1H,2H,2H–perfluorooctyltriethoxysilane (98%, Sigma-Aldrich) and O_2-plasma (60 W, 45 sccm, 10 min) cleaned SiO_2 wafer at 80^{o}C for 12 hr. The jewelry crystals (2854 butterfly flat back, crystal F 001, Swarovski element) were cleaned ultrasonically in IPA for several minutes and purged with nitrogen gas.

X-ray photoelectron spectroscopy (XPS) characterization

XPS spectra were obtained using AXIS Ultra DLD (Kratos, UK) with a monochromatic Mg Ka (1253eV) X-ray source of 40eV pass energy under ultra-high vacuum (~10^{-9} torr). High-resolution scans were acquired from 390 to 410 eV and 80 to 90 eV for analysis of N 1s peak (~399.5eV) and Au $4f_{7/2,5/2}$ (~84.1/84.9 eV). Ratio between Au and N was calculated with the peak areas and the atomic sensitivity factor.

Atomic force microscope (AFM) analysis

Substrates were cut with 1 x 1 cm^2 in size and prepared following the cleaning procedures. Then, α-synuclein-coated gold nanoparticles (αS-AuNP) in 200 μl of 50 mM citrate (pH 4.5) were placed on each substrate. The prepared samples were subjected to AFM (Multimode 8, Bruker, Billerica, MA) analysis using tapping mode Nanoscope V system (Bruker). For height measurement, each sample was smoothly scratched with a PET stick prior to the AFM measurement.

Contact angle measurements

Samples were prepared according to the same procedure performed in the AFM experiment. All the contact angles and the images of water droplets were monitored by using a drop shape

analyzer (DSA100, Kruss, Germany). The static contact angle was examined after storing the samples at a humid chamber for 30 min to prevent evaporation.

Large-area monolayer formation of αS-AuNP adsorbed on SiO_2 wafer

$\alpha S\text{-}AuNP_{10nm}$ was prepared by incubating 1 ml of αS (1 mg/ml) and 8 ml of the AuNP colloidal solution. After the centrifugation, the αS-AuNP pellet was resuspended with 2 ml of 50 mM citrate (pH 4.5), which was then placed onto the SiO_2 wafer pre-cleaned with sonication in IPA and O_2-plasma treatment to remove organic contaminants. After incubation at 40^{o}C for 3 hr in a humid chamber, the sample was thoroughly washed with 20% methanol at 4^{o}C and dried with nitrogen gas.

Field-emission scanning electron microscope (FE-SEM) analysis

All the samples were completely dried in a desiccator and coated with a 2-nm-thick layer of platinum by a sputter coater (BAL-TEC/SCD 005 sputter coater, Switzerland). The samples were then analyzed with FE-SEM (SUPRA 55VP, Carl Zeiss, Germany) at 2.0 kV.

Transmission electron microscope (TEM) analysis

An aliquot of samples (10 μl) was placed onto carbon-coated 200-mesh copper grids (Ted Pella Inc. CA). After washing the grid with DW, the air-dried grid was examined with TEM (JEM 1010, JEOL, Japan).

Computational calculations for isoelectric point (pI) of αS

Isoelectric point (pI) of αS was obtained as an average value calculated with 15 different programs such as Isoelectric Point Calculator (IPC) protein, IPC peptide, Toseland, Thurlkill,

Nozaki Tan, DTASelect, EMBOSS, Grimsley, Patrickios, Rodwell, Sillero, Solomon, Lehninger, Wikipedia, and ProMoST (http://isoelectric.ovh.org/).

High-density single-layer coating of αS-AuNPs onto various materials

The high-density single-layered coat of αS-AuNPs was formed onto bare AuNPs (BBI solutions, UK), carbon nanotubes (CNTs; Sigm-Aldrich), carbon nanofibers (CNFs; Sigm-Aldrich), or 500-nm titanium dioxide (TiO_2; EPR-Ti-0.5, EPRUI Nanoparticles & Microspheres Co. Ltd, China). Following an incubation at 40^{o}C for 2 hr with agitation at 200 rpm, the αS-mediated three types of AuNP-AuNP core-satellites were generated in 800 μl of 10 mM MES at pH 5.5 by incubating the following mixtures: αS-$AuNP_{30nm}$ in a pellet and 400 μl of bare $AuNPs_{5nm}$ colloidal solution (type 1), αS-$AuNP_{30nm}$ in a pellet and 400 μl of bare $AuNPs_{10nm}$ colloidal solution (type 2), and αS-$AuNP_{100nm}$ in a pellet and 400 μl of bare $AuNPs_{100nm}$ colloidal solution (type 3). After the incubation, the samples were centrifuged at 16,100 x g for 1 min with fresh 20 mM MES at pH 6.5 three times to remove free AuNPs. Each αS-AuNP pellet was prepared with 200 μl of AuNP colloid solution and 25 μl of αS (1 mg/ml). For the αS-AuNP coating on CNT, 0.226 mg of multi-walled CNTs were incubated with a pellet of αS-$AuNP_{10nm}$ (400-μl AuNP and 50-μl αS) in 200 μl of 50 mM citrate (pH 4.5) at 40^{o}C for 2.5 hr with agitation at 200 rpm after sonication for 1 min. The samples were then centrifuged at 16,100 x g for 15 min with fresh DW three times. For the αS-AuNP coating on CNF, the mixture of 15 μg of CNF (Sigma-Aldrich) and a pellet of αS-$AuNP_{5nm}$ (three sets of 400-μl AuNP and 50-μl αS) was incubated in 200 μl of 50 mM citrate at 40^{o}C for 3 hr. The products were washed via centrifugation with fresh DW at 16,100 x g for 15 min three times. The CNFs were solubilized by the pre-treatment, in which 3 mg of CNFs (sigma Aldrich) were refluxed for 24 hr under sonication (bath-type) in a solution composed of 2.5

ml of sulfuric acid, 5 ml of nitric acid, and 2.5 ml DW. For the αS-AuNP coating on TiO_2 microsphere (EPRUI Nanoparticles & Microspheres Co. Ltd), the TiO_2 spheres (10 μl) were incubated with a pellet of αS-$AuNP_{10nm}$ (three sets of 400-μl AuNP and 50-μl αS) in 200 μl of 50 mM citrate (pH 4.5) at 40°C for 2.5 hr. Micro-channels and microwells were filled with αS-AuNP solution in 50 mM citrate at pH 4.5. After incubation in a humid chamber at 40°C for 3 hr, the micro-channels and microwells were completely washed with 20% methanol at 4°C to remove free αS-AuNPs, and then stored in a desiccator.

Electron-beam (e-beam) lithography for 2-Dimensional patterning of αS-AuNPs in single-layer

PMMA (Microchem, M.W. = 950k, 5 wt % in anisole) was spin-coated on a cleaned Si/SiO_2 wafer at 4,000 rpm for 40 s. On the PMMA-coated wafer, e-beam was irradiated to the designed patterns drawn with computer-aided design (CAD) software (NPGS, DesignCAD Express 16.2). After the e-beam exposure, the PMMA-coated wafer was dipped into methyl isobutyl ketone/IPA solution for 45 s to remove the e-beam exposed region. Following the development process, the sample was thoroughly washed with IPA and dried with nitrogen gas. The patterns were treated with O_2 plasma (60 W, 45 sccm, 1 min) to remove organic residues on the SiO_2 surface, which results in the developed patterns hydrophilic to exhibit conformal contact toward the particle-containing aqueous solution. Then, αS-$AuNP_{10nm}$ in 50 mM citrate at pH 4.5 was placed onto the patterned substrate, and the sample was incubated in a humid chamber at 40°C for 3 hr. After the particle adsorption, the remnants were washed off with 20% methanol at 4°C and the substrate was dried with nitrogen gas. Before the lift-off process, the substrate was entirely exposed to O_2 plasma (60 W, 45 sccm, 11 min) to prevent cross-linking between the protein molecules. Finally, the whole substrate was dipped

into acetone with gentle agitation to remove the PMMA layer and dried with nitrogen gas purging.

Fabrication of micro-fluidic device and 3-D microwell array

A PDMS master mold for micro-channels was prepared using soft lithography and the previously reported techniques.[2] In brief, O_2 plasma-treated (50 W, 45 sccm, 5 min) Si wafer was spin-coated with negative photoresist (SU-8 5, Microchem, Boston, MA), and the wafer was pre-baked at 95^{o}C for 10 min. Following an exposure with 405 nm ultraviolet (UV) light (Shinu MST, Korea) at 500 mJ, the wafer was baked at 95^{o}C for 10 min. The unexposed region of the photoresist was removed with SU-8 developer (Microchem). Then, the resulting wafer was used as a master mold for PDMS precursor Sylgard 184 (Dow Corning, Midland, MI). The precursor solution with curing agents was poured on the wafer, baked at 90^{o}C for 40 min, and replicated. In the case of micro-fluidic device, the PDMS mold was punched for inlets and reservoirs, and attached on glass slide after O_2 plasma treatment (50 w, 45 sccm, 1 min).

Fabrication and characterization of memory devices

Indium-tin-oxide (ITO) coated polyethylene terephthalate (PET) substrates were used as purchased from Sigma-Aldrich (ITO thickness: 130 nm, surface resistivity: 60 Ω/sq) for a shared gate-electrode platform. These transparent plastic sheets were thoroughly cleaned by subsequent rinsing with acetone and isopropanol, followed by nitrogen blow-dry. A thin-film (~ 40 nm) of PEDOT:PSS (Clevios™, Heraeus) was deposited by spin-coating at 3,000 rpm for 60 s, with an immediate annealing step at 100^{o}C for 10 min, for mainly serving as a morphological stabilizer for ITO. PMMA (Sigma-Aldrich, M.W. = 120k) solution was prepared at the concentration of 80 mg/ml in toluene and heated at 70^{o}C with a magnetic

stirrer. The uniformly mixed PMMA solution was spin-coated at 1,000 rpm for 45 s, and annealed at 120^{o}C for 1 hr, creating a 850-nm thick gate-dielectric layer. αS-AuNPs suspended with 50 mM citrate at pH 4.5 were adsorbed onto the PMMA-coated substrate in a humid chamber at 40^{o}C for 3 hr. After the adsorption, the substrate was washed thoroughly with DW at 4^{o}C. Pentacene (Sigma-Aldrich, triple-sublimed grade, ≥99.995%) was then deposited onto the αS-AuNP layer by thermal evaporation in a vacuum chamber using a shadow mask for the patterned semiconducting channels. The pentacene deposition was conducted at a stable rate of 0.25 Å/s under the base pressure of 2×10^{-6} Torr. To finalize the device fabrication, 50 nm of Au source/drain electrodes were vacuum-evaporated in a dedicated chamber, defining the channel width of 500 μm and the channel length of 50 μm (base pressure: 4×10^{-6} Torr, deposition rate: 0.2-0.3 Å/s). The electrical characteristics of the flexible field-effect-transistors (FETs) were measured by using a parameter analyzer (4200-SCS Parameter Analyzer, Keithley, Cleveland, OH) in the dark and under ambient atmosphere.

Oxygen reduction reaction (ORR) performance test

For CNT-αS-AuNP preparation, 1.2 mg of multi-walled carbon nanotubes (MWCNT, Sigm-Aldrich) were reacted with αS-AuNPs under bath-sonication in 2 ml of 10 mM citrate, pH 4.5. αS-AuNPs were slowly added dropwise to the reaction solution of MWCNTs. The CNT-αS-AuNP composites were prepared with various sizes of AuNPs (CNT-AuNP$_{5nm(16.3\%)}$, CNT-AuNP$_{10nm(16.3\%)}$, and CNT-AuNP$_{20nm(16.3\%)}$) at different proportions (CNT-AuNP$_{5nm(8.8\%)}$, CNT-AuNP$_{5nm(16.3\%)}$, and CNT-AuNP$_{5nm(31.7\%)}$). The weight percent of AuNPs was obtained by monitoring the absorption intensity of αS-AuNPs at the maximum absorption wavelength of 518 nm. The resulting CNT-αS-AuNP complexes were washed with three consecutive

centrifugations at 16,100 x g for 15 min while resuspending the precipitates with fresh DW. The final composites were lyophilized with a freeze-dryer (FDU-2200, Eyela, Japan). The outer αS layer of the complexes was removed by O_2-plasma treatment (100 W, 10 sccm, 20 min). Electrochemical measurements were conducted in a standard three electrode cell with Pt-wire counter electrode and saturated Ag/AgCl reference electrode using Autolab potentiostat (PGSTAT). All the potentials were obtained relative to the reversible hydrogen electrode (RHE), which was calibrated by the hydrogen oxidation reaction. The Au/CNT samples were mixed with Nafion resin (Nafion® perfluorinated resin solution, 5 wt % in the mixture of lower aliphatic alcohols and water. contains 45% water, Sigma-Aldrich, 15 wt %) for a binder and dissolved in IPA. Before ORR measurement, the pre-scan was carried out between 0.05-1.0 V vs. RHE to clean the electrode surface. The ORR activity was measured in 0.1 M KOH solution saturated with O_2 at 298 K with a scan rate of 10 mVs^{-1} using a rotating ring disk electrode (Pine instrument). The rotating speed was maintained at 1,600 rpm. The capacitance term was calibrated by measuring CV under Ar saturated condition. The electron transfer number was calculated based on the ratio between ring current and disk current. Ring electrode (Pt) potential was held at a potential of 1.5 V vs. RHE during the measurement.

Plasmon-enhanced dye-sensitized solar cell

The αS-AuNPs prepared through the reaction between 50 μl αS (1 mg/ml) and 400 μl of the AuNP colloidal solution were adsorbed onto 10 μg of TiO_2 spheres (EPR-Ti-0.7, EPRUI Nanoparticles & Microspheres Co. Ltd) in 50 mM citrate (pH 4.5) at 40°C for 3 h. The resulting αS-AuNP-TiO_2 complexes were collected after three subsequent centrifugations at 100 x g for 10 min after resuspending the precipitates with DW. The solvent was then completely changed to ethanol by carrying out the same centrifugation (100 x g, 10 min)

three times. For the SiO_2 outer-shell formation surrounding the composites, the αS-AuNP-TiO_2 complex was mixed with 300 μl ammonium hydroxide, 125 μl DW, and 4,985 μl ethanol. TEOS (250 μl at 1 v/v % in IPA, Acros Organics, Belgium) was added dropwise to the mixture with continuous stirring at 600 rpm. After 18 hr of incubation, the resulting complexes were washed by centrifugation with fresh ethanol (3,000 x g, 3 min) three times. The final products of SiO_2-coated αS-AuNP-TiO_2 complex were collected and dried in a rotary evaporator. The complexes were then mixed with a paste consisted of ethyl cellulose, lauric acid, and terpineol. Before the deposition of αS-AuNP-TiO_2 complex, FTO glass was pre-treated with $TiCl_4$ in 60^oC for 1 hr and heated at 500^oC for 30 min. The paste containing αS-AuNP-TiO_2 complex was screen-printed to an active area of 0.25 cm^2 on the FTO glass. The sample was dried at room temperature and annealed at 500^oC for 30 min. The N719 (Solaronix, Auboone, Switzerland) was loaded by immersing the modified FTP glass into 0.5 mM N719/ethanol solution for 18 hr and the free dyes were washed off with absolute ethanol several times. The dye-sensitized electrode was integrated with a platinum-coated counter electrode using 60 μm thick Surlyn film (DuPont, Wilmington, DE). The assembled electric cell was sealed and filled with the liquid electrode of 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, and 0.5 M 4-tert-butylpyridine in acetonitrile. The J-V curve of the cell was measured using a 500 W xenon lamp (SXIL model 05A50KS source unit). IPCE (K3100, McScience, Korea) spectra were obtained in the wavelength range between 350 and 800 nm under short-circuit condition.

Cell culture

Cell adhesion experiments on the fluorinated wafer were performed with four different types of mammalian cells: primary human umbilical vein endothelial cells (HUVECs; Lonza, Basel,

Switzerland), primary human lung fibroblasts (LFs; Lonza), human epithelial HeLa cells, and human dopaminergic neuroblastoma cells (SH-SY5Y). HUVECs, LFs, HeLa, and SH-SY5Y were grown in the endothelial growth medium (EGM-2; Lonza), fibroblast growth medium (FGM-2; Lonza), Dulbecco's modified Eagle's medium supplemented with 10% (v/v) fetal bovine serum, and DMEM supplemented with 10% fetal bovine serum, respectively, at 37^{o}C with 5% CO_2. On the fluorinated wafer with 0.5 cm x 0.5 cm in size, HUVECs, LFs, HeLa, and SH-SY5Y were seeded at 1 x 10^6, 1 x 10^6, 2 x 10^5, and 1.6 x 10^5 cells/ml. After incubation for 12 hr, cell fixation and immuno-staining of the cells were carried out. For the cell culture in micro-fluidic devices, HUVECs at 1 x 10^6 cell/ml were loaded into the channels, and then cultured for 17 hr.

Immunostaining and confocal laser scanning microscope (CLSM) examination

All the cultured cells were fixed with 4% paraformaldehyde after rinse with Dulbecco's phosphate-buffered saline (PBS). The fixed cells were permeabilized with 0.2% Triton X-100 for 15 min at room temperature, and treated with a blocking buffer (1% bovine serum albumin in PBS) for 30 min at 37^{o}C. Then, the cells were immunostained with filamentous actin (F-actin) probe, Alexa Fluor 488 phalloidin (Molecular Probes, Invitrogen, Carlsbad, CA) for 20 min at room temperature. For the cells in micro-channel device, 4',6-diamidino-2-phenylindole (DAPI) staining was additionally conducted according to the manufacturer's instruction (Sigma-Aldrich). To visualize the αS-AuNP coat on micro-channel surfaces, the channels were stained with anti-αS antibody (LB509, Santa Cruz Biotechnology) and Alexafluoro 594-conjugated secondary antibody (Invitrogen). The fluorescence images were acquired with CLSM (LSM 710, Carl Zeiss, Germany).

HeLa cell detachment by the photodynamic effect of αS-AuNP single-layer coat

HeLa cells were cultured in Dulbecco's modified Eagle's medium supplemented with 10% (v/v) fetal bovine serum at 37^{o}C with 5% CO_2. The HeLa cells were seeded at 2 x 10^5 cells/ml on the slide glass with 0.5 cm x 2 cm in size. After incubation for 24 hr, the cells adhered on the glass in the media and Alexa Fluor 488 phalloidin-stained cells were observed with optical microscope and CLSM, respectively. The slide glass was washed with PBS, and then the light at a wavelength of 530 nm illuminated the HeLa cells on the glass in PBS with a luminescence spectrometer (LS-55, Perkin-Elmer) for 30 sec. Both regions of the glass with or without the light irradiation were examined with optical microscope and CLSM.

SUPPORTING FIGURES

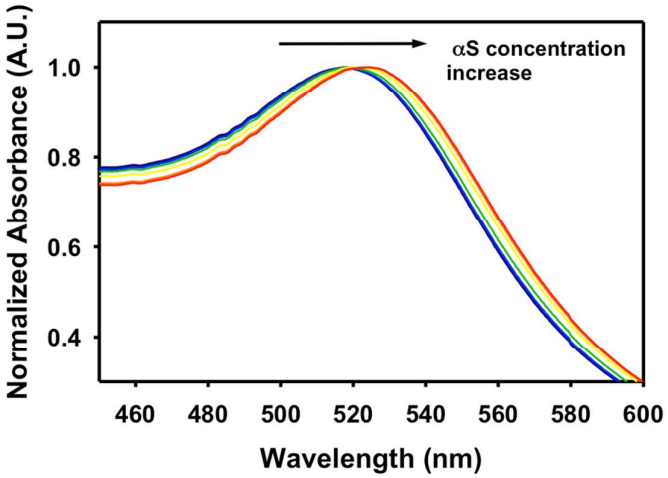

Figure S1. SPR shift of the citrate-capped AuNPs with α-synuclein at various concentrations. UV-visible spectra of the citrate-capped AuNPs reacted with 0-9 μM α-synuclein (purple-blue, 0 nM; blue, 0.09 μM; green, 0.3 μM; yellow , 0.9 μM; red, 9 μM).

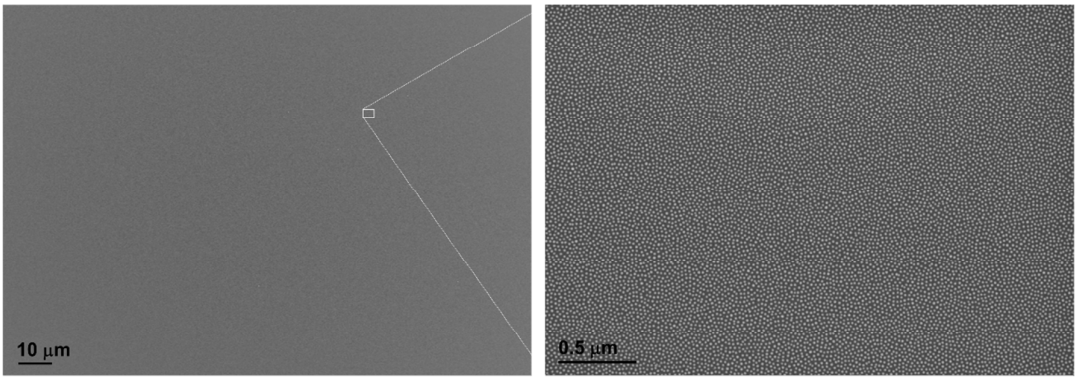

Figure S2. SEM images of the αS-AuNP single-layer on Si/SiO_2 wafer. Low- (left) and high- (right) magnification images are presented.

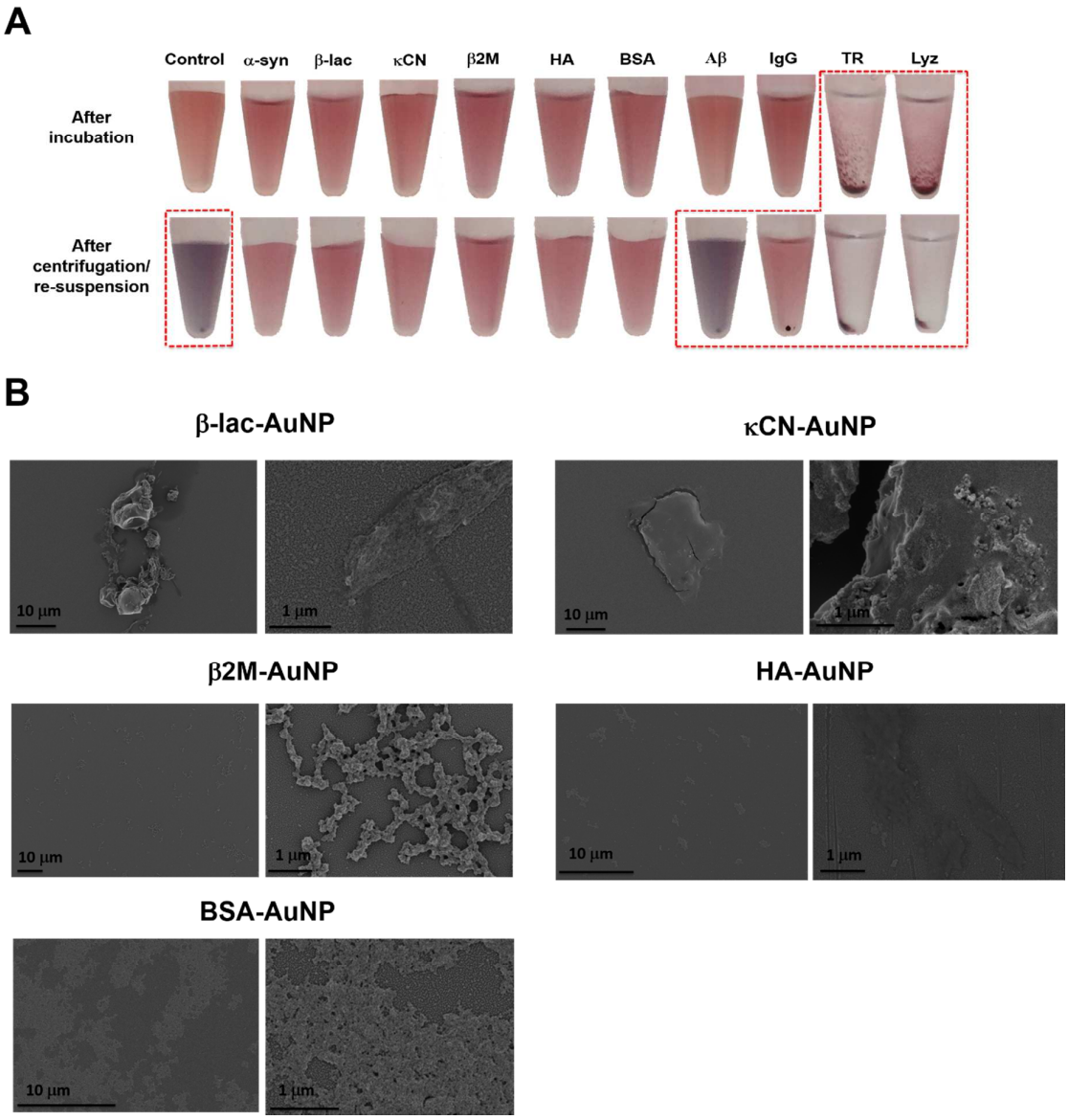

Figure S3. Preparation of AuNP conjugates with various proteins and surface adsorption of the resulting conjugates. (A) Optical images of the protein-AuNP complexes before and after centrifugation/re-suspension process. Samples in red-boxes indicate the agglomerate formation. (B) SEM images of the protein-AuNP conjugates adsorbed onto SiO_2 wafer.

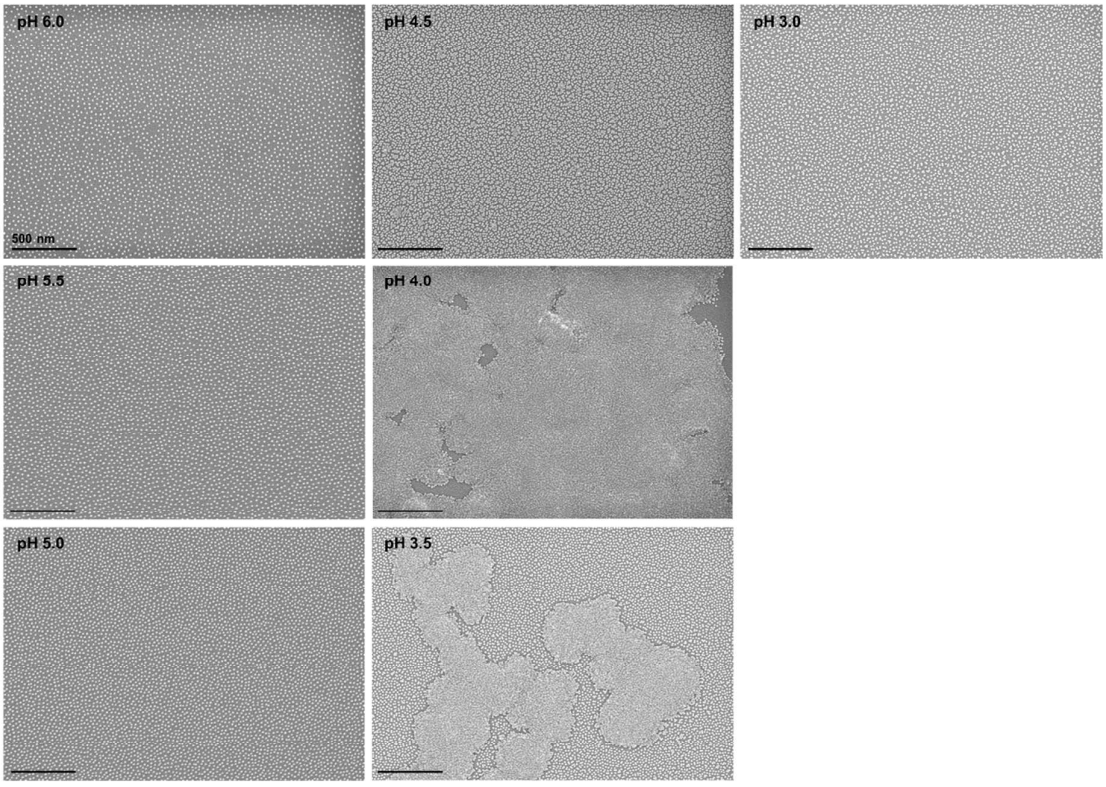

Figure S4. SEM images of αS-AuNPs adsorbed onto Si/SiO_2 wafer at various pHs. A double-component buffer solution comprising citric acid and sodium phosphate dibasic was employed to adjust the pH indicated between 3.0 and 6.0.

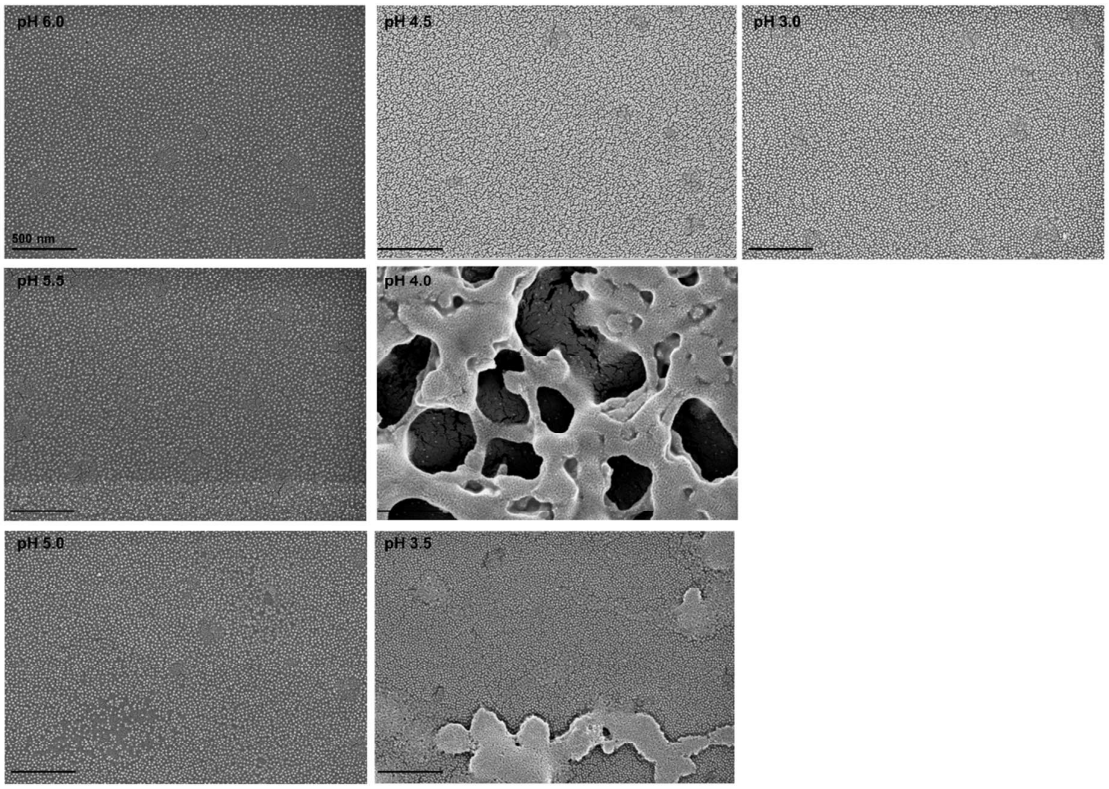

Figure S5. SEM images of αS-AuNPs adsorbed onto PMMA substrate at various pHs. The pHs were maintained in the double-component buffer solution (citric acid/sodium phosphate dibasic).

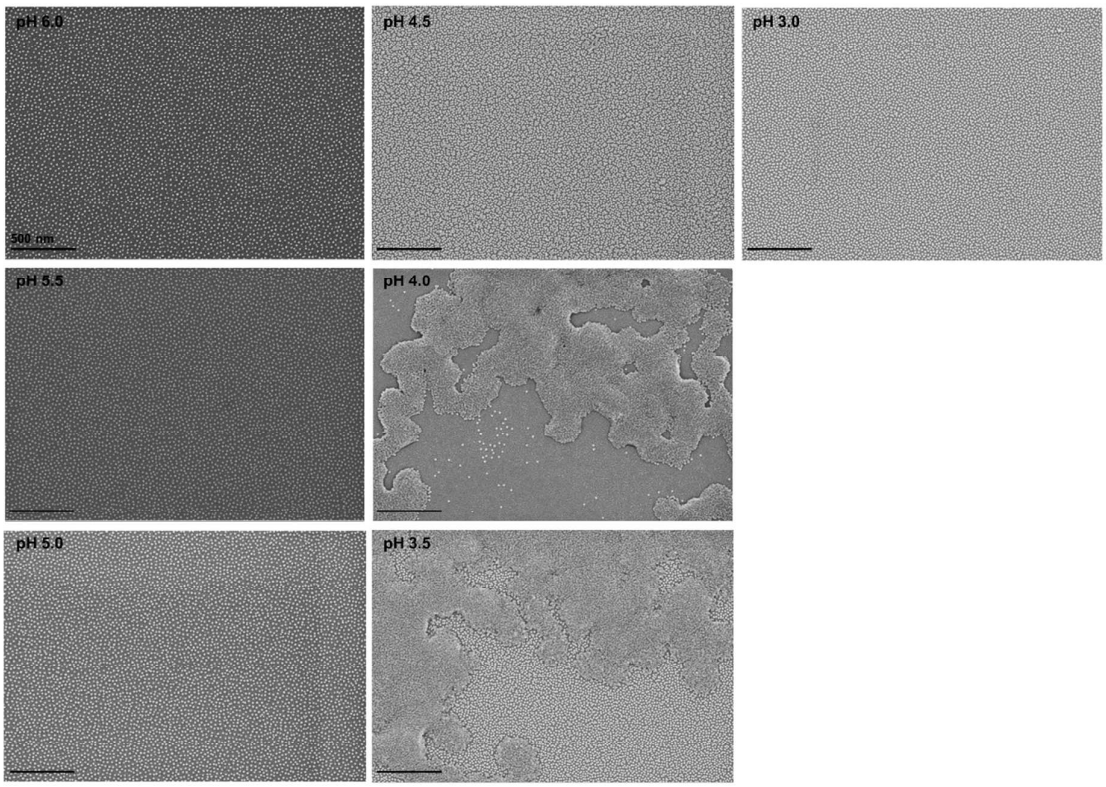

Figure S6. SEM images of αS-AuNPs adsorbed onto GaAs wafer at various pHs. The pHs were maintained in the double-component buffer solution (citric acid/sodium phosphate dibasic).

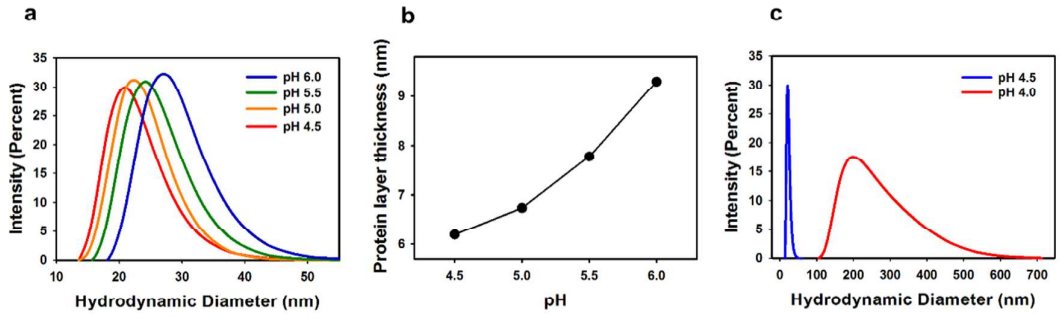

Figure S7. pH effect on the hydrodynamic diameter of αS-AuNP (10-nm AuNP). (a) Statistical distribution of the hydrodynamic diameters of αS-AuNPs measured with DLS at various pHs indicated. (b) Thickness of αS layer on the αS-AuNP conjugates obtained via the DLS measurements. (c) DLS spectra of the αS-AuNPs at either pH 4.5 or 4.0. Large agglomeration of the conjugates was shown to occur at pH 4.0.

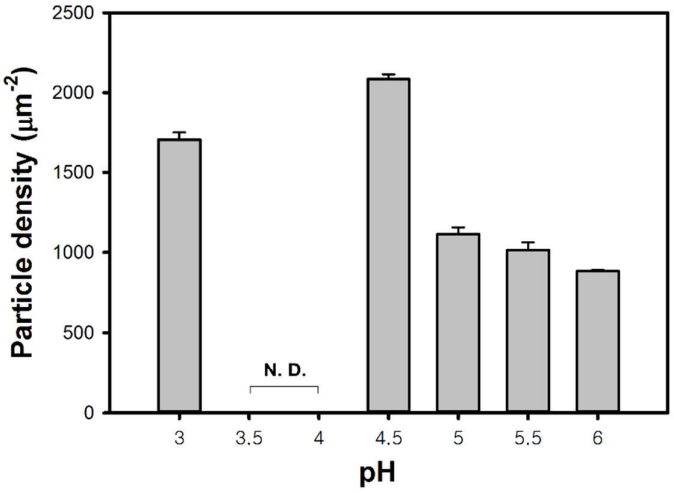

Figure S8. The particle density of αS-AuNPs adsorbed on PMMA substrate at various pHs. At pH 3.5 and 4.0, the particle density was not determined due to the agglomeration of αS-AuNPs.

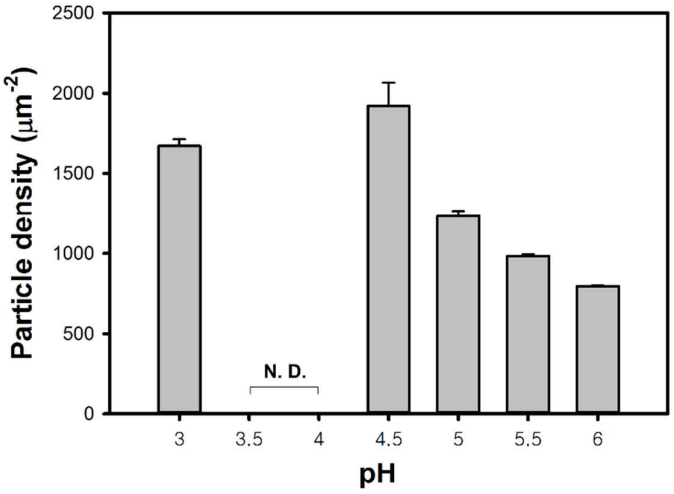

Figure S9. The particle density of αS-AuNPs adsorbed on GaAs substrate at various pHs. At pH 3.5 and 4.0, the particle density was not determined due to the agglomeration of αS-AuNPs.

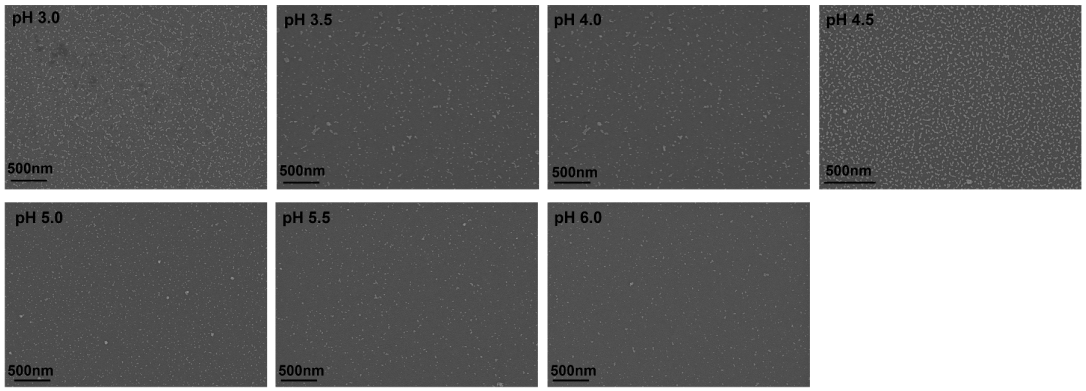

Figure S10. SEM images of the citrate-capped AuNPs adsorbed onto SiO_2 wafer at various pHs.

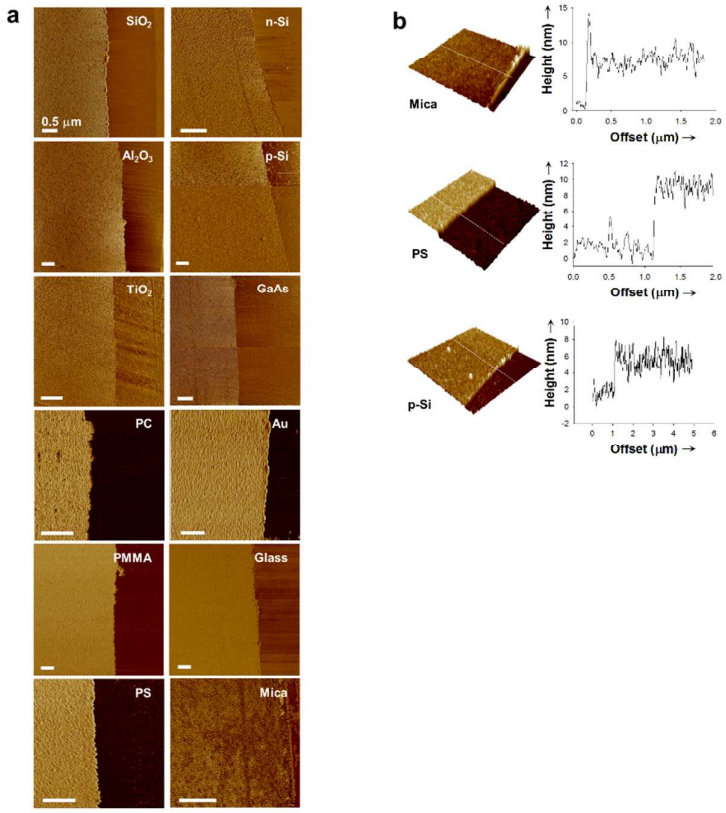

Figure S11. AFM analyses of the αS-AuNP single-layers adsorbed on various substrates. (a) AFM phase images of the αS-AuNP monolayers on various material surfaces: oxides (SiO_2, Al_2O_3, TiO_2), polymers (PC, PMMA, PS), semiconductors (n-Si, p-Si, GaAs), metal (Au), ceramic (glass), and natural mineral (mica). (b) AFM 3-D images and height profiles of the αS-AuNP monolayers on mica, PS, and p-Si.

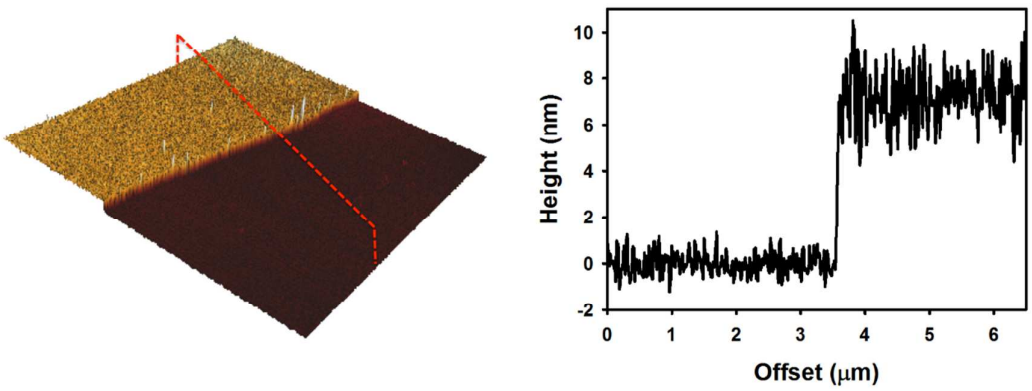

Figure S12. Height profile of the αS-AuNP single layer adsorbed onto SiO_2 wafer measured with Nanowizard® Sense AFM and Super Sharp tip.

Figure S13. Schematic representation of the αS-AuNP single layer and the residual α-synuclein molecules on the surface after scrapping off the layer with a PET stick.

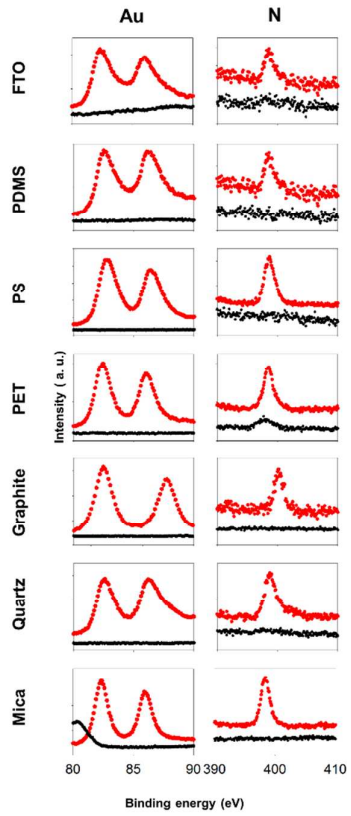

Figure S14. XPS measurements of the αS-AuNP single-layers on the substrates of FTO, PDMS, PS, PET, graphite, quartz, and mica. XPS spectra are provided to show the Au 4f doublet (left column) and the N 1s (right column) peaks.

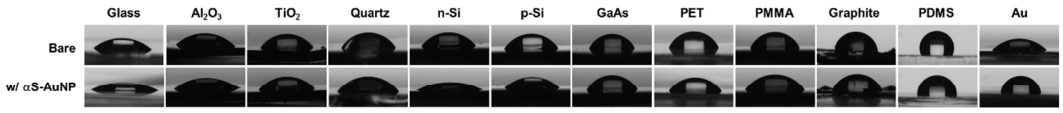

Figure S15. Water contact angles. Water droplet images are shown to assess contact angles on the surfaces of glass, Al_2O_3, TiO2, quartz, n-Si, p-Si, GaAs, PET, PMMA, graphite, PDMS, and Au in the absence or presence the αS-AuNP monolayer coat.

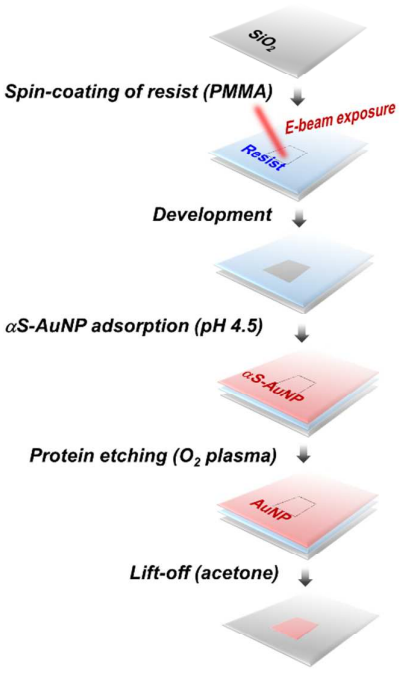

Figure S16. Schematic representation of a procedure for the AuNP two-dimensional (2-D) patterning. The protocol consists of SiO_2 substrate preparation, spin-coating of resist, e-beam exposure, development, αS-AuNP adsorption, O_2 plasma treatment, and lift-off step.

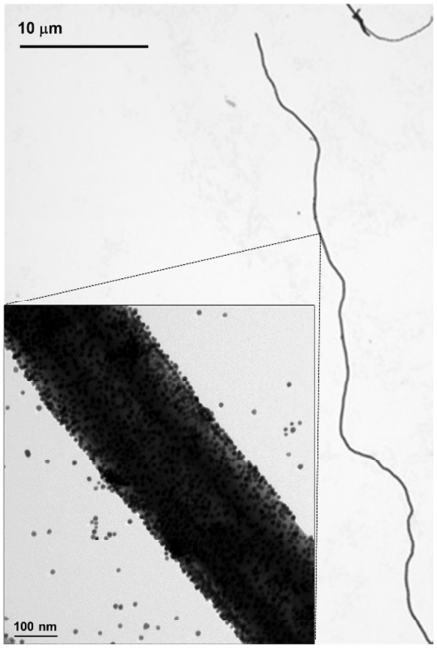

Figure S17. TEM image of the CNF decorated with AuNPs. High-magnification image is provided in inset.

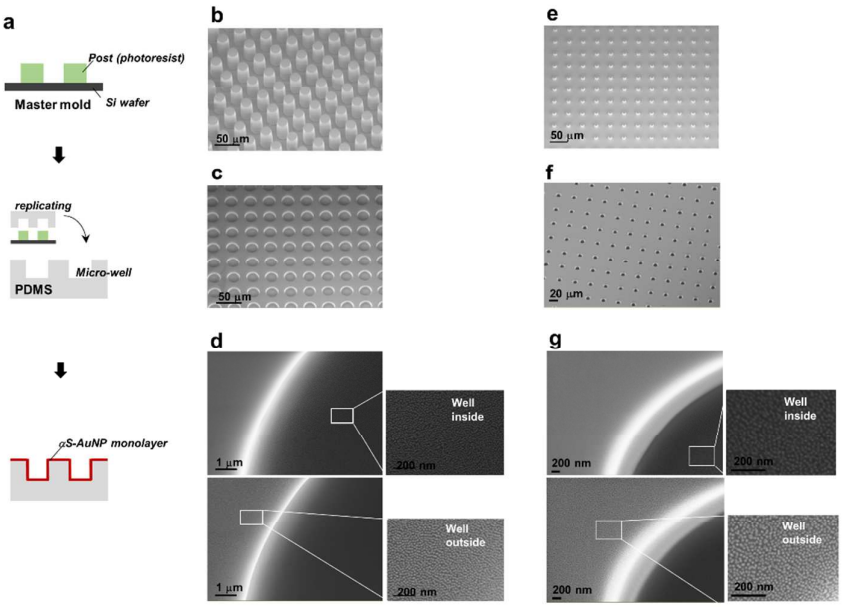

Figure S18. αS-AuNP single-layer coating on micro-structured surfaces. (a) Schematic illustration for the procedure of αS-AuNP single-layer adsorption onto PDMS micro-structured surface. After photo-lithography step, the resulting 3-D patterns of cylindrical post array (photoresist, SU-8 5) on Si wafer serves as a master mold for replicating PDMS micro-well structures, on which αS-AuNP monolayer is produced. (b) SEM images showing the master mold with a post array (post width = 20 μm; height = 30 μm) with separation distance of 20 μm. (c) SEM images of PDMS micro-well array (well width = 20 μm; depth = 30 μm) with separation distance of 20 μm. (d) SEM images focused on αS-AuNP monolayer on bottom surface inside a well (up) and upper surface outside a well (down). High-magnification images of the surfaces are also presented. (e) SEM images showing the master mold with a post array (post width = 10 μm; height = 10 μm) with separation distance of 20 μm. (f) SEM images of PDMS micro-well array (well width = 10 μm; depth = 10 μm) with separation distance of 20 μm. (g) SEM images focused on the αS-AuNP monolayer on bottom surface inside a well (up) and upper surface outside a well (down). High-magnification images of the surfaces are also presented.

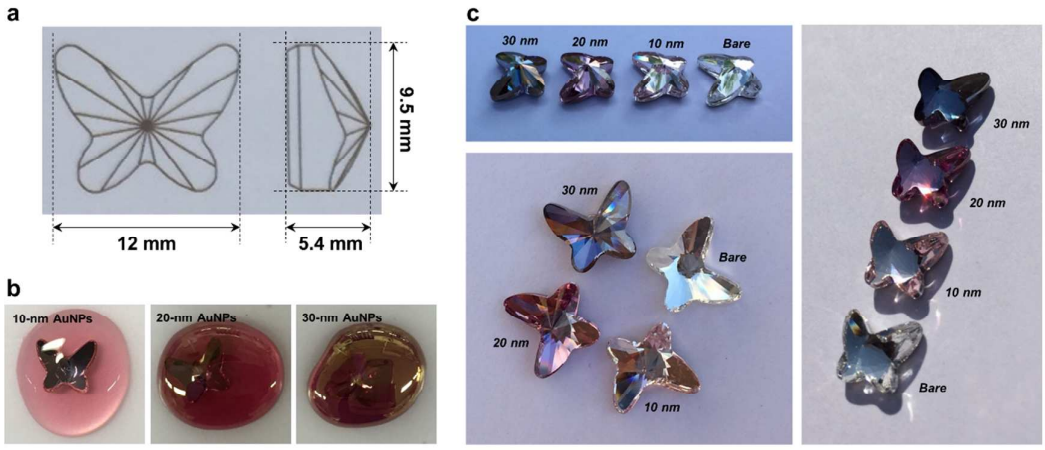

Figure S19. αS-AuNP single-layer coating on the surfaces of three-dimensional (3-D) macro objects. (a) Schematic diagrams showing the structure of butterfly-shaped glass crystal with the front- (left) and side-view (right). (b) Optical images of the crystals immersed in the solution of αS-AuNP$_{10nm}$ (left), αS-AuNP$_{20nm}$ (middle), and αS-AuNP$_{30nm}$ (right). (c) Optical pictures of glass crystals taken at different angles showing discriminative colors of white (bare crystal), light pink (αS-AuNP$_{10nm}$-coated crystal), red (αS-AuNP$_{20nm}$-coated crystal), and blue (αS-AuNP$_{30nm}$-coated crystal).

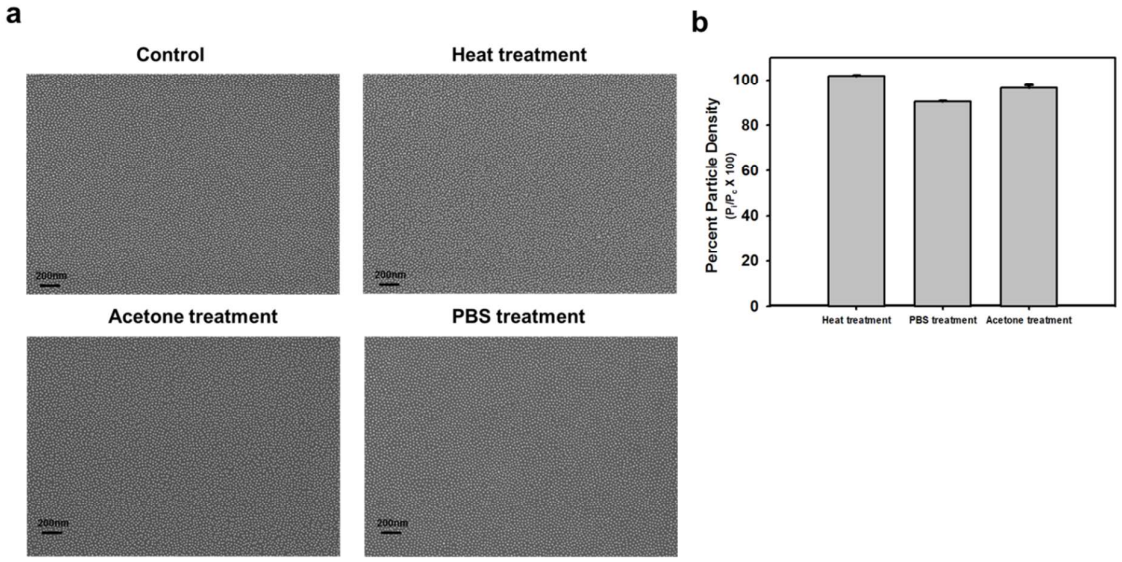

Figure S20. Stability of the αS-AuNP single-layer coat on Si/SiO_2 wafer. (a) SEM images of αS-AuNP single-layer on Si/SiO_2 wafer before and after the treatments indicated. (b) Percentage of particle density compared to the pristine αS-AuNP monolayer on Si/SiO_2. P_i, number of particles on SiO_2 surface after the treatments; P_c, number of particles on SiO_2 surface before the treatments

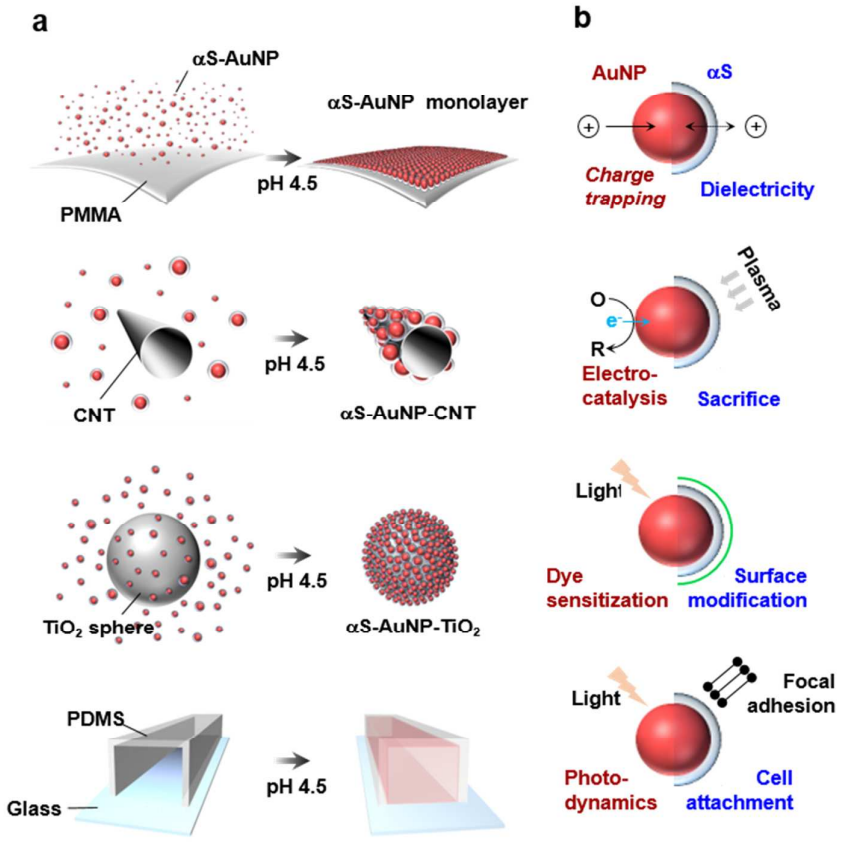

Figure S21. High-density single-layer of αS-AuNPs onto diverse substrates and their roles. (a) Schemes representing adsorption of close-packed αS-AuNP single-layer onto four different types of material's surface: PMMA layer (top), CNT (second top), TiO_2 microsphere (third top), and PDMS/glass microchannel (bottom). Change in pH is indicated by black arrows. (b) Drawings for multiple roles of αS-AuNPs. Four different modes of the conjugate's functions are schemitized for the inside AuNP/the out-layered αS proteins: charge trapping/dielectricity (top), electro-catalysis/scarificing (second top), dye-sensitization/surface modification (third top), and photo-dynamics/cell attachment (bottom).

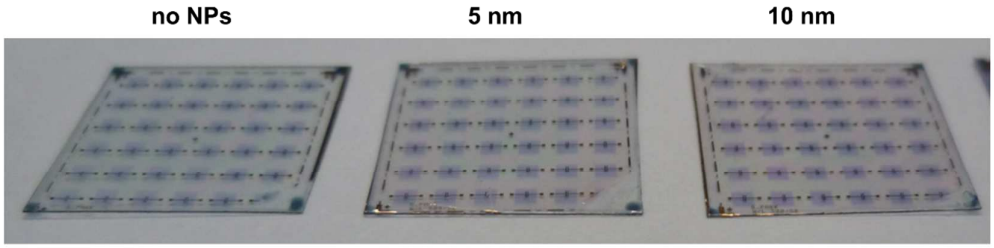

Figure S22. Optical images of organic field-effect-transistor (FET) memory with no NPs (left), αS-AuNP$_{5nm}$ (middle), or αS-AuNP$_{10nm}$ (right). The αS-AuNP memory devices are pink-transparent.

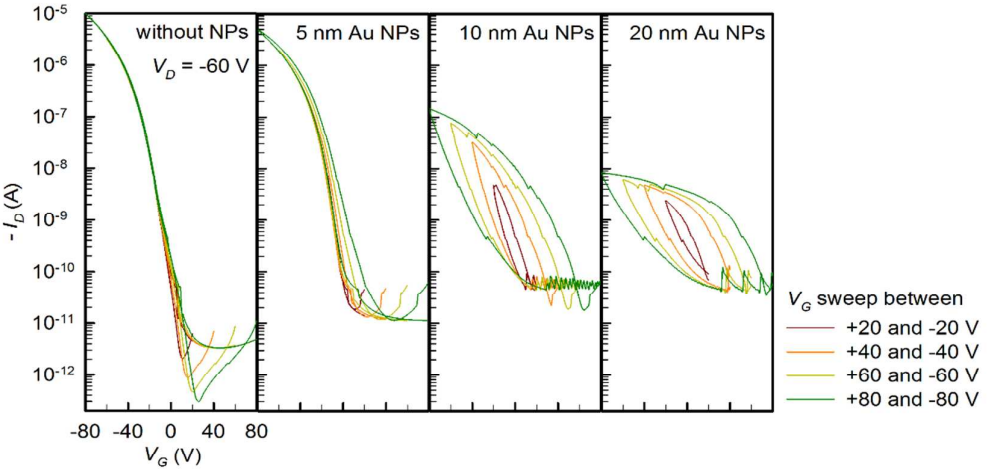

Figure S23. Transfer characteristics of FET memory without αS-AuNP and with αS-AuNP$_{5nm}$, αS-AuNP $_{10nm}$, or αS-AuNP $_{20nm}$. V_G sweep ranges were +20 to -20 V (brown), +40 to -40 V (orange), +60 to -60 V (light green), and +80 to -80 V (green).

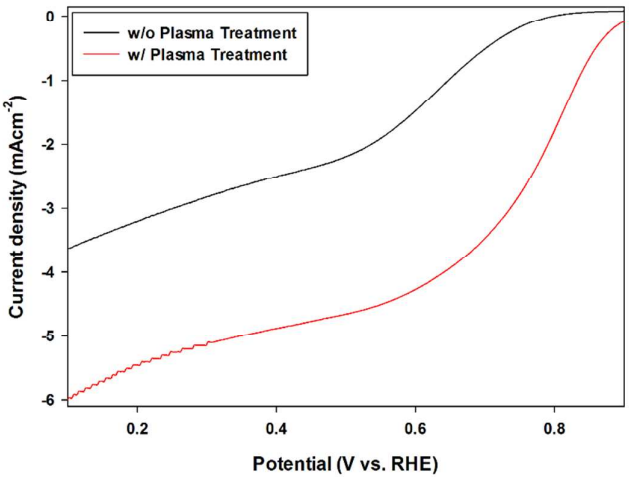

Figure S24. Line-sweep voltammetry (LSV) curves for oxygen reduction reaction (ORR) of the αS-AuNP-CNT complex without (black) or with (red) O_2 plasma treatment.

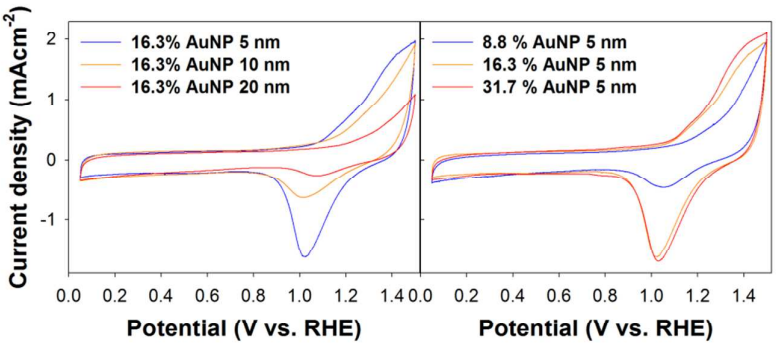

Figure S25. CV curves of ORR for the plasma-treated αS-AuNP-CNT complexes containing either different proportions of AuNPs [left graph; $AuNP_{5nm(8.8\ Au\ wt\%)}$-CNT (blue line), $AuNP_{5nm(16.3wt\%)}$-CNT (orange), and $AuNP_{5nm(31.7Au\ wt\%)}$-CNT (red)] or different sizes of the particles [right graph; $AuNP_{5nm(16.3wt\%)}$-CNT (blue line), $AuNP_{10nm(16.3wt\%)}$-CNT (orange), and $AuNP_{20nm(16.3wt\%)}$-CNT (red)].

Figure S26. Optical image of the αS-AuNP-TiO_2 solution.

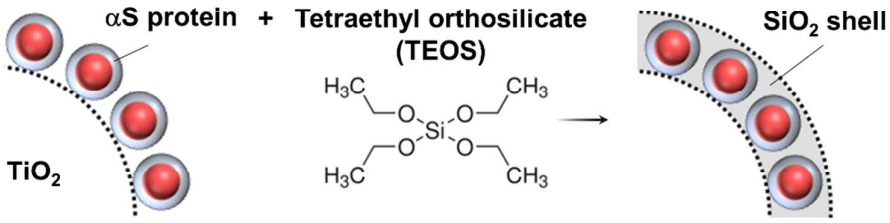

Figure S27. Diagram showing a reaction of αS protein with tetraethyl orthosilicate (TEOS) to form outer SiO_2 shell.

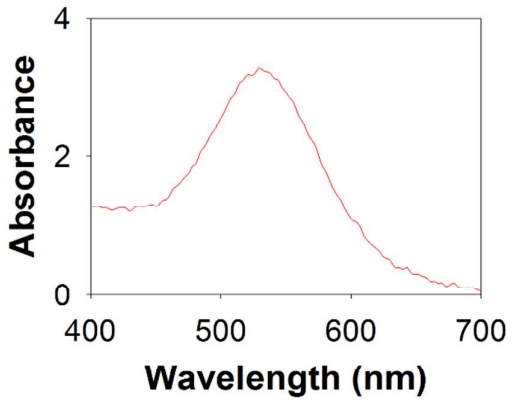

Figure S28. Surface plasmon resonance (SPR) spectrum of the αS-AuNP single-layer on glass.

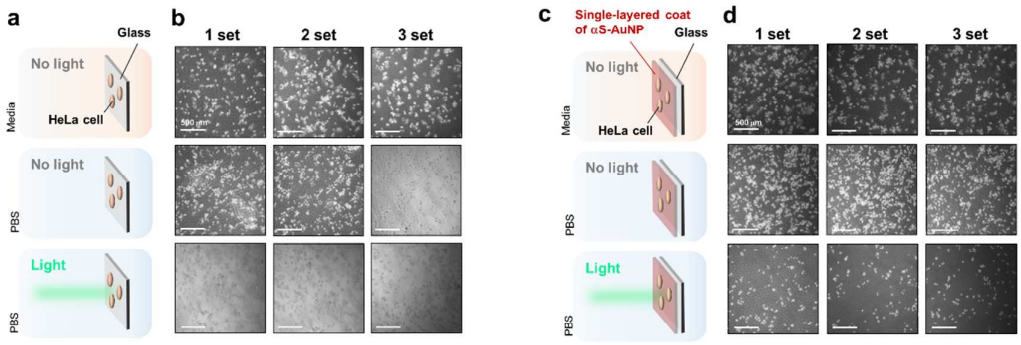

Figure S29. HeLa cell detachment from the glass (a and b) without and (c and d) with αS-AuNP coat upon a light illumination at 530 nm. (a) Schematic representation of HeLa cells on a bare glass in culture medium without light (top), PBS without light (middle), and PBS with light (bottom). (b) Microscopic optical images of HeLa cells on the bare glass in triplicated experiments under the conditions of culture medium without light treatment (top raw), PBS without light (middle raw), and PBS with light exposure (bottom raw). (c) Schemes of HeLa cells on the αS-AuNP-coated glass in culture medium without light (top), PBS without light (middle), and PBS with light (bottom). (d) Microscopic optical images of HeLa cells on the αS-AuNP-coated glass in triplicated experiments under the conditions of culture medium without light exposure (top raw), PBS without light (middle raw), and PBS with light (bottom raw).

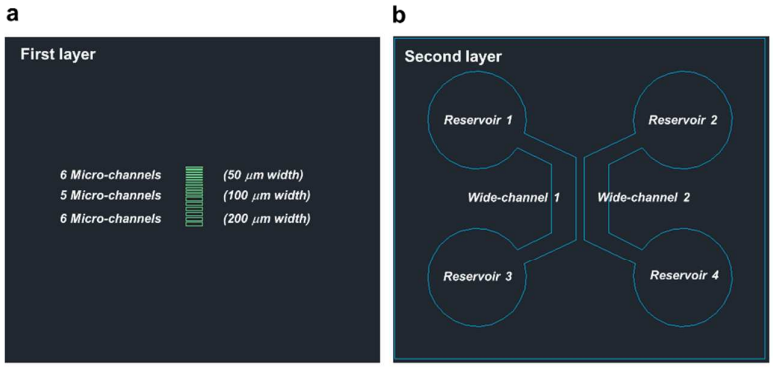

Figure S30. CAD design for the micro-fluidic device. (a) Designs for the first layer of 17 micro-channels and (b) the second layer of 2 wide-channels and 4 reservoirs.

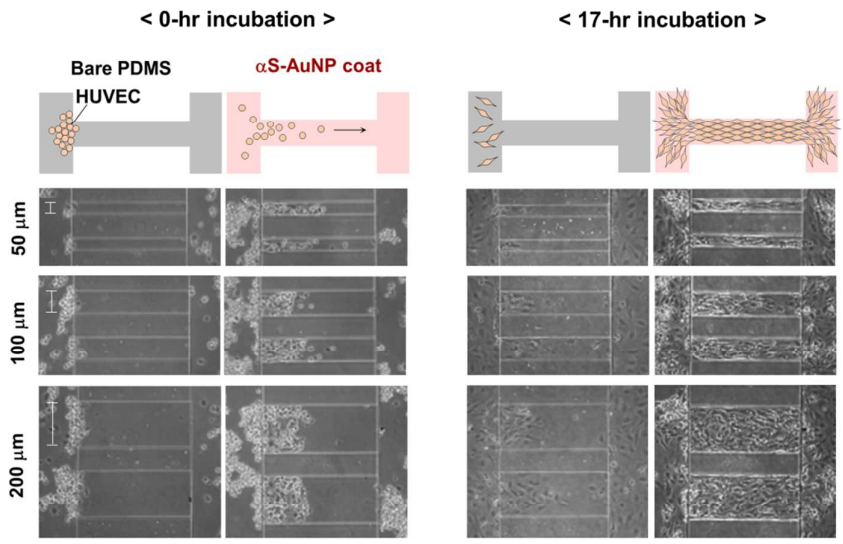

Figure S31. Drawings (first row) and optical microscope images of HUVECs in micro-channels with the width of 50 μm (second row), 100 μm (third row), and 200 μm (fourth row). Data sets for the 0-hr culture of HUVECs in the PDMS without (first column) and with αS-AuNPs coated (second column) are provided. The other sets for the 17-hr culture of HUVECs in the PDMS without (third column) and with the αS-AuNPs (fourth column) are also provided.

Table S1. Evaluation of water contact angles of various substrates coated with αS-AuNP single-layer.
θ_{adv} and θ_{stat} are advancing and static contact angles, respectively.

	Bare surface θ_{adv} (θ_{stat})	αS-AuNP coated surface θ_{adv} (θ_{stat})
PMMA	71.6 (66.5)	63.7 (54.9)
PC	80.9 (75.5)	62.3 (58.3)
PS	88.0 (78.2)	65.5 (60.6)
PDMS	112.3 (102.9)	93.5 (88.8)
Fluorinated wafer	106.6 (95.2)	78.2 (71.7)
PET	73.7 (66.2)	66.3 (55.6)
SiO_2	<10	39.7 (24.5)
FTO	29.7 (27)	53.3 (48.6)
Mica	<10	67.9 (56.4)
Au	52.1 (40.1)	59.3 (46.5)

References

(1) Paik, S. R.; Lee, J.-H.; Kim, D.-H.; Chang, C.-S.; Kim, J. Aluminum-Induced Structural Alterations of the Precursor of the Non-Aβ Component of Alzheimer's Disease Amyloid. *Arch. Biochem. Biophys.* 1997, *344*, 325-334.

(2) Xia, Y. N.; Whitesides, G. M. Soft Lthography. *Angew. Chem. Int. Ed.* 1998, *37* (5), 550-575.