Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Vertically-Aligned ZnO Nanorods Doped with Lithium for Polymer Solar Cells: Defect Related Photovoltaic Properties

Pipat Ruankham, Takashi Sagawa,* Horoshi Sakaguchi and Susumu Yoshikawa*

Institute of Advanced Energy, Kyoto University, Uji, Kyoto, 611-0011, Japan

Corresponding Authors: t-sagawa@iae.kyoto-u.ac.jp, s-yoshi@iae.kyoto-u.ac.jp

A. Energy-Loss Spectroscopy in a Scanning Transmission Electron Microscope (STEM-EELS) Study

In order to investigate the presence of Li atom in ZnO nanorod arrays, the 25 atom% Li doped ZnO nanorods was chosen as sample for STEM-EELs study. The Li element maps, in Figure S1, show that Li-rich phase is on the top of ZnO nanorods, confirming the Li incorporation into ZnO crystal during hydrothermal growth.

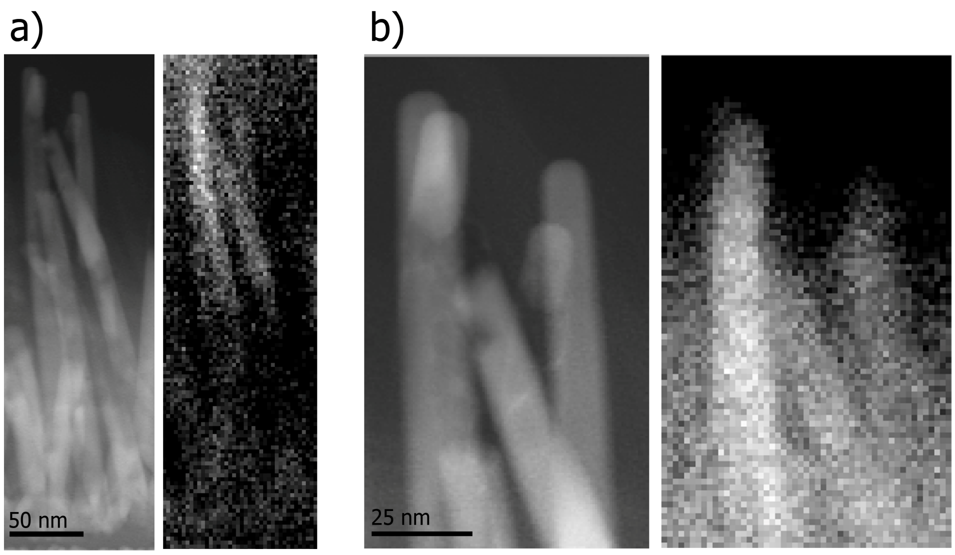

Fig. S1 The STEM image (left) and Li map (right) of 25 atom% Li doped ZnO nanorods, with scale bar a) 50 nm and b) 25 nm.

B. X-ray Diffraction (XRD) Analysis

The XRD patterns of ZnO nanorods with different Li-doping concentration on ITO substrates are shown in Figure S2.

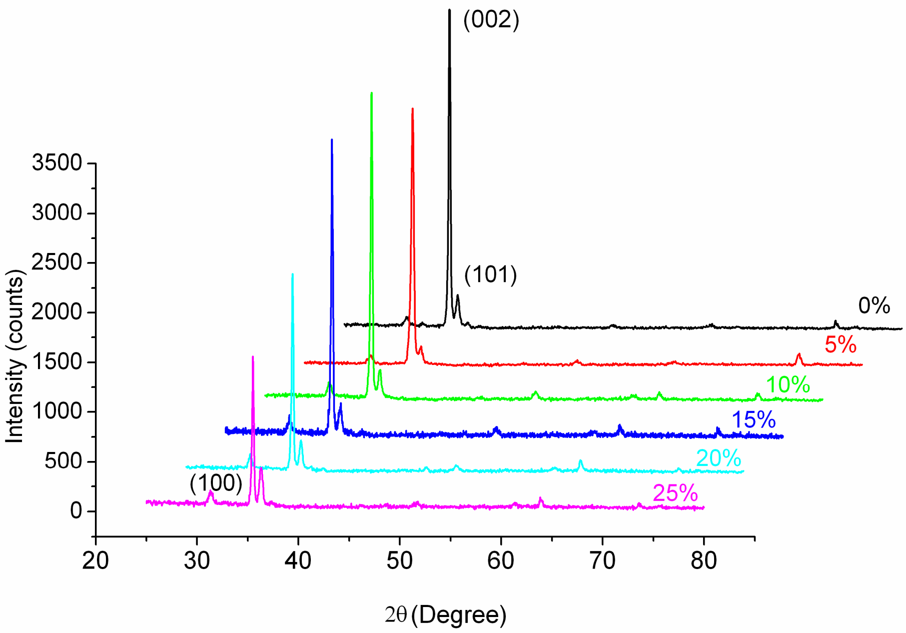

Fig. S2 The XRD patterns of $Zn_{1-x}Li_xO$ nanorods.

To better approximate the position and the FWHM of XRD peaks, XRD spectra were characterized using the Peak Fitting module. The crystal size (D) was calculated from the (002) peak width by using the Scherrer's equation

$$D = \frac{0.9\lambda}{\beta_{1/2}\cos(\theta)} \quad (1)$$

where D, λ, $\beta_{1/2}$ and θ are the mean crystal size, the X-ray wavelength, full-width at haft-maximum (FWHM) and Bragg diffraction angle, respectively. The lattice parameter of *c* was calculated using Equation (2) for the film:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (2)$$

where *d* is lattice spacing, *a* and *c* are lattice parameters.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

C. Room Temperature Photoluminescence of $Zn_{1-x}Li_xO$ Nanorods

Photoluminescence studies were carried out using a He-Cd laser operating at wavelength of 325 nm. The PL spectra of Li-doped ZnO nanorods at various Li content are shown in Figure S3. These spectra can be divided by Gaussian fitting.

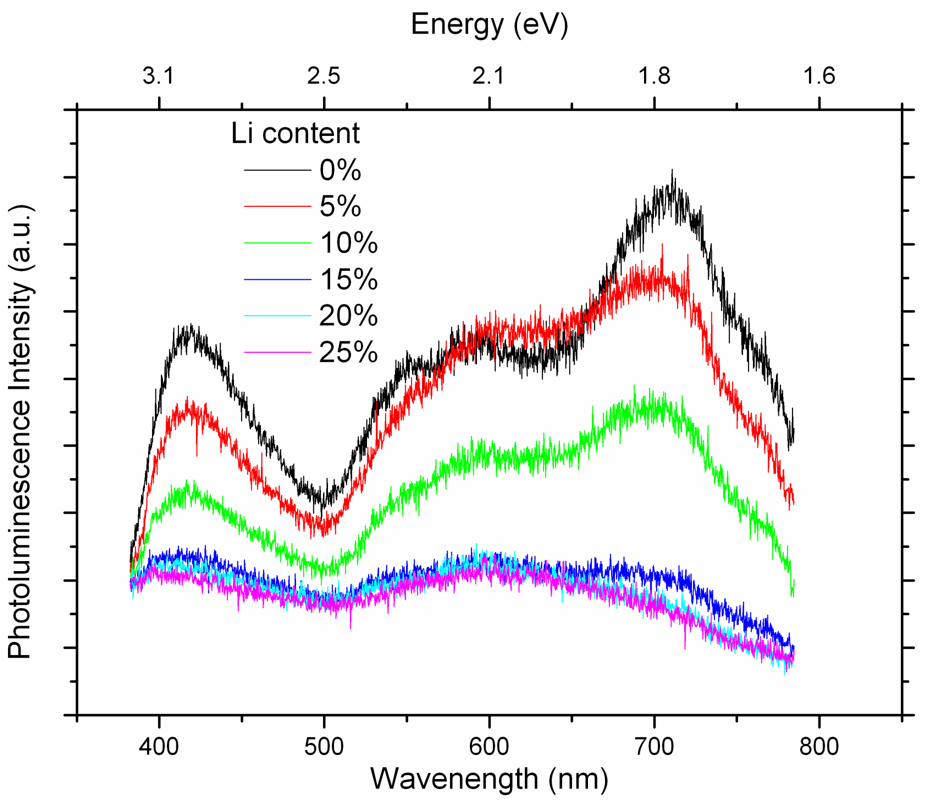

Fig. S3 The PL spectra of Li-doped ZnO nanorods at various Li content (0% - 25%)

D. Photoemission Yield Spectroscopy in Air (PYS) Study

In order to understand the electric conductivity due to the Li incorporation, the PYS were performed in air with the Riken Keiki AC-2 system, which are shown in Figure S5. Threshold energy of photoemission corresponds to the first ionization potential.

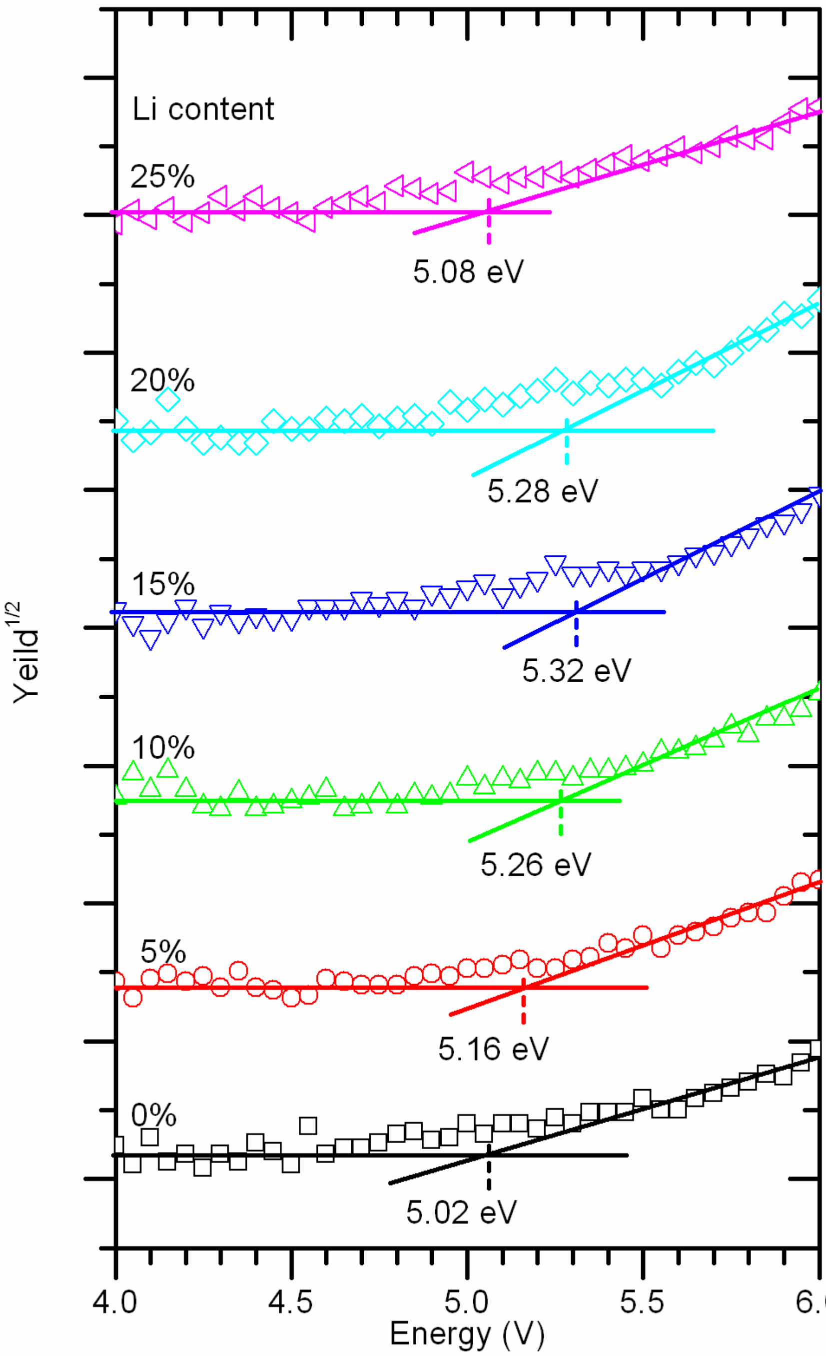

Fig. S4 Photoemission yield of Li-doped ZnO nanorods at various concentration of dopant

E. Optical Energy Gap Measurement

Transmittances and absorbances of Li doped ZnO nanorods coated on glass substrate were collected using UV-vis spectrophotometer (UV-2450 SHIMADZU), as shown in Figure S4.

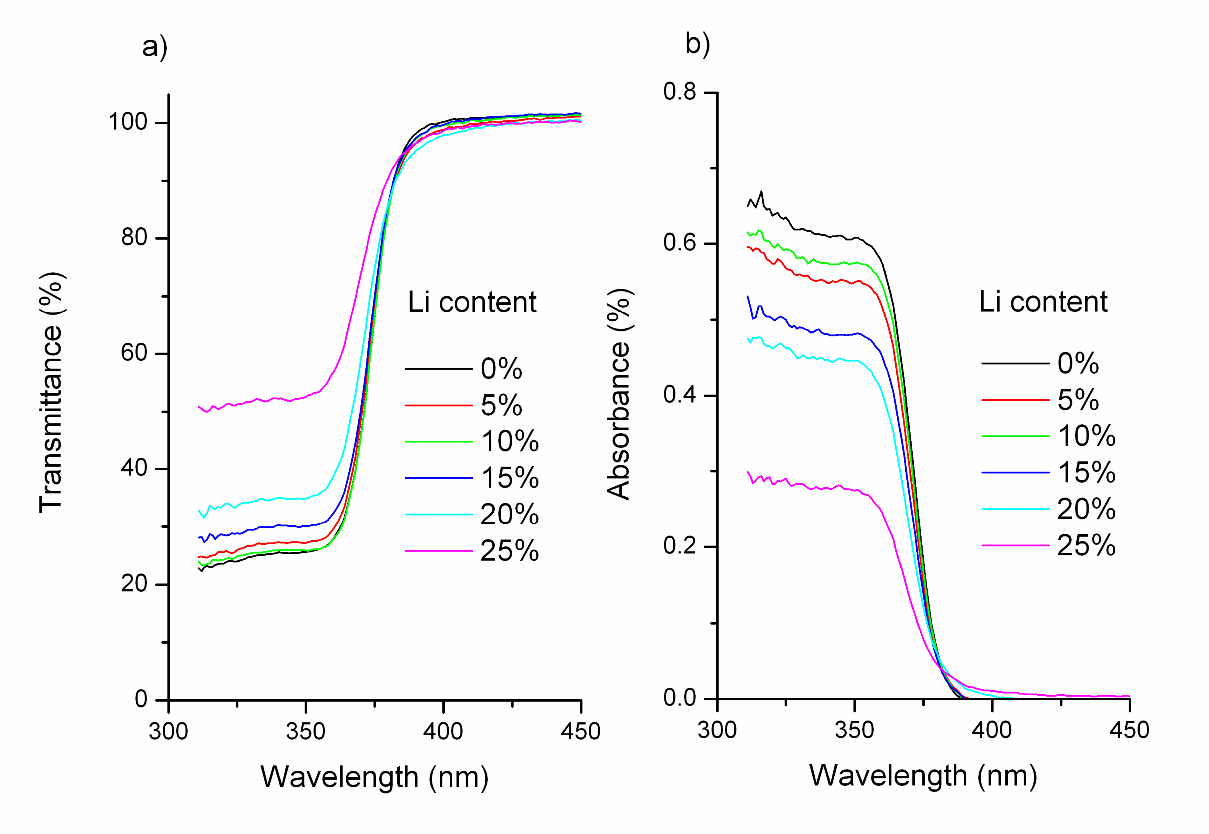

Fig. S5 Transmittances and absorbances of Li doped ZnO nanorods at various Li content coated on glass substrate.

The absorption coefficient (α) was calculated from Lambert-Beer-Bouguer law ;

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \tag{3}$$

where d and T is thickness of the film and transmittance, respectively. The optical band gap of the films was determined using Equation (4) (S. M. Sze, Physics of Semiconductor Devices ,Wiley-Interscience, 2006);

$$\alpha = A(h\nu - E_g)^m \tag{4}$$

where ν, E_g and m are wavelength, optical energy gap and constant which determines types of optical transition (m = 1/2 for allowed direct transition and m = 2 for allowed indirect transition).

F. Fitting of Current-Voltage Characteristics by Equivalent Circuit Model

To investigate the effect of Li incorporation into ZnO crystal on photovoltaic performance, the single diode model (S. Choi, W. J. Potscavage, B. Kippelen, J. Aapl. Phys. 2009, 106) was performed by Equation (5);

$$J = J_0\left\{\exp\left(\frac{V - JR_S A}{nkT/e}\right) - 1\right\} + \frac{V - JR_S A}{R_P A} - J_{ph} \qquad (5)$$

where J is the current density, J_0 is the diode reverse saturation current density, J_{ph} is the light-generated current density, q is the electronic charge, V is the applied voltage, A is the device active area, R_S is the series resistance, n is the ideality factor, k is Boltzmann's constant, T is temperature, and R_P is the shunt resistance. The fitting parameters were J_0, n, R_S, R_P. The J-V characteristics for all devices were fitted well as shown in Figure S6.

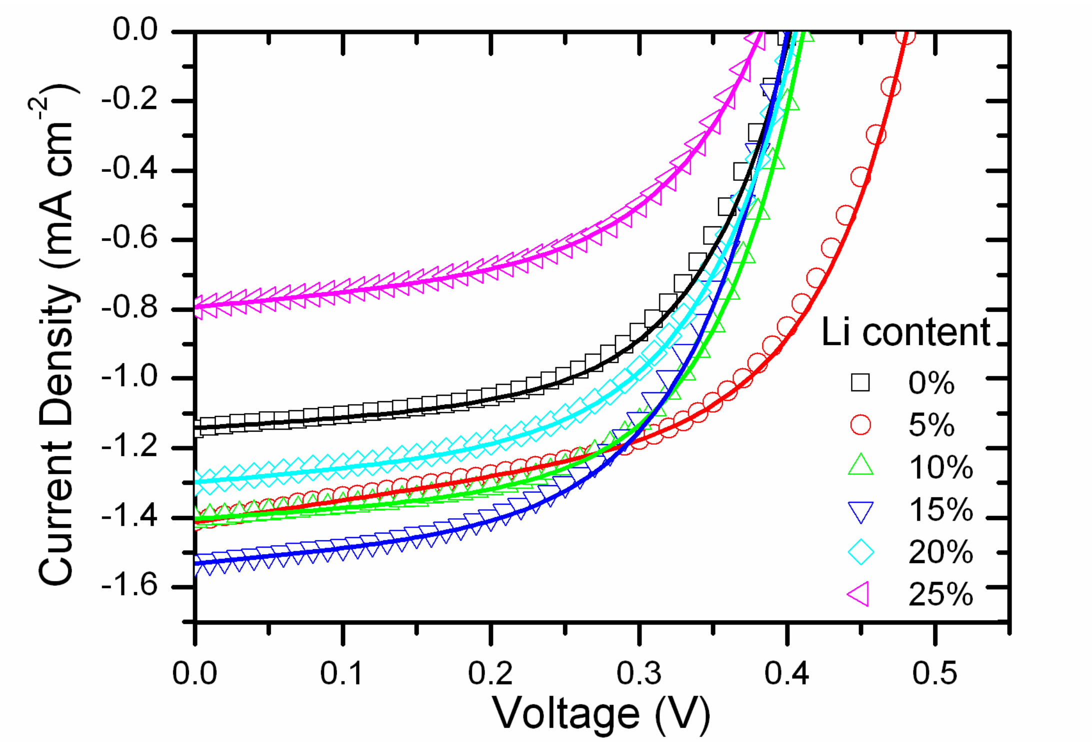

Fig. S6 Experimental (shapes) and fitted (solid lines) J-V characteristics for hybrid Li-doped ZnO nanorod/P3HT solar cell under illumination.

Reference

1 B.D. Cullity; S.R. Stock, *Element of X-ray Diffraction*, 3rd ed., Prentice Hall, 2001