Supplementary Information for

Highly efficient planar perovskite solar cells with a TiO_2/ZnO electron transport bilayer

Xin Xu, Huiyin Zhang, Jiangjian Shi, Juan Dong, Yanhong Luo, Dongmei Li, and Qingbo Meng*

Key Laboratory for Renewable Energy (CAS), Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condense Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

**Corresponding authors: 86-10-8264 9242 Email addresses: qbmeng@iphy.ac.cn*

1. The XRD pattern of different ETL

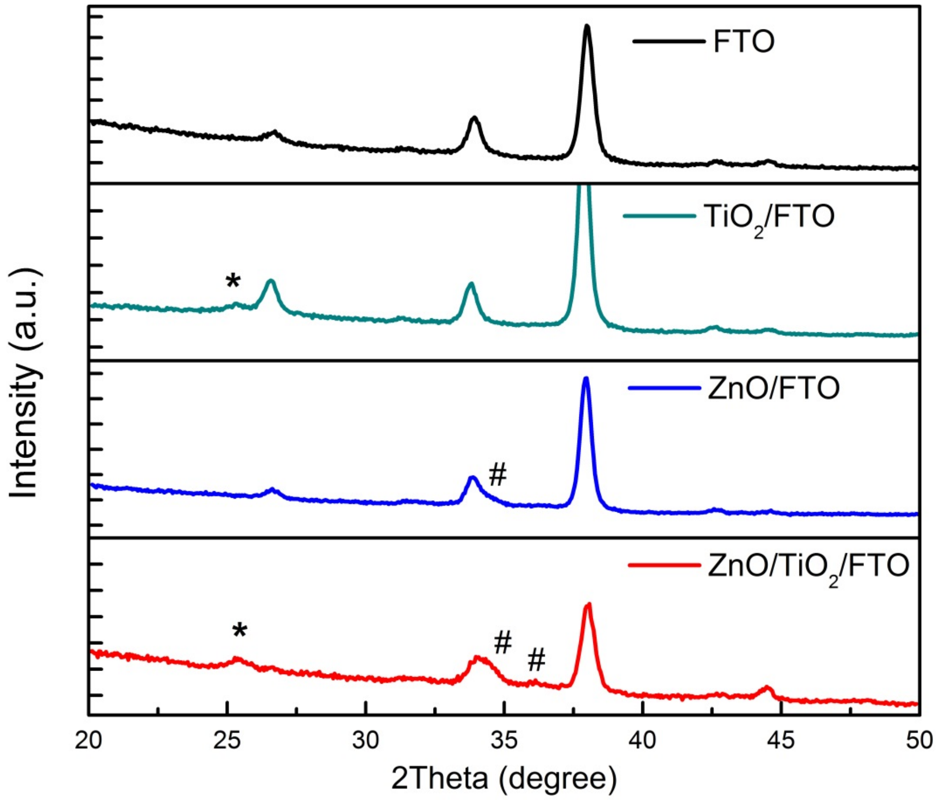


Figure S1 Grazing Incidence X-ray Diffraction (GIXRD) patterns of different electron transport layers. Asterisk (*) refers to TiO2, hash (#) refers to ZnO and other peaks belong to FTO substrate.

2. Band alignment of TiO_2/ZnO interface

The band offset at the TiO_2/ZnO surface can be calculated by the following equation:

$$\Delta E_V = \left(Zn2p_{\frac{3}{2}} - ZnO^{VBM}\right) - \left(Ti2p_{\frac{3}{2}} - TiO_2{}^{VBM}\right) - \Delta E_{CL}$$

When employ the XPS data, we conclude that the valance band offset between the TiO_2 and ZnO is 0.19eV, that the ZnO is higher than TiO2. Thus the TiO2 and ZnO will form a type-Ⅱband structure, which will benefit for the charge separation and transport in ETL [1, 2].

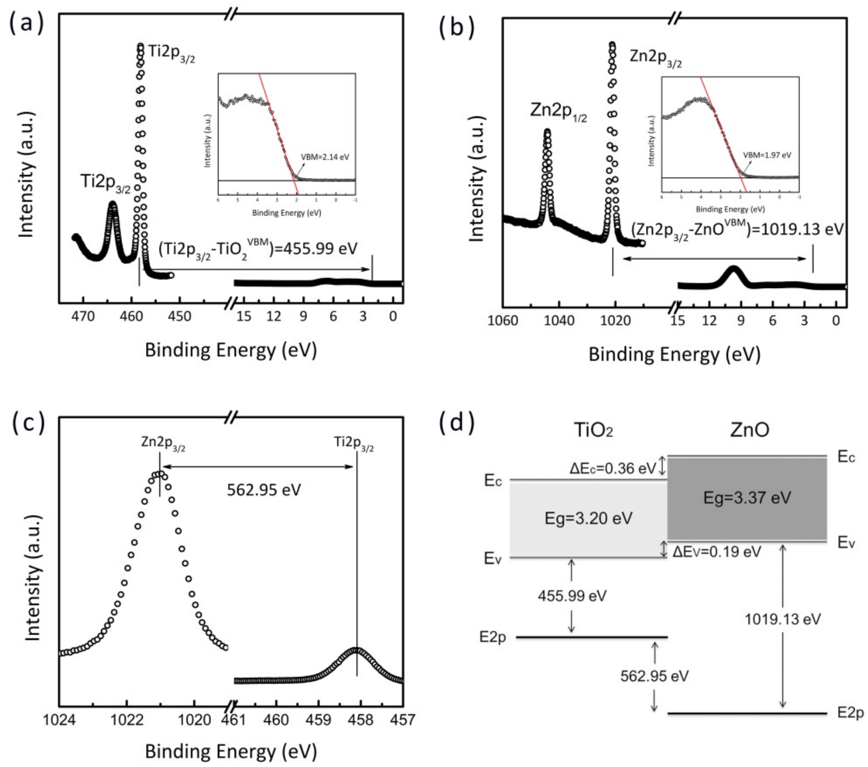
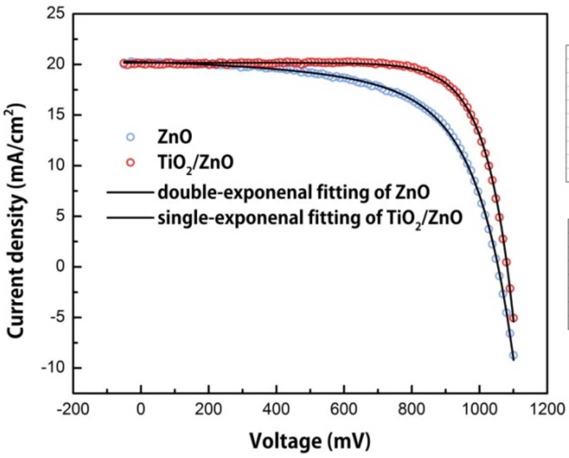


Figure S2 XPS spectrum of (a) core-level Ti 2p and valance band of TiO_2, (the inset is the detailed spectrum near the valance band maximum.) (b) core-level Zn 2p and valance band of ZnO, (the inset is the detailed spectrum near the valance band maximum.) and (c) high resolution spectra of Zn 2p3/2 and Ti 2p3/2 of TiO_2/ZnO bilayer. (d) Band alignment of TiO2/ZnO.

3. Exponenal fitting of I-V curves of planar perovskite solar cells with different ETLs.



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-	0.01943		
Adj. R-Square	0.99949		
		Value	Standard Error
Current densit	y0	20.66171	0.13967
Current densit	A1	-5.16578E-4	1.54924E-4
Current densit	t1	-102.38645	2.59165
Current densit	A2	-0.42548	0.11427
Current densit	t2	-419.81328	59.02437

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-	0.01128		
Adj. R-Square	0.99949		
		Value	Standard Error
Current densit	y0	20.16488	0.01181
Current densit	A1	-2.17502E-5	1.30029E-6
Current densit	t1	-78.72337	0.34533

Figure S3 *I-V* curves of planar perovskite solar cells with ZnO and TiO_2/ZnO ETL. The dark lines are the exponential fittings respectively.

It could be seen that the TiO_2/ZnO ETL perovskite solar cells can be fitted with single exponent while the ZnO ETL devices is well fitted by double exponent. The results suggest that the perovskite absorber might contact the FTO to form a Schottky diode in ZnO ETL devices, which will increase shunt paths. When the TiO_2 is employed into the ETL, the recombination paths will be reduced.

4. Thickness optimization of planar perovskite solar cells with different electron transport layer

Devices using ZnO ETL

When the ZnO is 20nm, the devices exhibit bad performances with low open-circuit voltages and fill factors. The power-conversion efficiency began to increase with ETL thickness increasing. But when an 80nm-thick ETL is used, the efficiency became to decrease again due to the reduced fill factors. After optimization, we found that device with a 50nm-thick ZnO layer ETL performed the best. Merely increasing ETL thickness cannot further improve the performance of planar perovskite solar cells.

Table S1 Performances of ZnO ETL perovskite solar cells with different ZnO thickness.

ZnO thickness	J_{SC} (mA/cm^2)	V_{OC} (mV)	*FF*	PCE (%)
20nm	19.61	923.6	0.545	9.864
50nm	19.56	1048.6	0.634	13.011
80nm	19.6	1025.6	0.555	11.158

Devices using TiO_2/ZnO ETL

When a layer of TiO_2 was added under the ZnO layer, the performance of devices was significant enhanced, with an obvious increasing in fill factors. The best performance can be achieved with TiO_2/ZnO 10nm/50nm.

Table S2 Performances of TiO_2/ZnO ETL perovskite solar cells with different TiO_2 thickness. All ZnO thicknesses here are optimized to 50nm.

TiO_2 thickness	J_{SC} (mA/cm^2)	V_{OC} (mV)	*FF*	PCE (%)
30nm	17.95	1079.4	0.691	13.388
10nm	19.36	1074.3	0.741	15.416
<5nm	19.05	1079.4	0.6	12.34
$TiCl_4$ treat	18.65	1090.3	0.647	13.158

Devices only using TiO_2 ETL

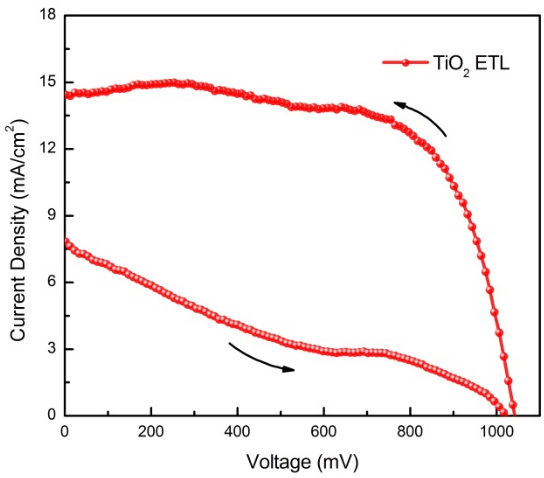


Figure S4 *I-V* curves of planar perovskite solar cells using spin-coating TiO_2 (50nm) as ETL. Scan rate: 100mV/s.

Great hysteresis can be seen in the I-V curves. Huge difference of PCEs between forward (from short circuit to forward bias, 2.1%) and backward (from forward bias to short circuit, 10.2%) exists due to the poor electron collection of TiO_2. This result suggested that the TiO2 made by spin coating method may not suit for planar perovskite solar cells, if without modification.

5. Performances of TiO_2/ZnO perovskite solar cells under different scan rate.

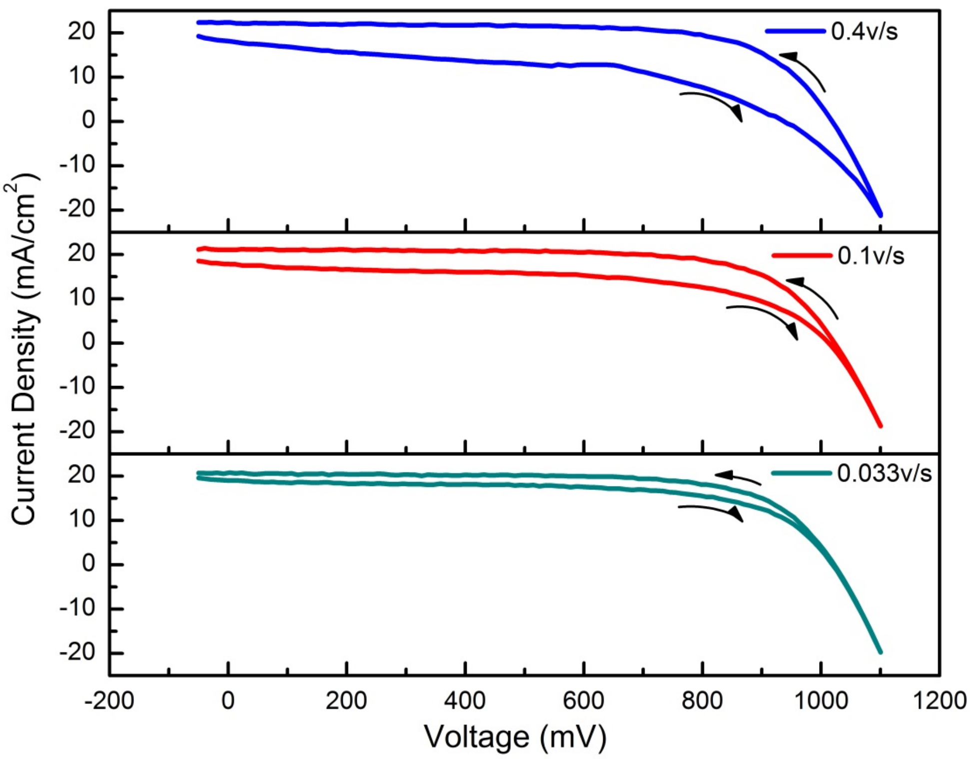


Figure S5 Performances of TiO2/ZnO perovskite solar cells under different scan rate.

Devices were tested under different voltage scan rate of 0.4V/s, 0.1V/s and 0.033V/s. This result suggested that the hysteresis reduced when the scan rate decreased. Compared to devices only using TiO_2 as ETL, the hysteresis can be well improved.

6. The stabilities of devices with TiO_2, ZnO and TiO_2/ZnO ETLs.

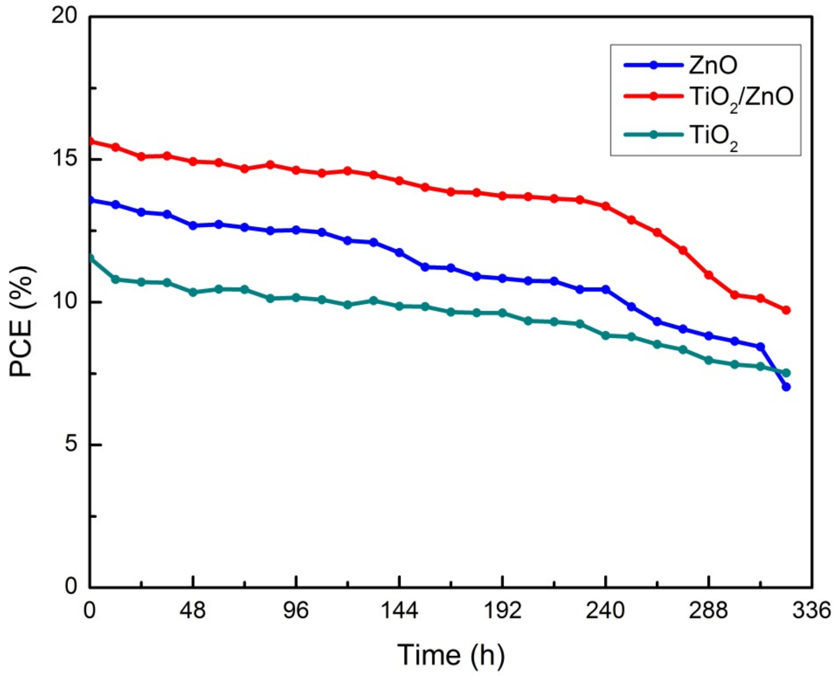


Figure S6 The stabilities of devices with different ETLs. The solar cells were stored in dark with 30%RH humidity and measured by every 12 hours.

[1] S.-J. Roh, R.S. Mane, S.-K. Min, W.-J. Lee, C.D. Lokhande, S.-H. Han, Appl. Phys. Lett. 89 (2006) 253512.

[2] K. Shen, K. Wu, D. Wang, Mater. Res. Bull. 51 (2014) 141-144.