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Supplementary Information

Long-term stable organic semiconductor photocathode-based photoelectrochemical module system for hydrogen production

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1. Materials and Preparation of Precursor Solutions

PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), EH-IDTBR (5,5'-[[4,4,9,9-tetrakis(2-ethylhexyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl]bis(2,1,3-benzothiadiazole-7,4-diylmethylidyne)]bis[3-ethyl-2-thioxo-4-thiazolidinone]), PTB7-Th (poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)]), and ZnO nanoparticle (NPs) were purchased from 1-Material. The PEDOT:PSS stock solution was filtered with a 0.45 μm PTFE syringe filter. EH-IDTBR and PTB7-Th were individually dissolved to 20 mg/ml in chlorobenzene (Sigma-Aldrich; ACS grade), and then mixed in a ratio of 1.5:1. The blended solution was stirred for over 30 min.

2. Fabrication of the organic photovoltaic (OPV) cells

Indium tin oxide (ITO) substrates were cleaned by sonication sequentially in the acetone, methanol, and isopropyl alcohol. To form the hydrophilic surface on the cleaned ITO substrate, UV–ozone treatment was carried out for 40 min. First, the PEDOT:PSS layer was spin-coated at 5000 revolutions per minute (rpm) for 30 s, and then it was annealed on a hot plate at 100 °C for 10 min. Next, the photoactive layer (PTB7-Th:EH-IDTBR) was spin-coated on the PEDOT:PSS layer at 3500 rpm for 40 s. Subsequently, ZnO NPs were spin-coated on the photoactive layer at 4500 rpm for 40 s. All spin coating processes were performed under ambient air conditions. Finally, the silver (Ag) top electrode (area: 5 mm × 5 mm, thickness: 190 nm) was deposited via a thermal evaporation process.

3. Fabrication of the organic semiconductor (OS)-based photoelectrochemical (PEC) device.

To fabricate Pt/Ti/Ag/OS photocathodes, we first spread and flattened the Indium–gallium eutectic alloy (EGaIn) (Sigma-Aldrich, 99.99% trace metal basis) on the Ag top electrode of as-fabricated OPV using a 1 ml syringe with a needle. Then, Ti foil (Sigma-Aldrich, 99.5% Ti foil, 0.25 mm) was covered on the EGaIn region. For the back contact, a copper (Cu) wire was utilized to connect to the exposed ITO region using silver paste. Thereafter, the entire device was passivated with an epoxy resin (Loctite, EA 9460, Henkel) to prevent electrical short-circuit by an electrolyte. For Pt decoration on the Ti foil, we followed the procedure in the previous work.[1] The Ti foil-passivated OS photocathode was immersed and stirred in the

K_2PtCl_4 solution (5.16×10^{-3} mol, 10 mL, deionized water) for 20 s and kept in the same solution for 40 s. For Pt/Ag/Os photocathode, we used the same method for Pt decoration without Ti foil passivation.

4. Fabrication of large-scale OS-based PEC module

The large-scale OS-based PEC module was fabricated through a parallel connection using twelve OS photocathodes. Twelve OS photocathodes were attached to the sliding glass and connected with a copper wire and silver paste. The entire device was passivated with an epoxy resin and decorated with the Pt NPs in the same way as fabrication of the OS photocathode.

5. Characterization of PEC performance

The PEC performance was measured using a potentiostat (Ivium-n-Stat, Ivium Technologies) with a standard three-electrode system under 0.5 M H_2SO_4 electrolyte (pH 1). The fabricated PEC device (OS photocathode), a Pt coil, and a saturated calomel electrode (SCE, E^0= 0.241 eV) were used as the working, counter, and reference electrodes, respectively. The applied potentials versus reference electrode were converted to the reversible hydrogen electrode (RHE) using the Nernst equation:

$$E_{RHE} = E_{SCE} + 0.059 \times pH + E^0_{SCE} = E_{SCE} + 0.059 \times pH + 0.241$$

where E_{SCE} is the experimentally measured potential vs. SCE. The calibrated light of a xenon lamp (Model 10 500, ABET Technology) illuminated the back of the OS photocathode with 1 Sun (AM 1.5G) intensity. The linear sweep voltammetry (LSV) was conducted at a scan rate of 50 mV s^{-1} with 10 mV intervals. For chronoamperometry (CA) measurement, a graphite rod was used as a counter electrode instead of a Pt wire to avoid unnecessary Pt deposition on the OS photocathode. The hydrogen yield of the OS photocathode was evaluated via the gas chromatography system (Agilent Tech 7820A, 5 A° molecular sieve column) using a thermal conductivity detector, and the Faradaic efficiency (FE) was calculated. The half-cell solar to hydrogen (HC-STH) efficiency of the photocathodes was calculated as follows:

$$HC-STH=\frac{|J_{ph}|\times E_{RHE}\times FE\%}{P}$$

where P is the intensity of illuminated light, and J_{ph} is the photocurrent density.

The outdoor PEC measurement of the large-scale OS-based module was performed from 11 am to 2 pm on August 12 at Gwangju Institute Science and Technology, while the intensity of real sunlight was measured for every minute using a silicon diode (91150-KG5 Reference Cell and Meter, Newport). The potentiostat (Ivium-n-Stat, Ivium Technologies) was connected to a large-capacity battery (KPC-PS300, KOKIRI) during the measurement. A standard three-electrode system was used with the large-scale module, a Pt coil, and an SCE as the working, counter, and reference electrodes, respectively. All electrodes were immersed in a 0.5 M H_2SO_4 electrolyte bath as shown in Figures 4a and 4d. The photocurrent was measured at 0 V versus reversible hydrogen electrode (V_{RHE}) by CA measurement.

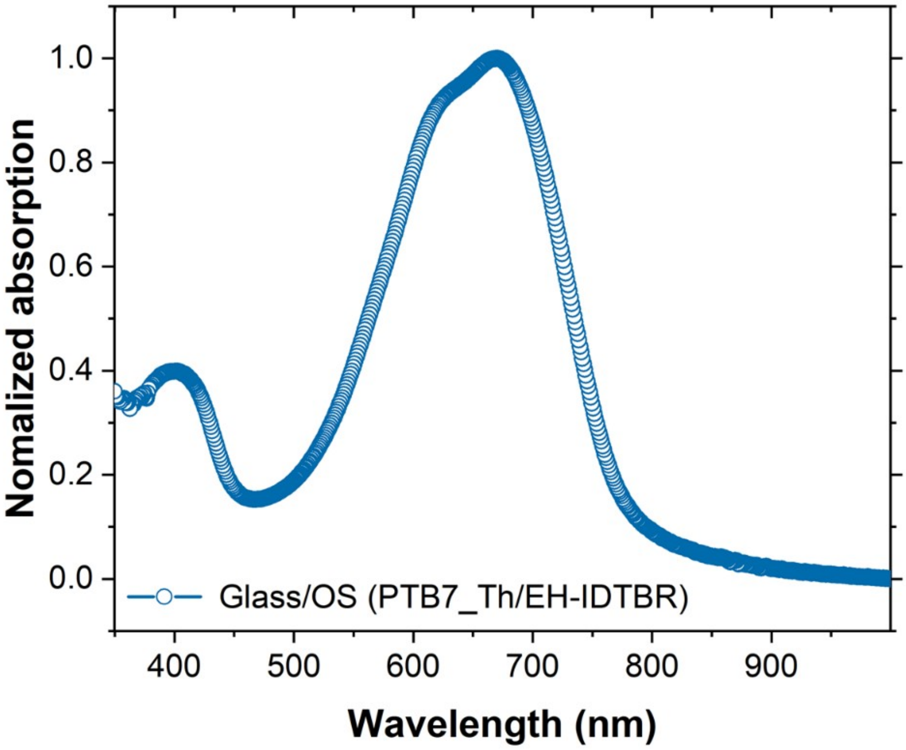

Figure S1. UV-vis absorption spectrum of OS/glass.

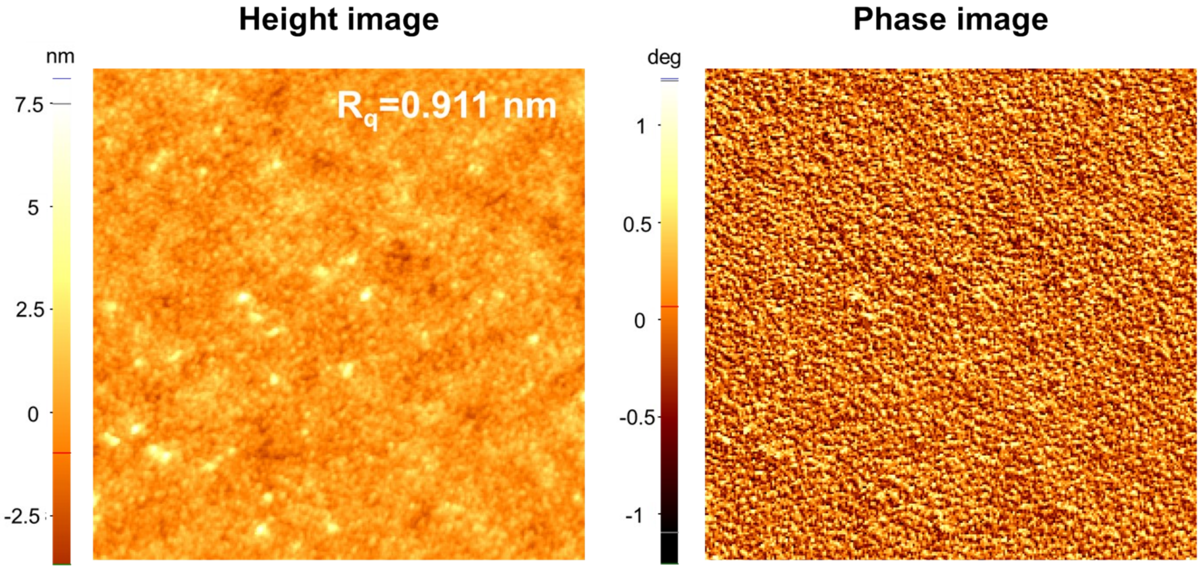

Figure S2. Atomic force microscope height and phase images (5 µm × 5 µm) of PTB7-Th/EH-IDTBR. The root mean square average of height deviation is 0.911 nm.

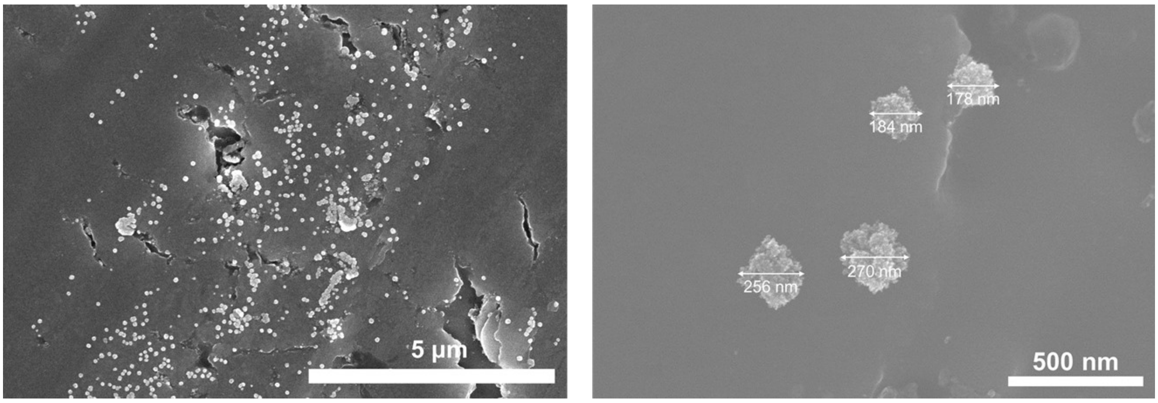

Figure S3. SEM images of Pt NPs on Ti foil. Pt nanoparticles are well dsipsered on the Ti foil. The size of Pt nanoparticles is 170~300 nm, approximately.

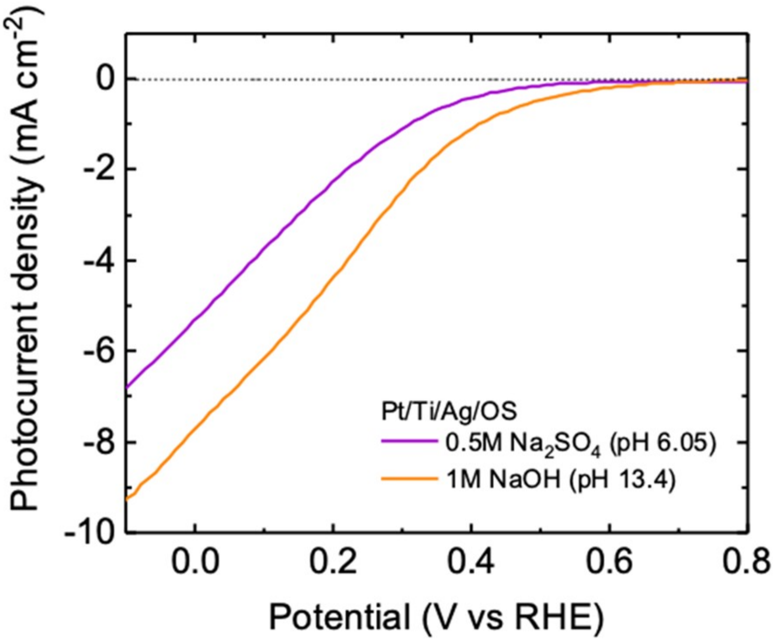

Figure S4. LSV curves of the Pt/Ti/Ag/OS photocathode under 0.5 M Na_2SO_4 (purple line) and 1 M NaOH (orange line).

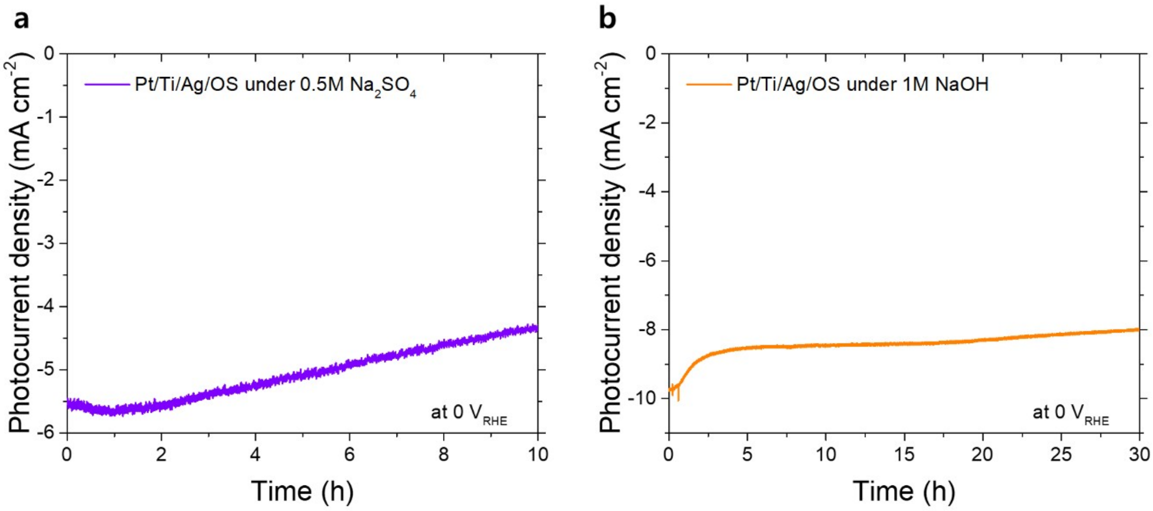

Figure S5. Chronoamperometry measurements of Pt/Ti/Ag/OS at 0 V_{RHE} (a) under 0.5M Na_2SO_4 and (b) under 1M NaOH.

References

[1] V. Andrei, R. L. Z. Hoye, M. Crespo-Quesada, M. Bajada, S. Ahmad, M. De Volder, R. Friend and E. Reisner, *Adv. Energy Mater.*, 2018, 8, 1801403.