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Electronic Supplementary Information

A new mussel-inspired polydopamine phototransistor with high photosensitivity: signal amplification and light-controlled switching properties

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Experimental Section

1. Materials and Measurements

The PDA patterning was obtained by using stainless-steel shadow masks with a thickness of 180 μm produced by laser beam machining and electrolytic polishing from Frontier Co., Korea. Si substrates with a thermally grown oxide layer were purchased from Buysemi Co., Korea. The PDMS, Sylgard 184 kit, was obtained from Dow Corning and (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (fluorinated silane) was supplied by United Chemical Technologies, USA. All of the other chemicals were purchased from Aldrich and used without further purification. Scanning electron microscopy (SEM, JEOL JSM7000F FESEM) operating at 15 kV was used to determine the size and thickness of the PDA thin film. Atomic force microscope (AFM) images were obtained in air using a Digital Instruments Nanoscope III (Veeco, USA) in the tapping mode. Hall effect measurements were performed using an Ecopia HMS-3000 system and the PDA thin films were deposited on glass substrate for the measurement. The electrical properties of the PDA-OPT were measured using a HP 4145B semiconductor parameter analyzer (Hewlett Packard). During

the measurement, the samples were kept at room temperature in an ambient atmosphere. A halogen lamp (12V, 100W) attached to the microscope of the probe station was used as the source of visible light. Raman spectra were measured using a Micro-Raman spectrometer (Renishaw) with a 514.4 nm line of argon laser as an excitation source. The capacitance-voltage characteristics were measured at frequencies of 1 MHz by an Agilent E4980A Precision LCR Meter in conjunction with a computer controlled system. X-ray diffraction (XRD) patterns of the PDA thin films deposited on SiO_2 substrate were measured with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, in the θ–2θ scanning mode at 30 kV and 40 mA by using Cu-$K\alpha$ radiation (λ = 1.5405 Å). Absorption spectrum of the PDA films was measured using a UV/Vis spectrophotometer (Schimadze UV-3600).

2. Fabrication of PDMS shadow masks

Figure S1 schematically illustrates the fabrication procedure of flexible PDMS shadow masks by a replica molding technique and their utilization as solution and vapor resists. The pristine stainless-steel shadow masks with a thickness of 180 μm were used to prepare the flexible PDMS shadow masks. The metal mask has rectangle holes with dimensions of 500 μm × 1000 μm. A 5 mm-thick flat PDMS plate prepared using a Si wafer as a template was attached to one side of the metal mask. Here, the array of discrete holes formed through the metal shadow masks functioned as a primary master. This primary master was treated with oxygen plasma (Harrick, 30 W) for 2 min, then coated with fluorinated silane under reduced pressure for 30 min. First, the PDMS mold was prepared by pouring a mixture of the PDMS prepolymer and curing agent (10 : 1 by weight) onto the primary master. The resulting PDMS mold had a thickness of 5 mm.

The secondary PDMS master was prepared by placing the upper side of the first PDMS mold onto a clean glass plate, treated with oxygen plasma and fluorinated SAMs, followed by

the PDMS molding conditions described above. To produce the flexible PDMS shadow mask, a mixture of the PDMS prepolymer and curing agent were poured on the secondary master, and the sample was placed in a desiccator under a reduced pressure for 1 h to remove the gas bubbles entrained between the first PDMS mold and glass plate. After curing the prepolymer inserted PDMS-on-glass samples in a conventional oven at 70 °C for 1 h and cooling down to room temperature, the flexible PDMS shadow mask was carefully separated from the first PDMS mold on the glass plate by tweezers. The prepared PDMS shadow masks were washed with acetone and dried in air. The flexible PDMS shadow mask with a thickness of 180 μm produced an array of rectangular holes on the mask, which were used as resists in the PDA thin film patterning.

3. Deposition of PDA Thin Film on SiO_2 Substrate

The substrates used for the TFT device consisted of thermally grown SiO_2 with a thickness of 300 nm on a doped silicon substrate with dimensions of 2×2 cm^2. In order to remove the trace organic contaminants, the substrates were cleaned with a piranha cleaning solution, 3:1 H_2SO_4/H_2O_2, for 30 min, and then rinsed with deionized water (resistivity of 18 MΩ) and isopropyl alcohol. The substrates were dried in oven, and retreated with oxygen plasma. To prepare the 0.01 M THAM buffer at a pH of 8.5 as a solvent for the PDA solution, a stock solution of 0.1 M THAM buffer at a pH of 7.4 was used. The stock solution was prepared by dissolving 1.21 g of THAM (99.0 %, Aldrich) in deionized water, and then the pH of the solution was adjusted to 7.4 using hydrochloric acid (37.0 %, Aldrich). The stock solution was diluted with deionized water to make the 0.01 M THAM buffer solution. The pH of the diluted solution was adjusted with a 0.1 M sodium hydroxide (97 %, Aldrich) solution to 8.5. The PDA solution was prepared by polymerizing the DA (0.24 g, 42 mM, Aldrich) that dissolved in 30 mL of the 0.01 M THAM buffer at a pH of 8.5. Patterned PDA thin films

were prepared on SiO_2/Si substrates by solution deposition using the PDMS shadow mask, as shown in Figure S1. The SiO_2/Si substrates covered by the PDMS masks were immersed in a 100 mL beaker filled with 30 mL of the PDA solution at room temperature for 1 h under an O_2 gas stream. After deposition of the PDA thin film, the substrate was removed and washed with deionized water and 2-propanol, dried under a stream of nitrogen. Then, the PDMS shadow mask was carefully peeled off from the substrate using a pair of tweezers. The film thickness variations of the PDA layer on SiO_2/Si substrates depending on a deposition time are shown in Figure S2.

4. Deposition of Source and Drain Electrodes on Patterned PDA Thin Film

The steel shadow mask with dimensions of 450 μm × 450 μm was aligned under a microscope onto the centre of the prepared PDA pattern on the SiO_2/Si substrates. Silver metal was thermally evaporated to a thickness of 100 nm at 3 Å per second through the holes of the PDMS shadow mask.

5. MIS Device Fabrication for Capacitance-Voltage Characteristics Measurement

For the capacitance-voltage characteristic measurements, PDA-based MIS devices were fabricated on a p-type silicon substrate ($N_d = 1.0 \times 10^{15}$ cm^{-3}, 1–10 Ω·cm) by thermal evaporation of gold (50 nm thickness) using a metal shadow mask. The silicon substrates with dimensions of 2 × 2 cm^2 were cleaned with a piranha cleaning solution, 3:1 H_2SO_4/H_2O_2, for 30 min, rinsed with deionized water (resistivity of 18 MΩ) and isopropyl alcohol. The substrates were dried in oven, and retreated with oxygen plasma. The PDA thin films as an organic dielectric material in a MIS device were deposited on the silicon substrate by immersion in a 70 mL vial filled with 30 mL of a PDA solution at room temperature under an O_2 gas stream for 1 h and 12 h, respectively. After deposition of the PDA thin film, the

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substrate was removed from the solution, washed with deionized water and 2-propanol, and then dried under a stream of nitrogen. The thicknesses of the PDA films were 30 nm for 1h and 300 nm for 12 h deposition, respectively. The C-V measurements were performed for the Au/pSi, Au/PDA(30nm)/pSi and Au/PDA(300nm)/pSi devices, respectively (Figure S5).

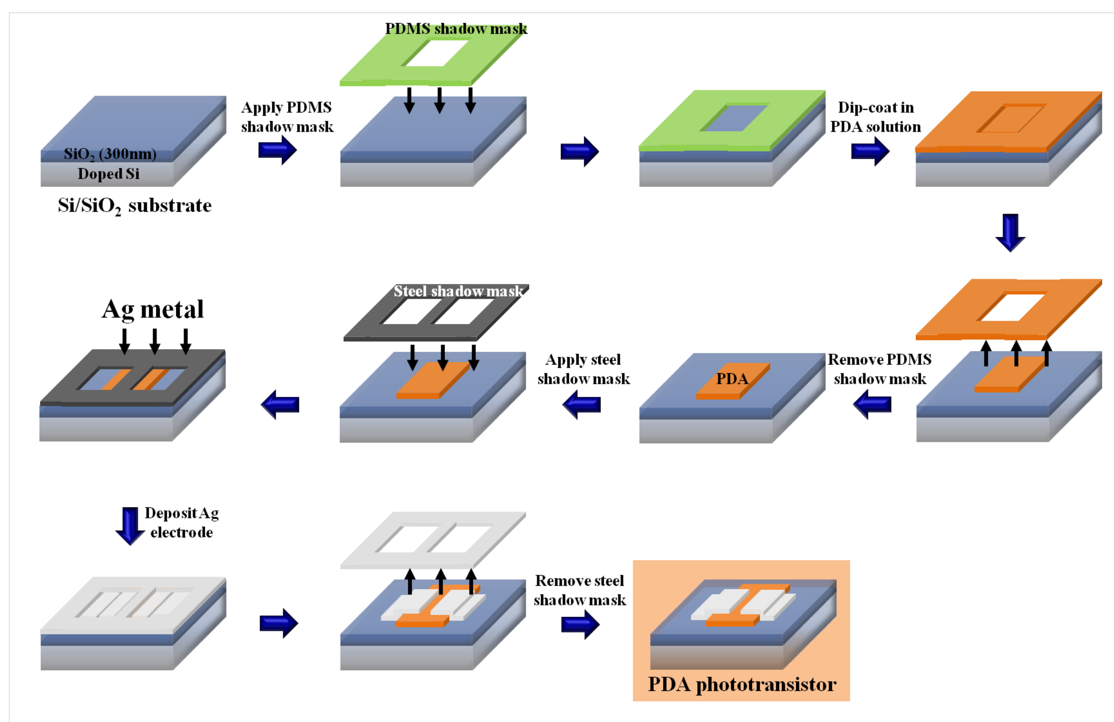

Figure S1. Schematic representation showing the fabrication procedures for fabricating PDA-based OPT using a flexible PDMS shadow mask prepared by twice replica molding.

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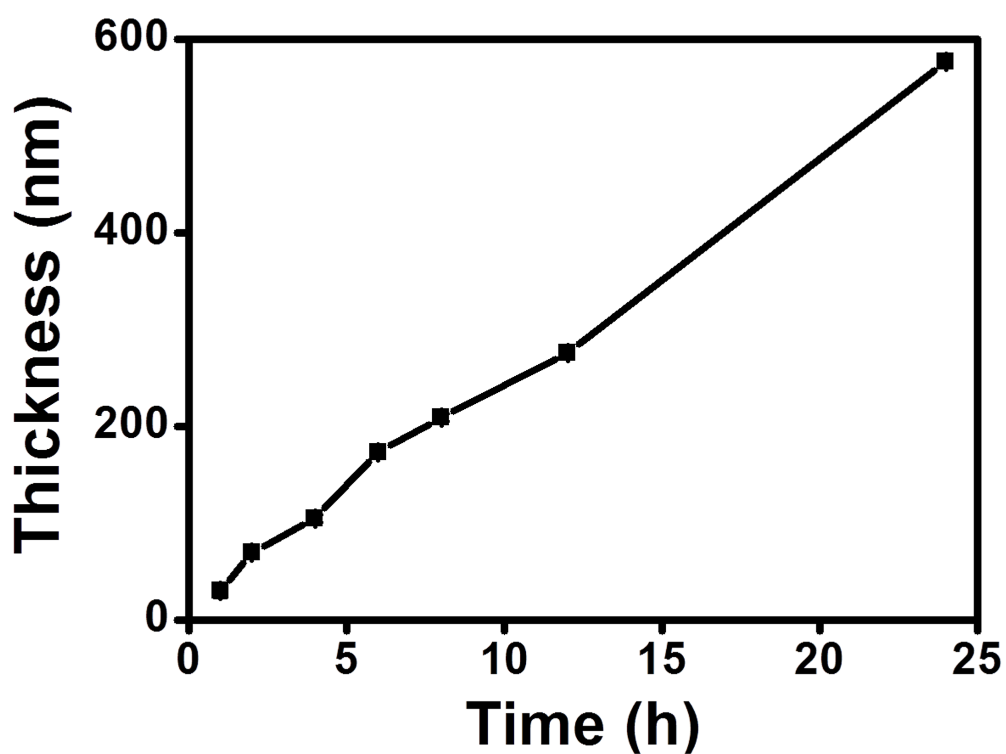

Figure S2. Film thickness of PDA layer deposited on SiO_2/Si substrate by dip-coating under O_2 gas stream showing the linear increment of film thickness depending on deposition time, in which the film thickness linearly increased from 30 (± 6) nm for 1 h to 576 (± 3) nm for 24 h deposition and the growth rate was about 0.42 nm/min.

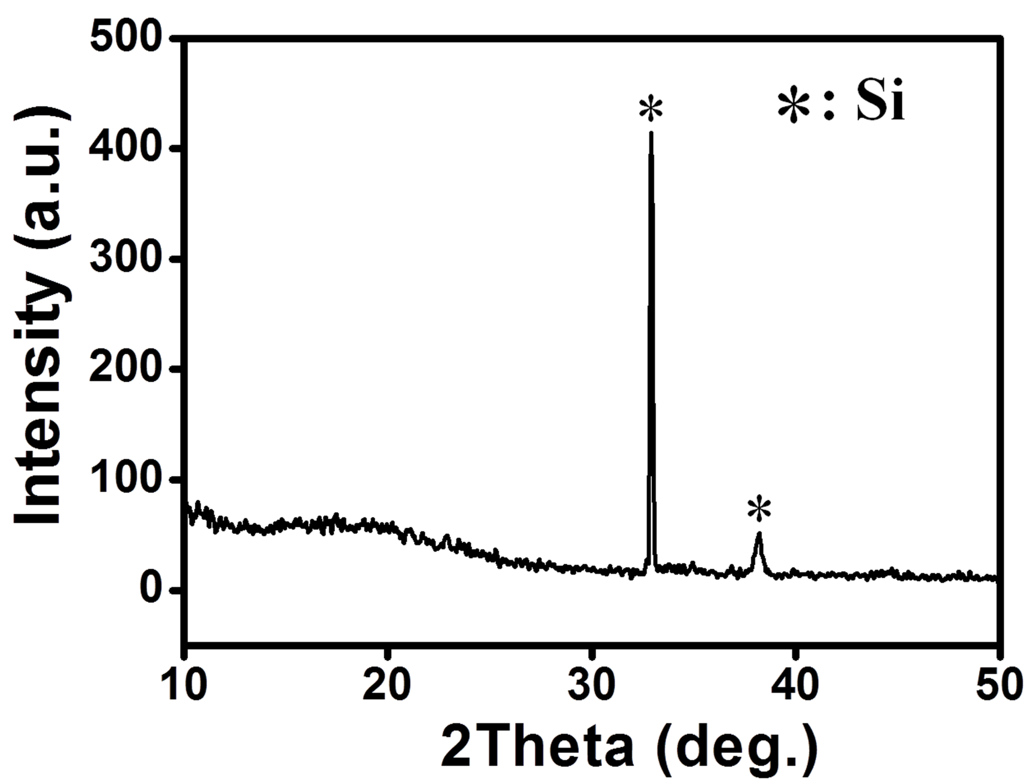

Figure S3. XRD data of O_2-induced PDA thin film (30 nm) deposited on SiO_2 substrate.

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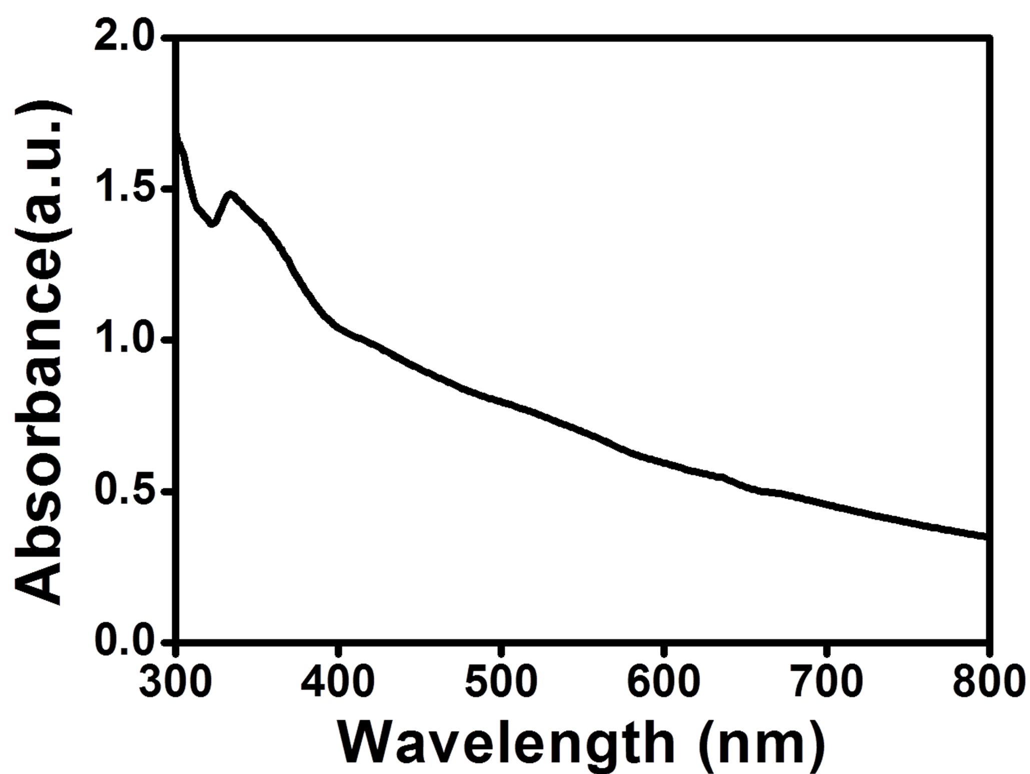

Figure S4. UV/vis absorption spectrum of the PDA thin film showing strong and broad absorption in UV and visible regions. The absorption band near 330 nm indicates the formation of intramolecular cyclized form.

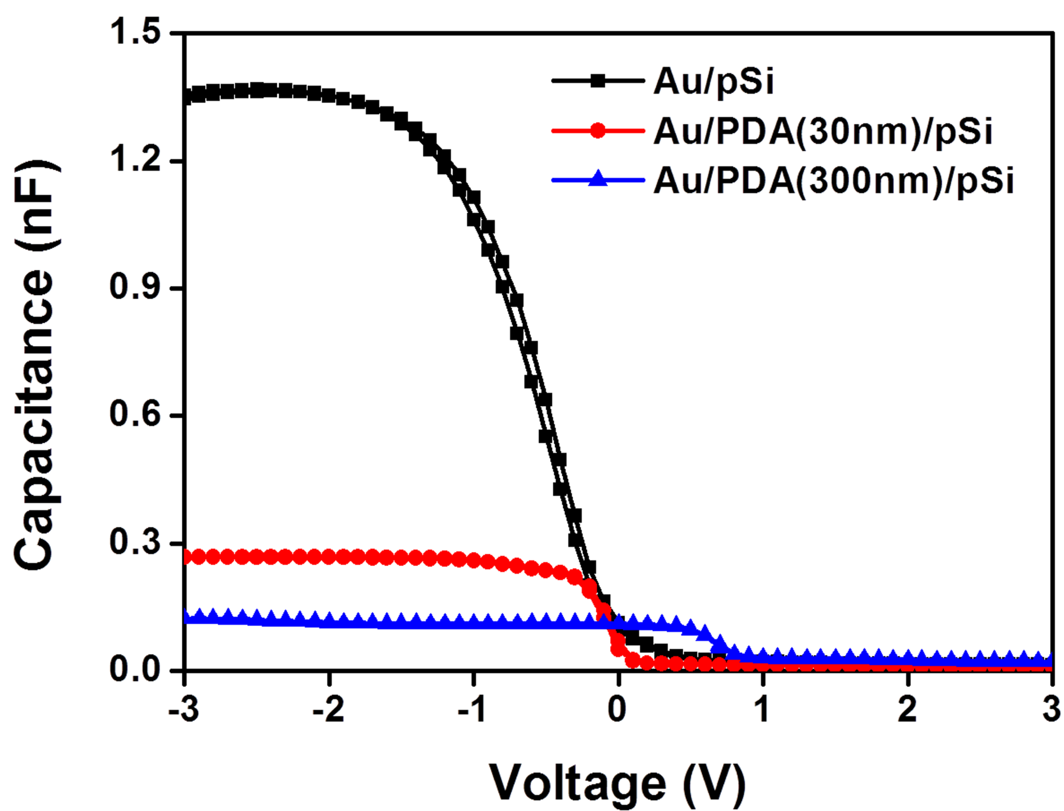

Figure S5. C-V characteristics of Au/pSi, Au/PDA(30nm)/pSi and Au/PDA(300nm)/pSi MIS devices measured at 1 MHz frequency, showing the lower accumulation capacitance for the thicker PDA thin film (300 nm).