Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

High-Efficiency Metal-Free Organic-Dye-Sensitized Solar Cells with Hierarchical ZnO Photoelectrode

Hsin-Ming Cheng [†] **and Wen-Feng Hsieh** [*,†]

[†]*Department of Photonics & Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan*

* Author to whom the correspondence should be addressed:
Tel: +886-3-5712121 ext. 56316;
Fax: +886-3-5716631;
e-mail: wfhsieh@mail.nctu.edu.tw

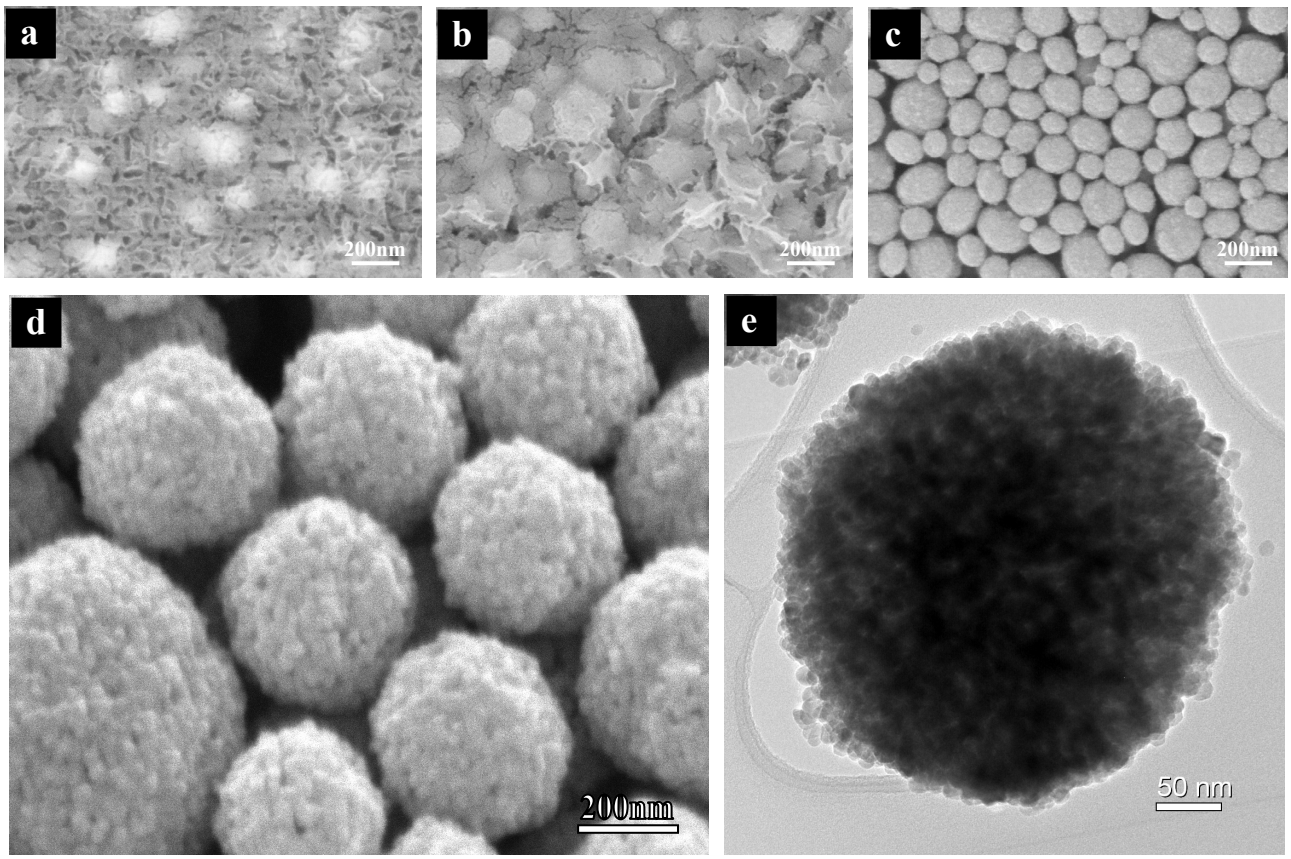

Figure S1. Parts (a)-(c) of figure S1 show the evolution of micrographs for various aging times via sol-gel method. Parts (d) and (e) show the FESEM and TEM images of the hierarchical ZnO secondary nanoparticle with agglomeration of primary single crystallites ranging from 6 to 12nm. (The detailed synthesis procedure has been presented exhaustively in our previous papers: H. M. Cheng, H. C. Hsu, S. L. Chen, W. T. Wu, C. C. Kao, L. J. Lin and W. F. Hsieh, *J. Cryst. Growth,* 2005, **277,** 192; H. M. Cheng, K. F. Lin, H. C. Hsu, C. J. Lin, L. J. Lin and W. F. Hsieh, *J. Phys. Chem. B*, 2005, **109,** 18385.)

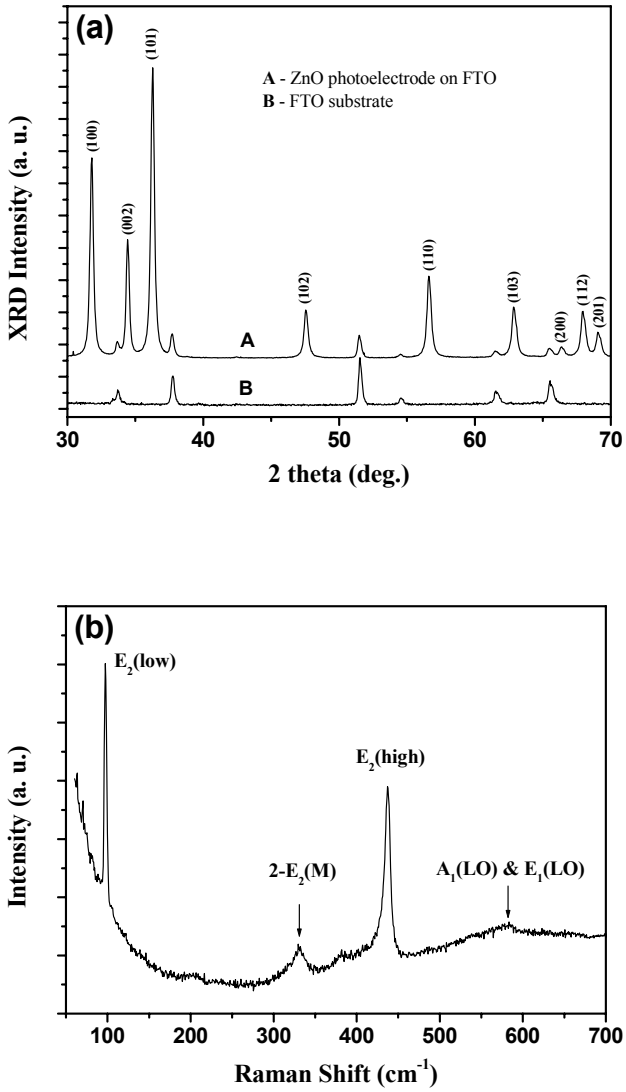

Figure S2. (a) θ-2θ XRD profiles of A: The printed ZnO photoelectrode on Fluorine doped tin oxide (FTO) substrate and B: Bare FTO substrate only. The XRD profiles corresponds to the presence of hexagonal wurzite crystallites (JCPDF Card # 36-1451) with cell constants of a = 3.251 Å and c = 5.208 Å. No excess peaks were detected, which indicates that all the binders have been completely decomposed during annealing. (b) Raman spectra of the ZnO photoelectrode, using a frequency-doubled Yb:YAG laser (λ = 515 nm). The remarkable E_2(low) and E_2(high) mode of ZnO are located at 97.5 cm^{-1} and 437 cm^{-1}, respectively. The peak at 331 cm^{-1} can be assigned to the second order Raman scattering arising from zone-boundary phonons 2-E_2(M) of ZnO. The weak and almost invisible signal around 582 cm^{-1} is contributed to the superimposition of A_1(LO) and E_1(LO). No substrate signals appeared because of the penetration limitation of 515-nm laser light. The good crystalline quality of ZnO nanostructures confirmed above ensure that the photoelectrode can offer good electronic conductivity and avoid the electron trapping within the structural defects.

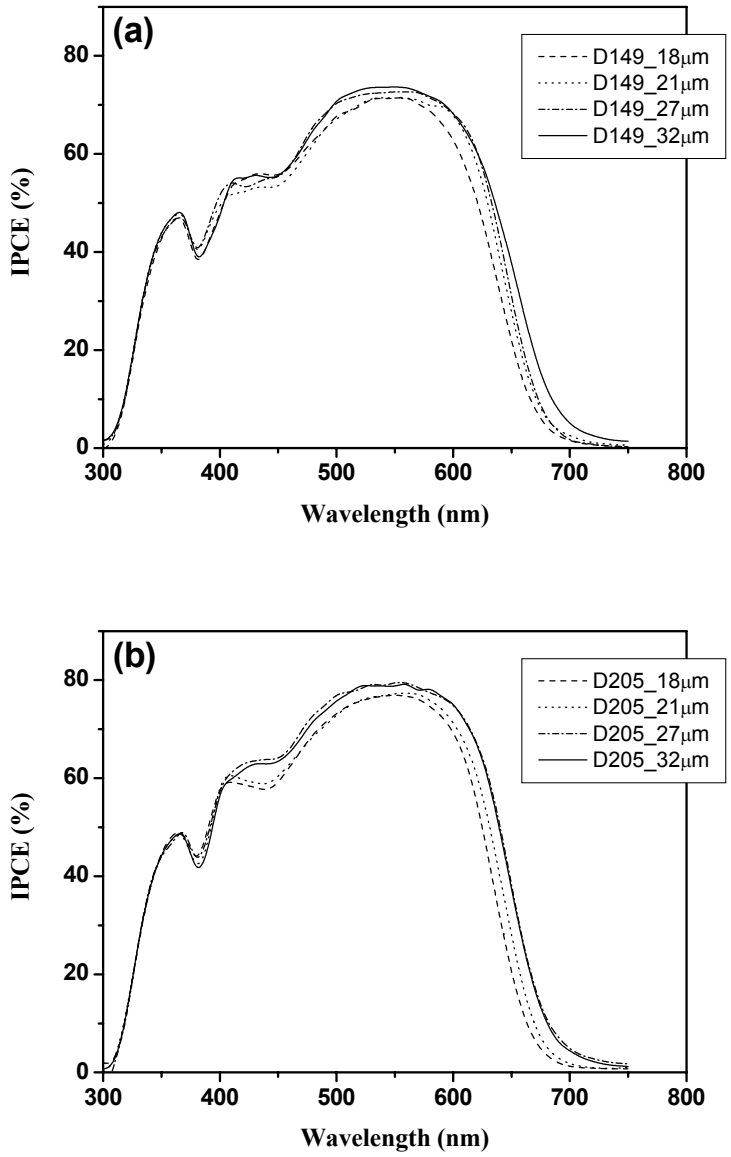

Figure S3. Figure (a) and (b) display the wavelength distribution of incident monochromatic photon to current conversion efficiency (IPCE) spectra of DSCs constructed using two indoline dyes (D149 and D205) with different ZnO photoelectrode thicknesses. The photocurrents at the peak approximately 367 nm, which are due to direct light harvesting by ZnO semiconductor, remain almost unchanged while increasing the photoelectrode thicknesses from 18 μm to 32 μm because of the small penetration depth for UV light. However, with the increase of thickness of ZnO photoelectrode, the maximum IPCE values increase from 71% up to 74% and 77% up to 79% at 550 nm for D149-, and D205-sensitized ZnO DSCs, respectively. Moreover, the values of IPCE increase significantly in the longer wavelength region (580 - 700 nm) with thicker photoelectrode films but saturated at the thickness about 30μm because the limitation of electron diffusion length. The numerous cracks in thick photoelectrode films (>32 μm) were also observed as a result of unpracticed-printing technology.

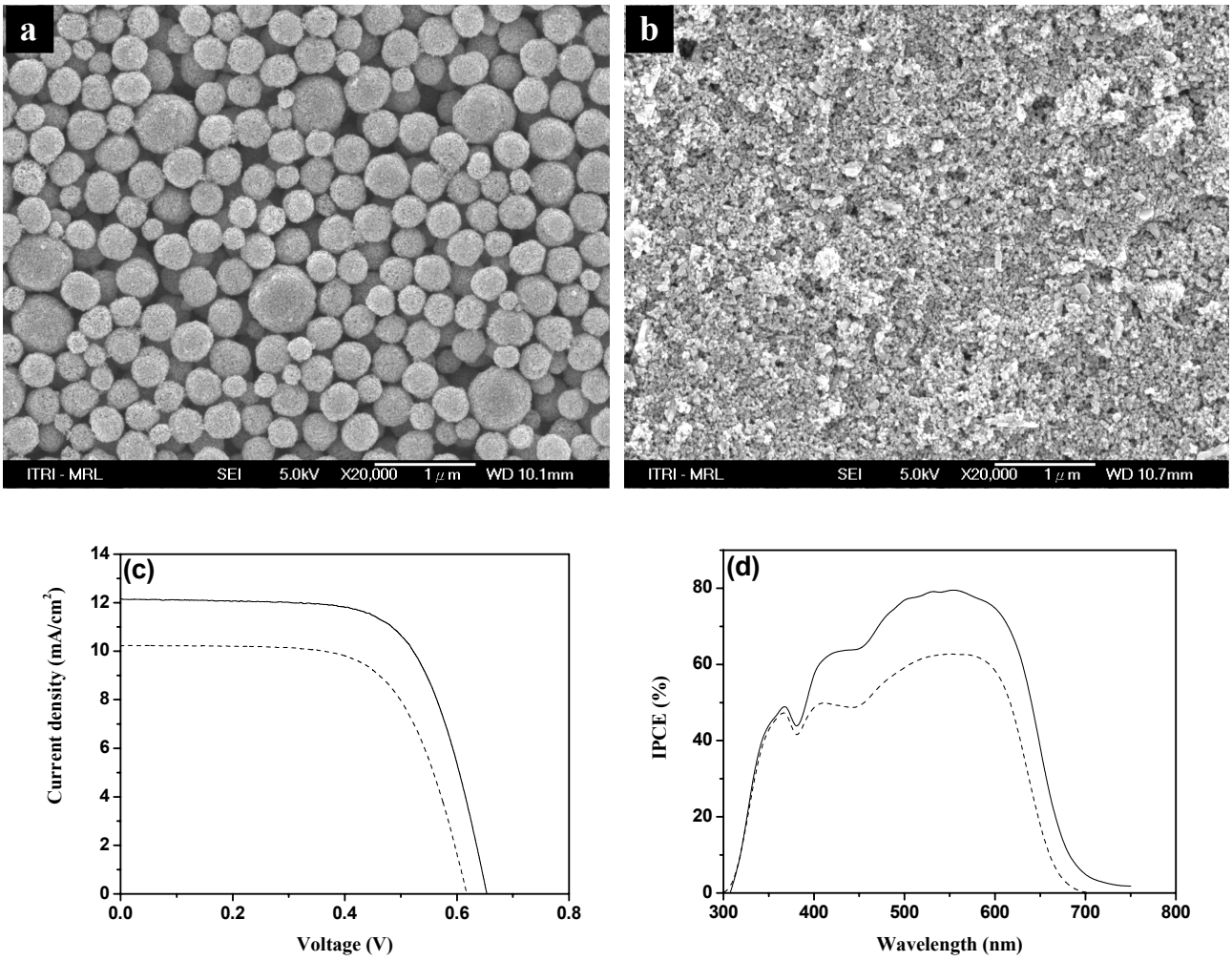

Figure S4. (a) FESEM image of hierarchical ZnO secondary nanoparticles. (b) FESEM image of non-aggregated ZnO nanoparticles from grinding the original ZnO secondary nanoparticles. (c) photocurrent–voltage (J-V) curves and (d) photocurrent action spectra of D205-sensertized DSCs composed with 27 μm-thick hierarchical ZnO photoelectrode (solid line) and 23 μm-thick grinded nanoparticles (size ~10 nm) with 4 μm-thick commercial ZnO particles (Merck Ltd. Particle Size ~200 nm) as a scattering layer on the top (dash line). For the grinded particles, the J-V curve reveals V_{oc} = 618 mV, J_{sc} = 10.22 mA cm^{-2}, FF = 0.66, and η = 4.16 %, for which the performance is poorer than the hierarchical ZnO potoelectrode. The IPCE spectrum also shows remarkable deterioration in the visible-wavelength (400-700 nm) region for the D205-sensertized DSC composed with grinded nanoparticles because insufficient light-traveling distance. The insufficient light-harvesting for non-aggregated ZnO potoelectrode also leads to increasing the non-excited area, which lowers V_{oc} further after averaging the electron density, as shown in J-V curves.