Electronic Supplementary Information

Ultrathin Two Dimensional Graphitic Carbon Nitride as an Solution-processable Cathode Interfacial Layer for Inverted Polymer Solar Cells

Lingyu Zhou,[ab] Yuxing Xu,[ab] Wei Yu,[a] Xin Guo,[a] Shuwen Yu,[a] Jian Zhang,[a,]* Can Li[a,]*

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian 116023,PR China.

[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

*Corresponding authors:

Tel.: +86 411 84379070

Fax: +86 411 84694447

E-mail addresses: canli@dicp.ac.cn.;

Experimental

Preparation of C_3N_4

Bulk C_3N_4 was synthesized by pyrolyzation of melamine. Briefly, 10 g of melamine was heated to 550°C for 110 min and maintained at this temperature for 4 h. Ultra-thin C_3N_4 nanosheets were obtained via ultrasonication-assisted liquid exfoliating of as-prepared bulk C_3N_4. The as prepared C_3N_4 was ground well into powder with a mortar, then dispersed in a solution consisting of H_2O and 2-propanol in a volume ratio of 1:2, followed by the consecutive sonication for 8 h. The unexfoliated C_3N_4 was removed by centrifugation. Afterwards, C3N4 nanosheets were dispersed in H_2O and IPA mixed solvents (1:2, vol%) with a concentration of 1 mg mL^{-1} for the deposition of C_3N_4 thin films.

Fabrication of inverted polymer solar cells

ITO coated glass substrates with a sheet resistance of 10 Ω sq^{-1} were cleaned via sonication in acetone, isopropyl alcohol and ethanol sequentially, followed by ultraviolet ozone (UVO) treatment for 15 min prior to thin film deposition. C_3N_4 nanosheets were deposited onto the ITO by multiply spin coating or dip coating. ZnO thin films were obtained by spin-coating ZnO precursor (consisting of 0.3 M zinc acetate dehydrate and 0.3 M ethanolamine in 2-methoxyethanol) on the cleaned ITO substrates, following annealing at 200°C for 10 minutes in a nitrogen-filled glove box and continuously annealed in air at 200°C for 1 hour. The thickness for ZnO cathode interface layer is found to be 15 nm. The BHJ active layers were spin-cast of the solution of PBDTTT-C:$PC_{71}BM$ (1:1.5, wt%) or PTB7:$PC_{71}BM$ (1:1.5 wt%) in 1,2-

dichlorobenzene/1,8-diiodoctane (97:3 vol%) in a N_2 filled glove box with the overall concentration of 30 mg mL^{-1}. Finally, 6 nm MoO_3 and 100 nm Ag were deposited sequentially by thermal evaporation under $5^{*}10^{-4}$ Pa through a shadow mask to define an active area of 6.4 mm^2.

Characterization of polymer solar cells

The current density-voltage (J-V) characteristics of the solar cells were measured by a Keithley 2400 source unit. The J-V curves and PCE parameters of V_{OC}, J_{SC}, FF were obtained under exposure to AM 1.5 Global solar simulator with an intensity of 100 $mW{\cdot}cm^{-2}$ (AAA Oriel solar simulator with AM 1.5G filter). External quantum efficiency (EQE) was characterized on the QTest Station 2000ADI system (Crowntech. Inc.).

The optical properties including UV-Vis absorption, transmission and diffuse reflectance spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer. The Fourier transform infrared spectra (FTIR) were collected using a Thermo Scientific Nicolet iS10 FTIR spectrometer. Atomic force microscopy (AFM) topography images were obtained by using a Multimode Nanoscope III-D atomic force microscope (Bruker) in the tapping mode. The work functions of the films were measured by scanning Kelvin probe method. XPS spectra were acquired with a Thermo Scientific (ESCALAB 250Xi) system using monochromatic Al Ka X-ray excitation; the base pressure within the XPS chamber was $7.1{*}10^{-7}$ Pa. The binding energy value for all spectra was calibrated using the C1s peak (284.6 eV) as a reference.

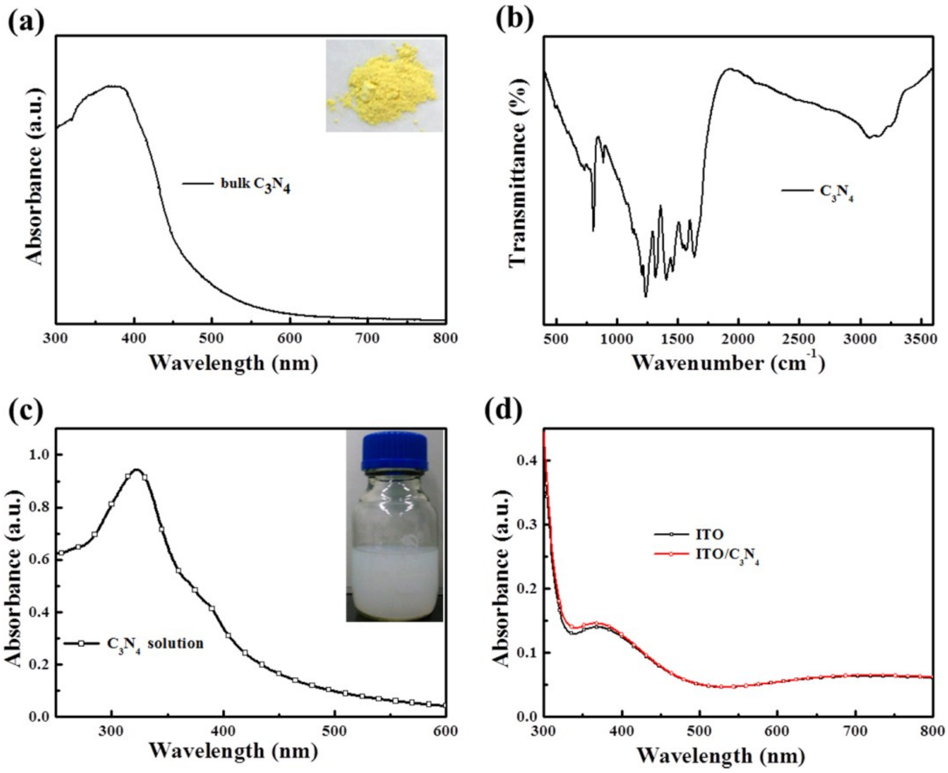

Figure S1. (a) UV-Vis diffuse reflectance spectra and (b) FT-IR spectra of the bulk C_3N_4. (c) The UV-vis spectroscopy C_3N_4 nanosheets in solution, the inserted graph showed C_3N_4 nanosheets dispersion after standing for 1 year. (d) The UV-vis spectroscopy of C_3N_4 films on ITO substrate.

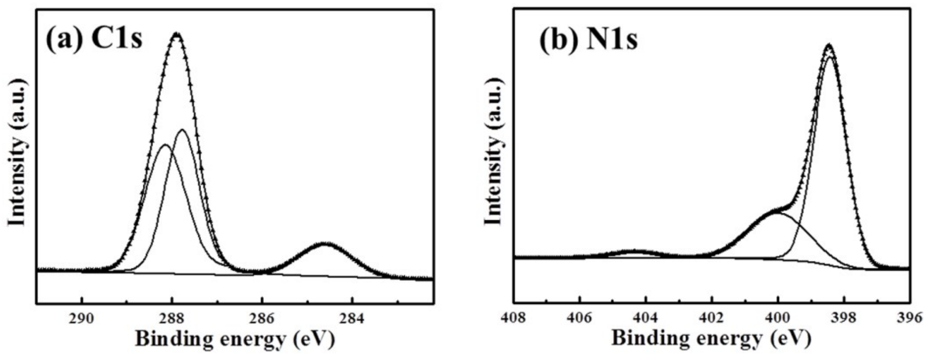

Figure S2 (a) High-resolution C1s spectra of C_3N_4 nanosheets, fitted to three energy components centered at around 288.2, 287.7 and 284.6 eV. (b) High-resolution N1s spectra of C_3N_4 nanosheets fitted to three energy components centered at around 398.4, 400.0 and 404.3 eV.

Figure S3. Contact angles of water droplet on (a) bare ITO without UVO treatment, (b) ITO with UVO treatment, and (c) ITO/C_3N_4 (three times spin-coating).

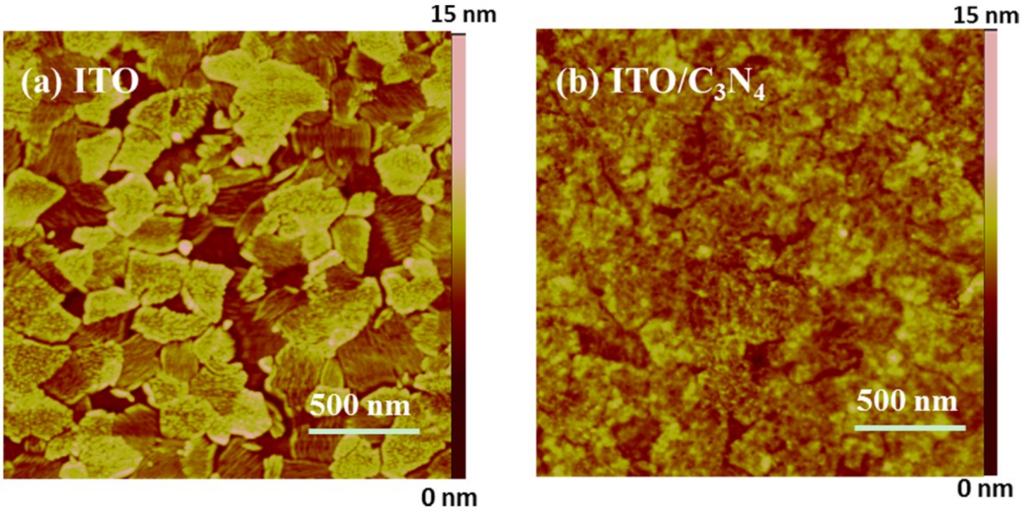

Figure S4 AFM topography images of (a) ITO and (b) ITO/C_3N_4 (three times spin-coating).

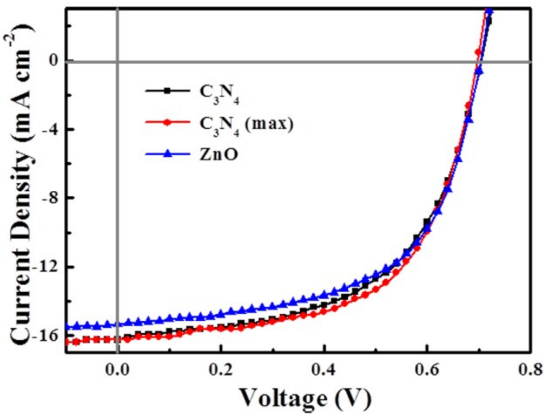

Figure S5 J-V curves of inverted organic solar cells with C_3N_4 or ZnO as cathode interfacial layer based on PBDTTT-C:$PC_{71}BM$ under the illumination of AM 1.5G 100 mV cm $^{-2}$.

Table S1 J–V characteristics of inverted organic solar cells with C_3N_4 or ZnO as cathode interfacial layer based on PBDTTT-C:$PC_{71}BM$.

Devices	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
C_3N_4	16.04	0.70	57	6.40
C_3N_4 (max)	16.17	0.70	61	6.90
ZnO	15.18	0.70	60	6.38

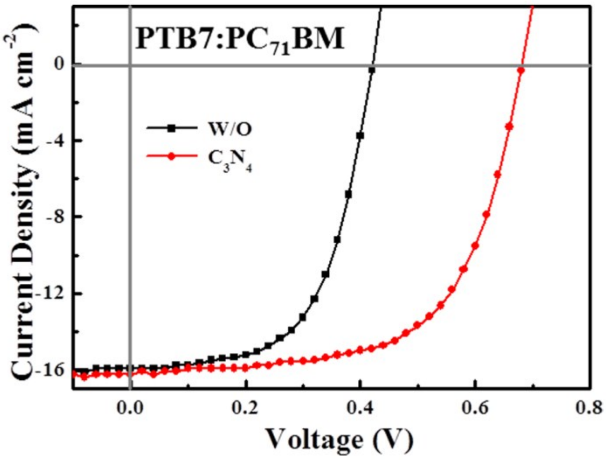

Figure S6. J-V curves of the devices based on PTB7:$PC_{71}BM$.

Table S2 Average device performance of inverted PSCs based on PTB7:PC71BM.

Devices	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
W/O	15.92	0.42	0.595	3.98
C_3N_4	16.21	0.68	0.624	6.88