Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Easy and green preparation of a graphene – TiO_2 nanohybrid using a supramolecular biomaterial consisted of artificially bifunctionalized proteins and its application for a perovskite solar cell

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Contents

1. General

Graphene was purchased from a commercial supplier (G-10L, EMJapan Co.,Ltd.) and used without further purification. CDT1 was synthesized according to our previous reports.[1] All other reagents were purchased from commercial suppliers (FUJIFILM Wako Pure Chemical Corporation, Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd, and Bio-Rad Laboratories, Inc.) and used without further purification. The centrifugation process was performed by a BECKMAN Optima TLX. The ultrasonication process was carried out by a BRANSON Digital sonifier S-450. A gel permeation chromatography (GPC) was performed by a GE healthcare HiPrep 26/60 Sephacryl S-300 High resolution. High performance liquid chromatography (HPLC) was carried out by a TOSOH LC-8020 equipped with a GE healthcare HiLoard 26/10 Q-Sepharose High Performance anion-exchanger column. A sodium dodecyl sulfate (SDS)-polyacrylamide gel electrophoresis (PAGE) was measured by Bio-rad PowerPac Basic. Mass spectrometry was performed using a Bruker Daltonics Autoflex2 spectrometer (MALDI-TOF). FE-SEM images were captured by a JEOL JSM-7400F. TEM images and electron energy-loss spectroscopy were obtained by a JEOL JEM-3100FEF. Raman measurements were performed by a JASCO NRS-2100 spectrophotometer. The UV/O_3 irradiation was carried out by a

SAMCO, Inc. UV-1. Fabrication processes under inert N_2 conditions was carried out in a UNICO Ltd. UL-1800A. Spin-coating processes were performed by a MIKASA Co., Ltd. MS-A100. Thermal evaporation processes were carried out an ULVAC KIKO Inc. VPC-410ST. The *I–V* measurements were carried out using by a Bunkoukeiki Co., Ltd. CEP-2000RR.

2. Biosynthesis, purification, and identification of CDT1

CDT1 was synthesized from *Escherichia coli* BL21(DE3) encoded with a pET-CDT1 plasmid. The pET-CDT1 plasmid was obtained by gene encoding from pET20b-NHBP-LiDps plasmid[1]. The encoded *Escherichia coli* BL21(DE3) was cultivated in LB medium with ampicillin at 37 °C for 24 h. The generated CDT1 (BL21(DE3)/pET-CDT1) was separated from the *E.coli* by using an ultrasonication process, followed by centrifugation at 6000 rpm for 5 min. Subsequently, the supernatant was heated at 60 °C for 20 min. After this period, the solution was centrifuged at 6000 rpm for 5 min. The solution containing CDT1 was purified by GPC. A 50 mM tris(hydroxymethyl)aminomethane-HCl (Tris-HCl) buffer at pH 8.0 with 150 mM sodium chloride (NaCl) was employed as an eluent solvent. CDT1 was further purified by HPLC. CDT1 obtained was identified by MALDI-TOF MS (Fig.S1) and Compute pI/Mw[2]. The purity of CDT1 was analyzed by the SDS PAGE (Fig. S2).

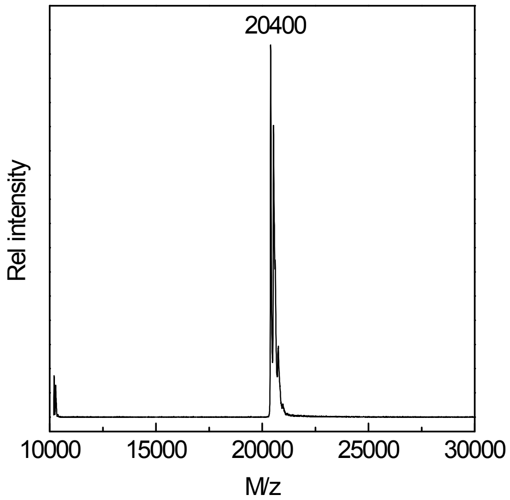


Fig. S1. MALDI-TOF MS spectrum of CDT-1.

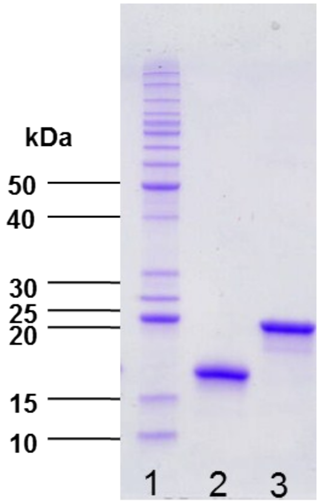


Fig. S2. SDS-PAGE image of 1) the BenchMark^{TM} protein ladder, 2) Listeria Dps, and 3) CDT-1.

Table S1**.** The protein sequence of CDT-1

MDYFSSPYYEQLFMKTINSVDTKEFLNHQVANLNVFTVKIHQIHWYMRGHFFTLHEKMDDLYSEF
NHBP-1
GEQMDEVAERLLAIGGSPFSTLKEFLENASVEEAPYTKPKTMDQLMEDLVGTLELLRDEYKQGIELT
DKEGDDVTNDMLIAFKASIDKHIWMFKAFLGKAPLEMRKLPDA
minTBP-1

3. Biomineralization of an iron oxide nanoparticle in CDT-1.

CDT1 (0.5 mg/mL) and ammonium iron(II) sulfate (1 mM) were mixed in a HEPES buffer (80 mM) at pH7.5. The mixture solution was incubated at 4 °C for 3 h, followed by centrifugation at 15000 rpm at 4 °C for 30 min. The supernatant containing CDT1 with the iron oxide nanoparticle was concentrated by centrifugal ultrafiltration at 30000rpm for 20h.

4. FE-SEM measurement

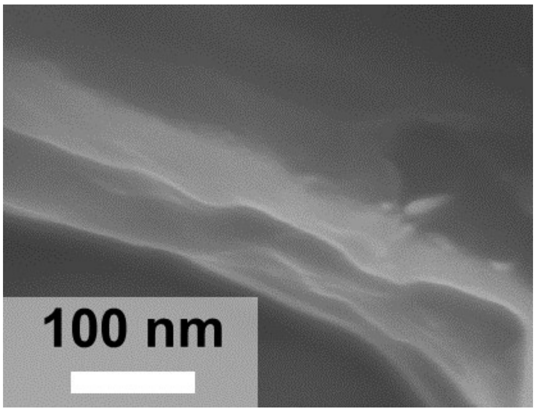
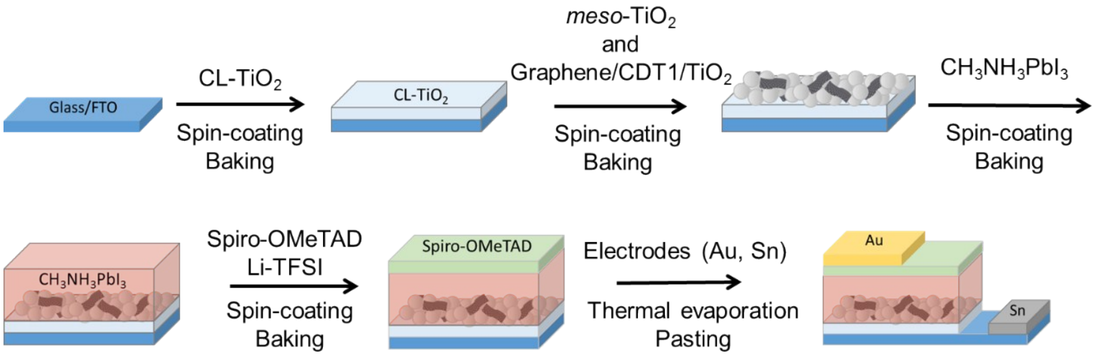


Fig. S3. A FE-SEM image of the graphene/CDT1 complex without the iron oxide core.

5. PSC fabrication process

The fabrication scheme of the PSC is illustrated in Fig. S3[3]. A FTO/grass substrate was washed with a nonionic detergent and acetone in an ultrasonic bath and treated by a UV/O_3 cleaner. A compact layer of TiO_2 (CL-TiO_2) was prepared on the FTO/grass substrate by a spin coating method (700 rpm for 8 s, 1000 rpm for 10 s, and 2000 rpm for 40 s). The substrate was then baked at 125 °C for 15 min. After this period, an ethanol solution of *meso*-TiO_2 (18wt%) and the graphene/CDT1/TiO_2 nanohybride (0 or

0.5wt%) was spin-coated on the CL-TiO_2, followed by drying at 125 °C for 5 min under ambient conditions. The substrate was then annealed at 450 °C for 1h. Subsequently, a perovskite layer was deposited onto the *meso*-TiO_2 layer by a continuous multi-stepped spin-coating method as follows. A mixture solution of dimethyl sulfoxide (DMSO) (71 μL) and *N*,*N*-dimethylformamide (DMF) (640 μL) (13/100, w/w) including lead (II) iodide (461 mg, 1 mmol) and methylammonium iodide (159 mg, 1 mmol) was dropped onto the substrate, followed by rotation of the substrate at 4000 rpm. After 6 s of rotation, diethyl ether (0.5 mL) was dropped onto the rotating substrate. The total rotation time for spin-coating was 25 s. Then, the substrate was baked at 2 steps (65 °C for 1 min, and 100 °C for 2 min) under inert (N_2) conditions. To fabricate a hole transport layer (HTL), a precursor solution was prepared by mixing of chlorobenzene (240 μL) including Spiro-MeOTAD (17 mg, 0.013mmol) and 4-*tert*-butylpyridine (6.36 μg, 0.05 μmol) and acetonitrile (4.2 μL) containing lithium bis(trifruoromethanesulfonyl)imide (5.6mg,19.5 μmol). The mixture solution (50 μL) was dropped onto the perovskite layer and spin-coated at 1000 rpm for 4 s and subsequent 4000 rpm for 26 s. After this period, a gold electrode was deposited on the HTL by thermal evaporation. Finally, a tin paste was pasted on the FTO electrode.



Scheme S1 Fabrication scheme of the PSC with the graphene/CDT1/TiO_2 nanohybrid.

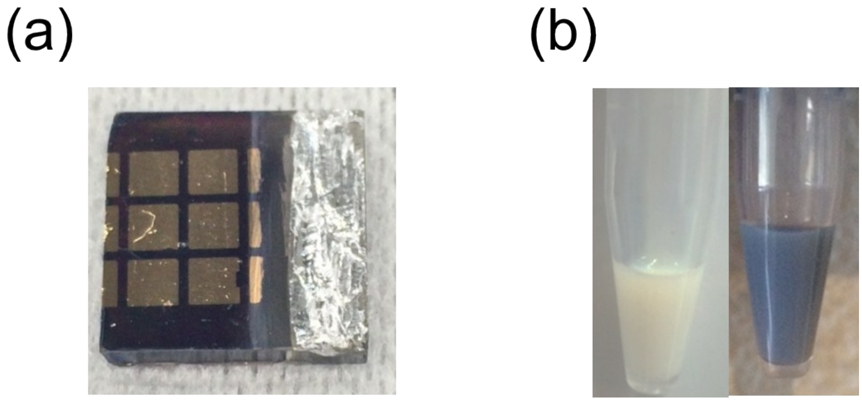


Fig. S4 Photographs of (a) the fabricated PSC and (b) the homogenous ethanol solutions including the *meso*-TiO_2 paste with (right) or without (left) and the graphene/CDT1/TiO_2 nanohybrid.

6. PSC characteristics

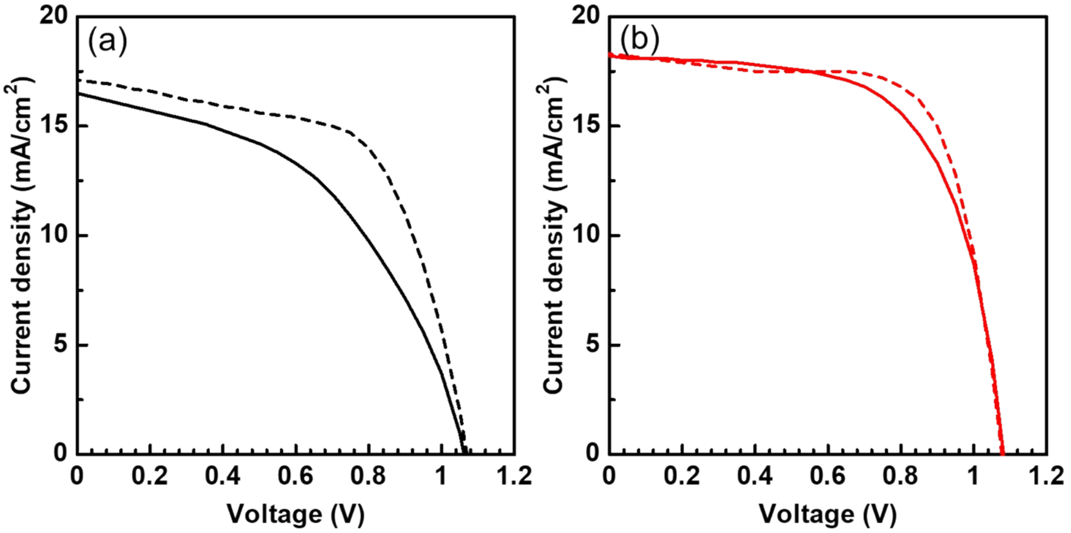


Fig. S5 *I*-*V* characteristics (solid line: forward, dash line: reverse) of PSCs without (a) or with (b) the graphene/TiO_2 nanohybrid.

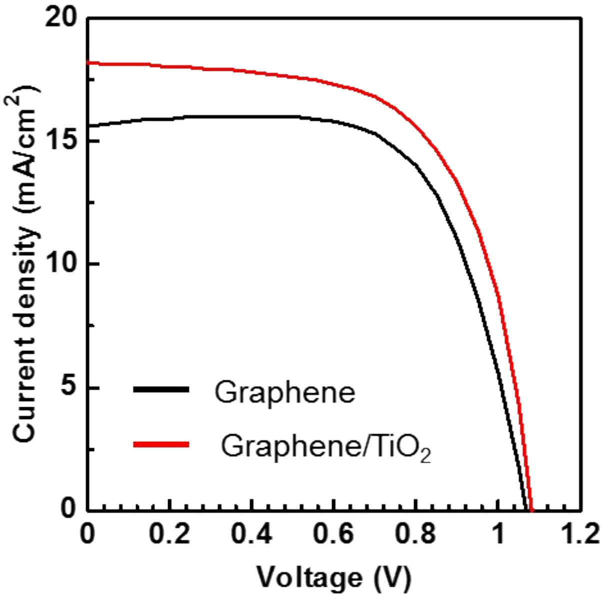


Fig. S6 *I-V* characteristics of PSCs with the graphene/TiO_2 nanohybrid (red line) or graphene (black) in the *meso*-TiO_2 layer.

Table S2 PSC characteristics of each device

	PCE (%)	FF	*V*oc (V)	*J*sc (mA/cm^2)
meso-TiO_2	8.4	0.48	1.06	17.5
graphene	11.2	0.67	1.07	15.6
graphene/TiO_2	12.5	0.64	1.08	18.2

7. References

1. M. Kobayashi, S. Kumagai, B. Zheng, Y. Uraoka, T. Douglas and I. Yamashita, *Chem. Commun*., 2011, **47**, 3475. (*b*) I. Inoue, B. Zheng, K. Watanabe, Y. Ishikawa, K. Shiba, H. Yasueda, Y. Uraoka, and I. Yamashita, *Chem. Commun*., 2011, **47**, 12649.
2. Compute pI/Mw tool, https://web.expasy.org/compute_pi/ (accessed May 2017)
3. Raifuku, Y. Ishikawa, S. Ito, Y. Uraoka, *J. Phys. Chem. C,* 2016, **120**, 18986.