Supporting information

Poly(3,4-propylenedioxythiophene)/Carbon Micro-spheres Bismuth Nanoflakes Composite and Multifunctional Co-doped Graphene for a Benchmark Photo-supercapacitor

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Experimental

Chemicals

Titania powder (P25) is a free gift from Evonic Corporation. Thiourea, Citric acid, sulfur powder, Triton X-100, titanium tetrachloride ($TiCl_4$), acetyl acetone, cadmium acetate ($Cd(CH_3COO)_2$), sodium sulfide (Na_2S), bismuth nitrate, 3,4-propylenedioxythiophene (ProDOT), lithium perchlorate ($LiClO_4$), poly(methyl methacrylate) (PMMA, average MW: 996000), propylene carbonate (PC), N-methyl-2-pyrrolidone (NMP), carbon black, PVdF (Polyvinylidene Fluoride), ethylenediamine, hydrazine hydrate, PEG 400, acetonitrile, methanol, ethanol, acetone, hydrochloric acid, acetic acid and sodium hydroxide were obtained from Merck. Ultrapure water with a resistivity of ~18.2 MΩ cm was procured from a Millipore Direct-Q3 UV system. Nickel (Ni) foam (1 mm thickness) was purchased from Gelon. Fluorine-doped tin oxide (FTO) coated glass substrates with a sheet resistance of ~16 Ω/sq were obtained from Pilkington and cleaned sequentially in a soap solution, 10% HCl solution, 10% NaOH solution, distilled water and acetone/ethanol (v/v 1:1). Fumed silica (SiO_2) was obtained from Cabot Corporation. Popped rice was bought from the local market.

Fabrication of photoanode films

Sulfur- and nitrogen- doped graphene particles (SNGP) were prepared by a hydrothermal method reported by Qu et al.[1] Citric acid (1 mmol), thiourea (3 mmol) were dissolved in deionized water (5 mL) and stirred for half an hour, and a clear solution was obtained. The solution was the transferred to a Teflon lined stainless steel autoclave. It was kept in an electric oven and heated to 160 °C for 8 h. The final product was obtained by iterative centrifugation (at 8000 rpm for 5 min.) and washing with ethanol and water. The final product (1 mg) was dispersed in deionized water (1 mL).

FTO substrates were dipped in an aqueous $TiCl_4$ (0.04 M) solution at 70 °C for 20 min. A dense layer of TiO_2 was applied using a paste of TiO_2 powder by doctor blade method to obtain the TiO_2/FTO film as per our previous report.[2] Briefly, 0.3 g of TiO_2 powder was mixed homogeneously in a clear solution of 1.5 mL acetyl acetone, 8.5 mL ultrapure water, and 20 mg Triton X-100. TiO_2 films were heated to 80 °C for 30 min, followed by annealing at 500 °C for another 30 min. One more layer of TiO_2 was deposited, followed by heating and annealing as done before. The TiO_2 film was again dipped in an aqueous $TiCl_4$ (40 mM) solution for 30 min. at 70 °C and the resulting film was rinsed in water and annealed at 500 °C for 30 min. CdS was deposited over the TiO_2 film by successive ionic layer adsorption and reaction (SILAR) method [2]; 0.1 M $Cd(CH_3COO)_2$ /methanol and 0.1 M Na_2S/methanol solutions were kept in two beakers. The TiO_2 film was dipped in the Cd^{2+} solution for 2 min., rinsed in methanol, followed by drying at 60 °C and again dipped in the Na^+ solution for 2 min., rinsed in methanol and followed by drying at 60

°C. Five more SILAR cycles were carried out and the TiO_2/CdS photoanode was obtained. To fabricate the TiO_2/SNGP/CdS or TiO_2/SNGP photanodes, the TiO_2 film was dipped in a SNGP (100 mg) solution in ultrapure water (5 mL) for 48 h, rinsed in ethanol and dried at ambient temperature. The resulting TiO_2/SNGP film was subjected to the above-described 6-SILAR cycles in the Cd^{2+} and S^{2-} baths and the TiO_2/SNGP/CdS photoanode was obtained. The dimensions of the FTO substrate were 1 cm × 2.5 cm and the active electrode area was roughly maintained between 0.1 to 0.11 cm^2.

PProDOT/CMS-BiNF based electrodes and cell fabrication

Carbon micro-sphere (CMS) was prepared by simple hydrothermal method. Popped rice (100 g) was soaked in ultrapure water (100 mL) placed in a Teflon lined autoclave and sealed. It was heated at 120 ^oC for 12 h. After heating, a black carbon residue was collected via centrifugation with ultrapure water and ethanol. Carbon and KOH were taken in a 1:2 weight ratio in minimum amount of deionized water and heated at 80 ^oC with continuous stirring for 12 h. Then it was washed with ultrapure water and dried, and the resulting black colored material is referred to as carbon micro-spheres.

To prepare the bismuth nanoflakes,[3] 0.1 M bismuth nitrate in acetic acid (5 mL), ethylenediamine (180 µL) as the capping agent, and hydrazine hydrate (40 µL) as the reducing agent were added to an aqueous solution (20 mL). The resulting clear solution was transferred to a 50 mL Teflon vessel and heated at 150 °C for 3 h. The brownish colored product (labeled as Bi nanoflakes) was obtained via centrifugation with ultrapure water and ethanol.

Carbon microsphere was mixed with carbon black and PVdF in a weight ratio of 80:10:10 by a dry grinding method using a mortar and pestle for 2 h. A few drops of NMP were added to this dry mixture and by using a glass rod, and a homogeneous slurry was prepared. The slurry was applied over Ni foam using doctor blading, and the coated Ni foam was heated at 70 °C for 12 h in a vacuum oven to yield the CMS@Ni foam electrode. Similarly, for coating a composite of CMS-BiNF on Ni foam, the slurry was prepared by taking Bi nanoflakes, carbon microsphere, carbon black and PVdF in a weight ratio of 20:60:10:10, and applied over Ni foam using the same above-mentioned procedure.

PProDOT was deposited on CMS-BiNF@Ni foam or CMS@Ni foam or Ni foam by electropolymerization, proposed by Reddy et al.[4] 0.1 M ProDOT, 0.1 M of lithium perchlorate and 1 mL of PEG-400 were dissolved in 20 mL of acetonitrile. The monomer solution was sonicated for 10 min. prior to deposition. In a three-electrode system, CMS-BiNF@Ni foam or CMS@Ni foam or Ni foam immersed in this solution was employed as the working electrode (WE). A stainless steel plate and an Ag/AgCl/KCl probe served as the CE and reference electrode. Under potentiostatic conditions, a fixed voltage of 1.2 V was applied to the WE for 300 s. The resulting films were bluish-black in color and were dried at 70 °C for 5 h to obtain the PProDOT/CMS-BiNF@Ni foam or PProDOT/CMS@Ni foam or PProDOT@Ni foam electrodes.

Instrumentation techniques

Surface morphologies of Ni foam, deposited Ni foam, PProDOT, CMS and Bi nanoflakes were analyzed using a scanning electron microscope (Zeiss Evo 18 Special Edition). Transmission electron microscopy (TEM) images of SNGP, Bi nanoflakes, PProDOT/CMS-BiNF material were measured on a JEOL 2100 microscope operating at an accelerating voltage of 200 kV by using samples deposited over carbon-coated copper grids, followed by their suspension and evaporation. X-ray photoelectron (XPS) spectra of SNGP was recorded on Thermo Scientific K-ALPHA

surface analysis spectrometer using Al Kα radiation (1486.6 eV) to understand surface elemental state and bonding. Raman spectra of PProDOT, carbon-microspheres and SNGP were recorded on a Bruker Senterra dispersive Raman microscope spectrometer, having a 532 nm laser excitation source. XRD patterns of pristine Bi nanoflakes, PProDOT, and CMS were recorded on a PANalytical, X'PertPRO instrument with a Cu-Kα (λ =1.5406 Å) radiation. Optical absorption spectra of photoactive solutions were recorded in absorbance mode on a UV-Vis spectrophotometer (T90+, PG Instruments). Fluorescence spectra of photoactive electrodes were performed on a Horiba Flouromax-4 fluorescence spectrometer. Lifetime decay analysis was performed using the time-correlated single photon counting (TCSPC) method on a Horiba Jobin Yvon data station HUB. A nano LED diode having emission pulses at 450 nm with 1 MHz repetition rate and a pulse duration of 1.3 ns, served as the excitation source. A Ludox solution (colloidal silica or prompt) was used to acquire the instrument response function. A LOT-Oriel Xe arc lamp with an irradiance of 1 sun (100 mW cm^{-2}, AM 1.5) connected to an Autolab PSTAT 302N electrochemical workstation (equipped with a NOVA 1.1 software) was employed to measure the current versus potential data of solar cells. Cyclic voltammetry studies, linear weep voltammetry, photo-charging, galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) studies were also done on the same instrument. LSV for conductance was also performed on the same instrument.

Table S1. Lifetime decay fitting parameters of photoactive electrodes at λ_{ex} of 370 nm inferred from bi-exponential fits.

Photoanode	B_1	τ_1 (ns)	B_2	τ_2 (ns)	τ (ns)	χ^2
CdS	49.46	0.24	50.54	17.50	17.2	1.14
SNGP/CdS	57.51	0.80	42.49	9.90	9.0	1.20
TiO_2/CdS	52.84	0.73	47.16	6.77	6.1	1.08
TiO_2/SNGP/CdS	44.86	1.63	55.14	1.73	1.7	1.21

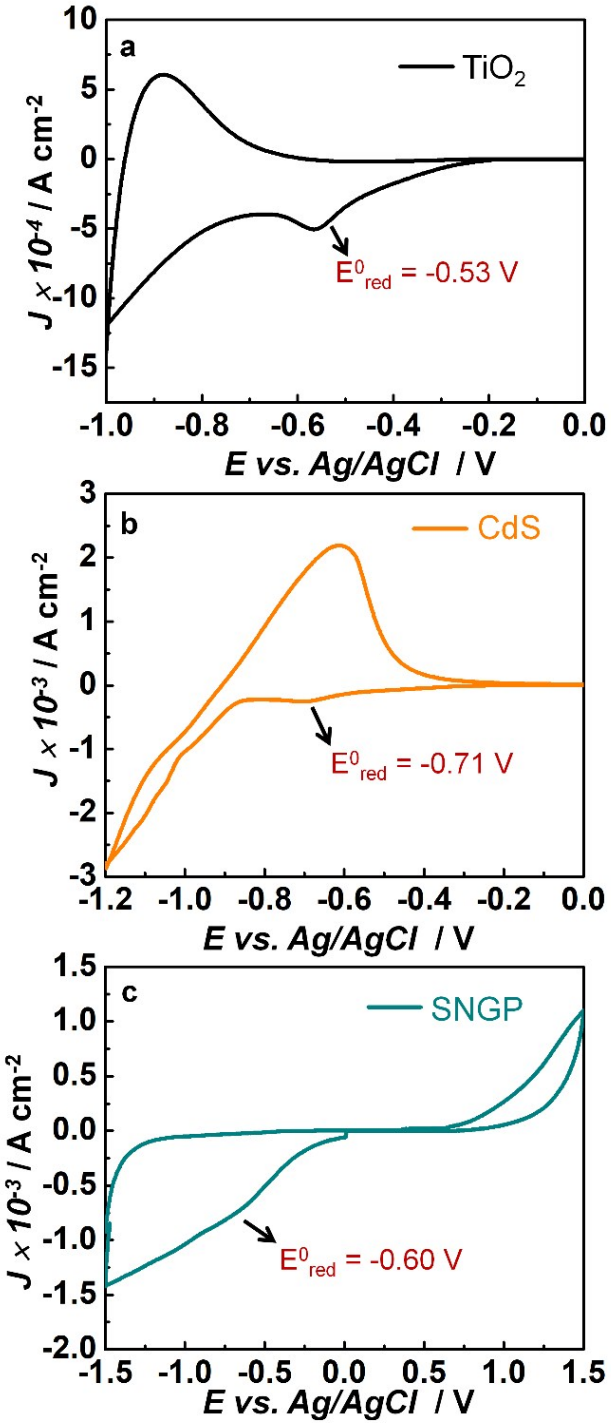

Figure S1. Cyclic voltammograms of (a) TiO_2, (b) CdS, and (c) SNGP coated on FTO substrates as working electrodes, Pt as the counter electrode and Ag/AgCl/KCl probe as the reference electrode in a 0.1 M KCl solution as the electrolyte and, recorded at a scan rate of 10 mV s^{-1}.

Table S2. Conduction band and valence band positions of photoactive electrodes (TiO_2, CdS and SNGP) used in the QDSCs prepared in this study (E^o(Ag/AgCl/KCl) = 0.198 V).

Material	E^o_{red} vs. Ag/AgCl/KCl (V) (from CV plots)	E^o_{red} vs. NHE (V)	CB (eV) = –(E^o vs. NHE + 4.5)	Optical band gap (E_g, eV)	VB (eV) –(E_g) + CB
TiO_2	–0.53	–0.33	–4.17	3.18	–7.35
CdS	–0.74	–0.54	–3.96	2.27	–6.23
SNGP	–0.60	–0.40	–4.10	1.90	–6.00

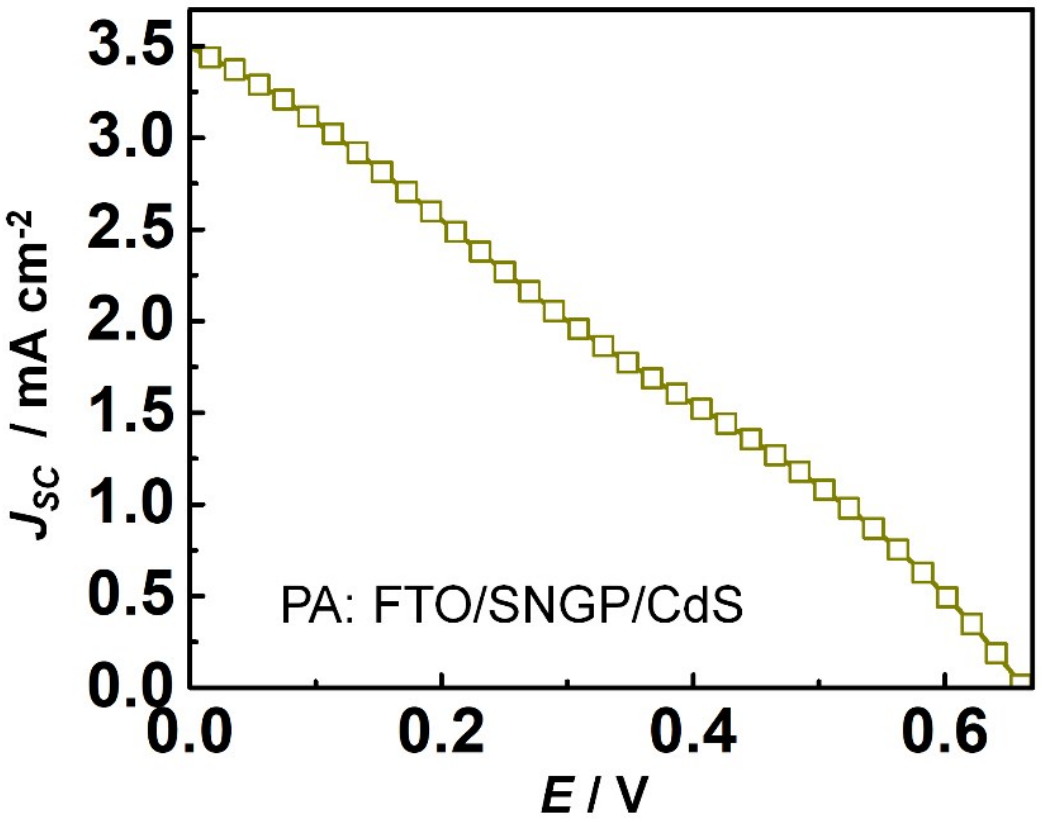

Figure S2. J-V plot of FTO/SNGP/CdS-S/S^{2-}/silica gel-PProDOT/CMS-BiNF@Ni foam cell under 1 sun.

Table S3. Solar cell parameters of solar cells having 5 cells with two photoanodes compared with four counter electrodes using polysulfide/silica gel electrolyte under 1 sun illumination (100 mW cm^{-2}), exposed area 0.1-0.11 cm^2.

Solar cell configurations	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
TiO_2/CdS– Ni				
1	11.82	0.676	0.416	3.33
2	11.73	0.677	0.416	3.31
3	11.54	0.683	0.418	3.30
4	11.76	0.672	0.415	3.28
5	11.60	0.671	0.417	3.25
Average	11.69±0.11	0.675±0.004	0.416±0.001	3.29±0.03
TiO_2/CdS– PP@Ni				
1	13.84	0.736	0.541	5.47
2	13.76	0.735	0.541	5.44
3	13.81	0.733	0.538	5.43
4	13.70	0.732	0.536	5.38
5	13.73	0.725	0.534	5.32
Average	13.76±0.05	0.732±0.004	0.538±0.003	5.40±0.06
TiO_2/CdS– PP/CMS@Ni				
1	14.56	0.783	0.589	6.72
2	14.46	0.781	0.588	6.65
3	14.62	0.775	0.584	6.62
4	14.30	0.784	0.590	6.61
5	14.44	0.779	0.585	6.59
Average	14.47±0.12	0.780±0.003	0.587±0.002	6.64±0.05
TiO_2/CdS– PP/CMS-BiNF@Ni				
1	15.40	0.807	0.630	7.83
2	15.27	0.809	0.628	7.77
3	15.33	0.804	0.626	7.76
4	15.38	0.800	0.630	7.75
5	15.29	0.794	0.626	7.61
Average	15.33±0.05	0.802±0.006	0.628±0.002	7.74±0.08
TiO_2/SNGP/CdS– Ni				
1	16.08	0.685	0.410	4.53
2	15.90	0.690	0.412	4.52
3	15.93	0.688	0.410	4.50

4	15.94	0.686	0.409	4.48
5	15.97	0.681	0.409	4.45
Average	15.96±0.07	0.686±0.003	0.410±0.001	4.50±0.03
TiO_2/SNGP/CdS– PP@Ni				
1	17.07	0.740	0.562	7.13
2	16.86	0.733	0.573	7.11
3	17.02	0.742	0.561	7.10
4	16.95	0.741	0.561	7.06
5	16.98	0.737	0.561	7.02
Average	16.97±0.08	0.738±0.003	0.563±0.005	7.08±0.04
TiO_2/SNGP/CdS– PP/CMS@Ni				
1	17.61	0.790	0.603	8.42
2	17.52	0.790	0.604	8.37
3	17.59	0.785	0.604	8.35
4	17.47	0.787	0.604	8.31
5	17.56	0.782	0.601	8.26
Average	17.55±0.05	0.787±0.003	0.603±0.001	8.34±0.06
TiO_2/SNGP/CdS– PP/CMS-BiNF@Ni				
1	18.20	0.822	0.634	9.50
2	18.13	0.820	0.633	9.43
3	18.16	0.818	0.633	9.41
4	18.19	0.814	0.632	9.36
5	18.33	0.815	0.625	9.35
Average	18.20±0.07	0.818±0.003	0.631±0.003	9.41±0.06
TiO_2/SNGP– PP/CMS-BiNF@Ni				
1	7.05	0.606	0.414	1.77
2	6.99	0.603	0.412	1.74
3	6.94	0.600	0.410	1.71
4	6.86	0.603	0.413	1.71
5	6.88	0.601	0.414	1.70
Average	6.94±0.08	0.602±0.002	0.412±0.001	1.72±0.03

PP: PProDOT, CMS: carbon micro-spheres, BiNF: Bi nanoflakes.

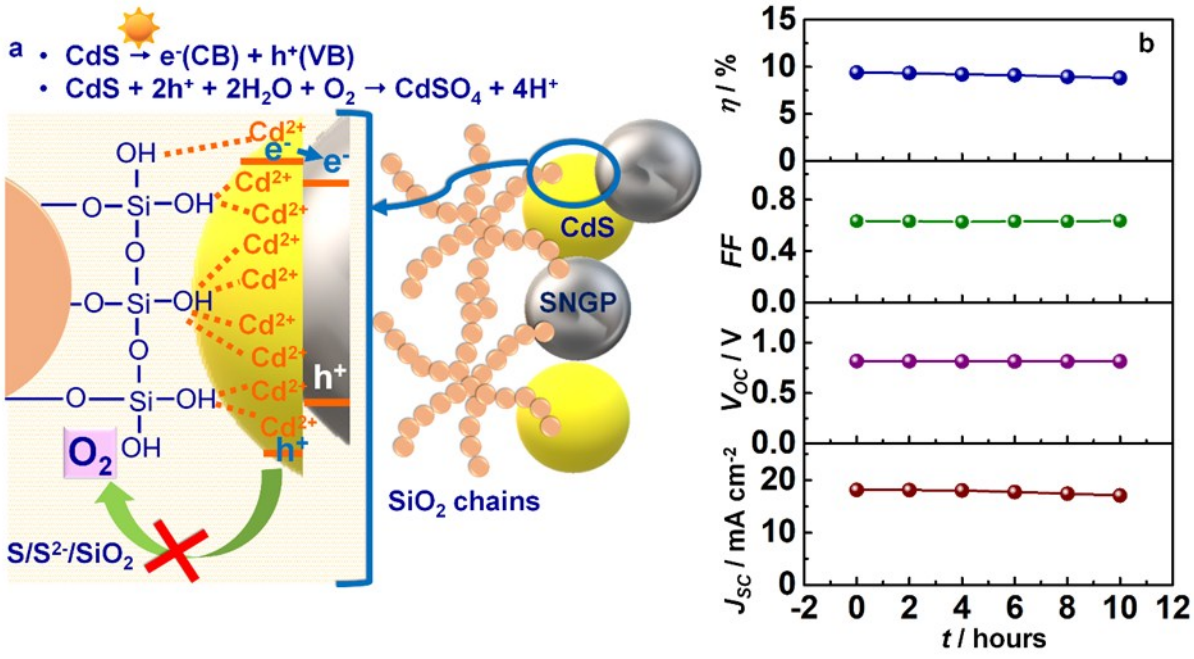

Figure S3. (a) Reactions for photodecomposition of CdS and cartoon illustrating how SiO_2 reduces photo-corrosion. (b) Variation of cell parameters: J_{SC}, V_{OC}, FF, and PCE on continuous illumination for 10 h.

Table S4. Solar cell parameters of a TiO_2/SNGP/CdS/-polysulfide/silica gel-PProDOT/CMS-BiNF with active area: 0.1 cm^2 under 1 sun illumination.

Illumination	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
0 h	18.16	0.818	0.633	9.40
2 h	18.13	0.816	0.631	9.33
4 h	18.05	0.814	0.626	9.20
6 h	17.76	0.814	0.631	9.12
8 h	17.45	0.814	0.630	8.95
10 h	17.08	0.815	0.634	8.82

Table S5. EIS parameters achieved from Nyquist plots of QDSC.

Photoanode	R_b (Ω cm^2)	R_{CE} (Ω cm^2)	Y_{oCE} (μ $Ω^{-1}$)	N_{rec}	R_{rec} (Ω cm^2)	Y_{orec} (m $Ω^{-1}$)	N_{rec}
TiO_2/CdS	22.2	13.6	193	0.880	11.5	1.06	1.100
TiO_2/SNGP/CdS	20.7	17.4	130	0.912	21.6	4.52	0.894

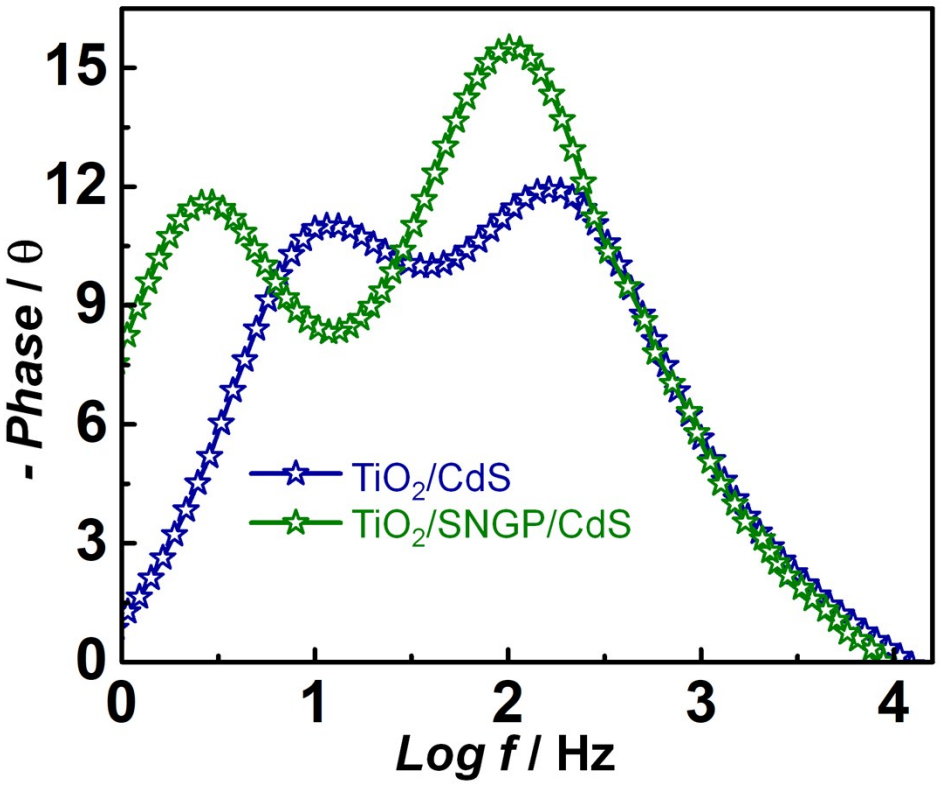

Figure S4. Bode phase plots (Log f versus phase angle) of TiO_2/CdS and TiO_2/SNGP/CdS photoanode using S/S^{2-}/silica gel electrolyte and PProDOT/CMS-BiNF@Ni foam CE.

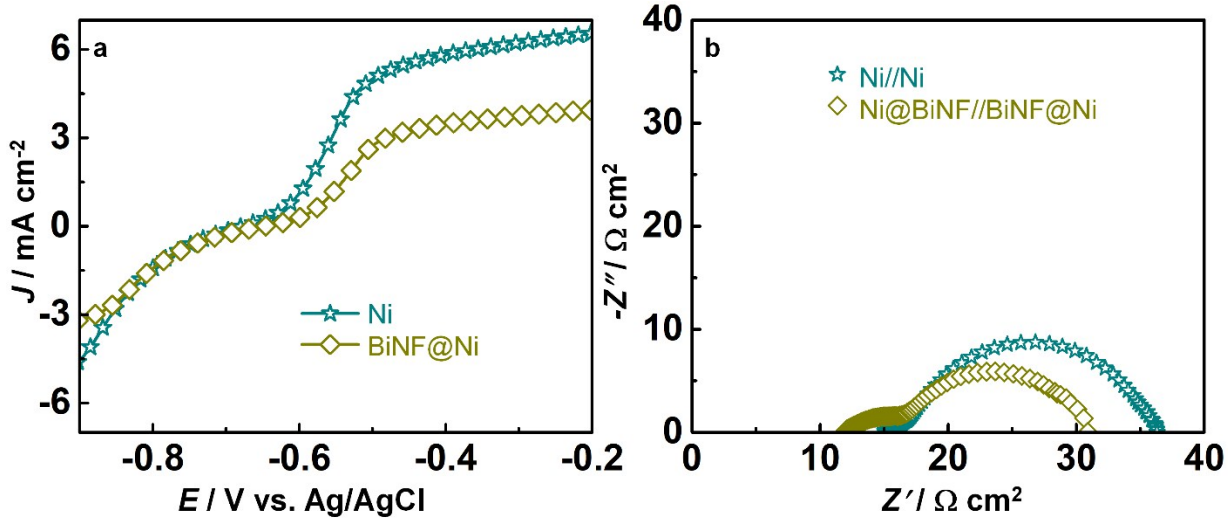

Figure S5. (a) LSV plots of CEs: Ni foam and BiNF@Ni foam in a three-electrode system using S/S^{2-}/silica gel electrolyte. (b) Nyquist plots of Ni//Ni and Ni@BiNF//BiNF@Ni with the gel electrolyte.

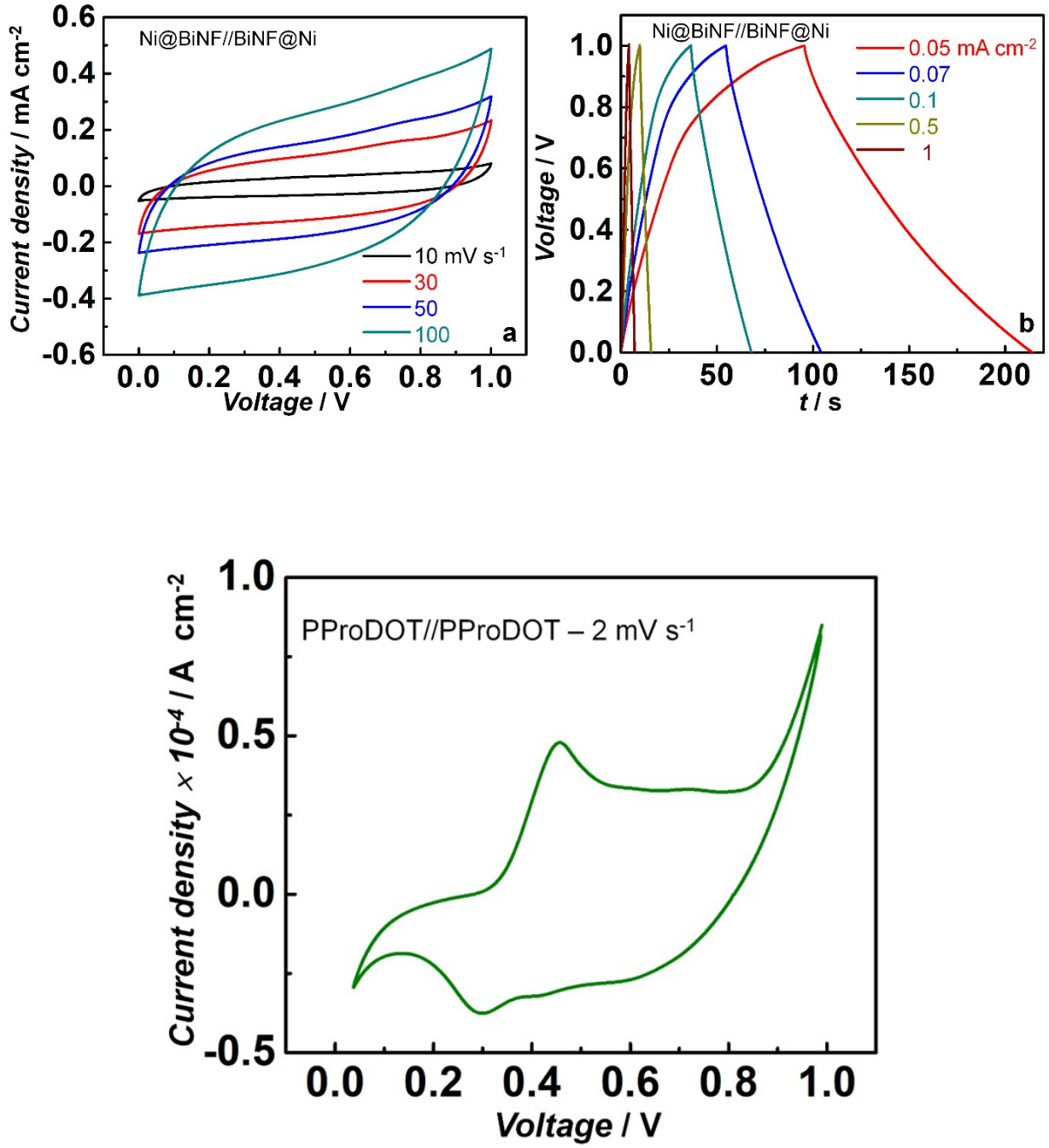

Figure S6. (a) CV and (b) galvanostatic charge-discharge (GCD) plots of Bi nanoflakes (BiNF) coated Ni foam based symmetric cells.

Figure S7. CV plot of symmetric supercapacitor PProDOT//PProDOT with a $LiClO_4$/PC/PMMA gel recorded at a scan rate of 2 mV s^{-1}.

Table S6. EIS parameters achieved from Nyquist plots of symmetric cell configuration of supercapacitor.

Supercapacitor	R_b (Ω cm^2)	R_{ct} (Ω cm^2)	Y_o ($\mu\Omega^{-1}$ cm^2)	N	Z_W ($m\Omega^{-1}$ cm^2)	C_{dl} (mF cm^2)
PP	5.37	15.3	457	0.697	37.0	35.3
PP/CMS	8.95	3.9	917	0.580	49.5	28.5
PP/CMS-BiNF	4.17	4.1	161	0.774	88.5	28.6

PP: PProDOT, CMS- carbon micro-spheres, BiNF: Bi nanoflakes.

Table S7. Literature values of $\eta_{conversion}$, $\eta_{overall}$ and $\eta_{storage}$ for PSC devices with the listed solar cell and supercapacitor electrodes/architecture.

Solar cell	Supercapacitor Electrode	PCE $\eta_{conversion}$ (%)	$\eta_{overall}$ (%)	$\eta_{storage}$ (%)	Reference
DSSC	PANI-SS wire	5.41	2.1	46	5
DSSC	Carbonized silicon wafer	4.8	2.1	43	6
DSSC	Plasma assisted hydrogenation treated bi-polar TiO_2 nanotube arrays	3.17	1.64	51.6	7
DSSC	CNT fiber twisted with modified Ti wire	2.20	1.5	68.4	8
DSSC	MWCNT-PANI	2.31	0.79	34.0	9
DSSC	Ti wire perpendicularly aligned with TiO_2 nanotube and horizontally aligned multi-walled carbon nanotube sheet	2.73	–	75.7	10
Perovskite solar cell	Polypyrrole/MWCNT	–	10	49	11
Perovskite solar cell	Carbon supported graphene/PEDOT	8.03	7	87.17	12
Perovskite solar cell	PEDOT-Carbon	6.37	4.7	73.77	13
Perovskite solar cell	PANI/CNT	2.55	0.76	70.9	14

QDSC	PProDOT/CMS-BiNF	9.41	6.8	72.3	This work

MWCNT: Multiwalled carbon nanotubes, PANI: Poly(aniline), PEDOT: Poly(3,4-ethyleenedioxythiophene), DSSC: Dye sensitized solar cell and QD: Quantum dot.

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