Supporting information

Efficient electron transport in ZnO nanowire/nanoparticle dye-sensitized solar cells via continuous flow injection process

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Light harvesting efficiency (LHE)

According to the definition, the incident monochromatic photo-ti-current conversion efficiency (IPCE) is expressed in terms of the light harvesting efficiency (LHE), the quantum yield of charge injection (ϕ_{inj}) and the efficiency of collecting the injected charge at the back contact (η_{CC}).

$$\mathrm{IPCE}(\lambda)=\mathrm{LHE}(\lambda)\cdot\phi_{inj}\cdot\eta_{CC} \qquad \text{(S-1)}$$

The light harvesting efficiency is given by

$$\mathrm{LHE}(\lambda)=1-10^{-\Gamma\sigma(\lambda)} \qquad \text{(S-2)}$$

Γ is the number of moles of sensitizers per square centimeter of projected surface area of the film and σ is the absorption cross section in unit cm^2/mol obtained from the extinction coefficient (unit:$M^{-1}cm^{-1}$) by multiplication with 100 cm^2/L.

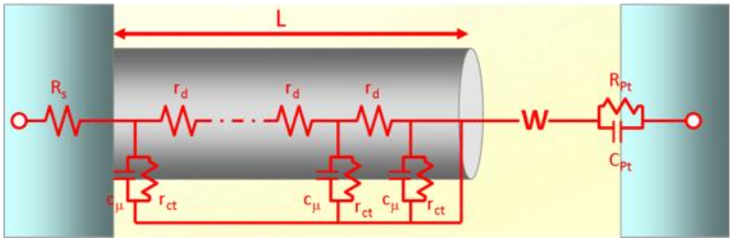
Recombination lifetime, τ_n

The kinetics of transport and recombination in dye-sensitized solar cells (DSSCs) have been investigated by several methods, such as electrochemical impedance spectroscopy (EIS)[S1-S2] as well as intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS).[S3-S4] “Recombination” in DSSCs is defined as including and mainly representing the back electron transfer by the back reaction of electrons with oxidized redox species.

EIS is a well-established technique in characterizing DSSCs because it shows all kinetic processes of DSSCs, such as electron transport in the photoanode, recombination property at photoanode/electrolyte interface, charge transfer at counter electrode/electrolyte interface, and electrolyte diffusion in an electrolyte.[S5-S7]

During EIS analysis, a bias voltage is applied to DSSCs, the electrons are injected into the photoanode from a back collection electrode, and the photoanode gets charged by propagation of the injected electrons. At the same time, some of the injected electrons in the conduction band of photoanode are recombined with I_3^- ion in a redox electrolyte. These processes are denoted as semicircles ar different frequency ranges in a Nyquist plot. The diffusion-recombination model was usually used to analyze these electronic processes. In this model, two basic diffusion theoreies, the continuity equation and the constitutive equation, combine with a first-order recombination reaction, and the term of $\tau_n \sim k_{eff}^{-1}$, where τ_n is electron lifetime and k_{eff}^{-1} is kinetic rate constant.

Under the open circuit voltage (V_{oc}) condition, a Nyquist plot just display a charge transfer resistance at the counter electrode/electrolyte interface (R_{pt}) and the photoanode (i.e., ZnO NW or ZnO NW/NP)/electrolyte interface ($R_{ct}=r_{ct}/L$) as shown in the following.



A diffusion resistance ($R_d=r_d \cdot L$) representing a degree of how effective charge transport by diffusion along with the photoanode. Therefore, the electron lifetime (τ_n), electron diffusion coefficient (D_n) and effective diffusion length (L_n) can be calculated by using R_{ct} and R_d and the corresponding chemical capacitance (C_μ) as follows.

$$\tau_n = R_{ct}C_\mu \;;\; D_n = \frac{L^2}{\tau_d} = \frac{L^2}{R_d C_\mu} \;;\; L_n = \sqrt{\tau_n D_n} \tag{S-3}$$

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[S2] J. Bisquert, G. G. Belmonte, F. Fabregat-Santiago, N. S. Ferriols, P. Bogdanoff, E. C. Pereira, *J. Phys. Chem. B*, 2000, **104**, 2287-2298.

[S3] J. van de Lagemaat, N. G. Park, A. J. Frank, *J. Phys. Chem. B*, 2000, **104**, 2044-2052

[S4] N. W. Duffy, L. M. Peter, K. G. U. Wijayantha, *Electrochem. Commun.*, 2000, **2**, 262-266.

[S5] J. Bisquert, *J. Phys. Chem. B*, 2002, **106**, 325-333.

[S6] Q. Wang, S. Ito, M. Grätzel, F. Fabregat-Santiago, I. Mora-Seró, J. Bisquert, T. Bessho, H. Imai, *J. Phys. Chem. B*, 2006, **110**, 25210-25221.

Table S1 Dye loading amount analysis for all kinds of ZnO-NW and ZnO-NW/NP photoanodes

Samples	Dye loading amount (nmol/cm^2)
NW-I	25.09
NW-II	27.17
NW-III	21.62
NW-IV	22.67
NW/NP-I	197.91
NW/NP-II	114.49

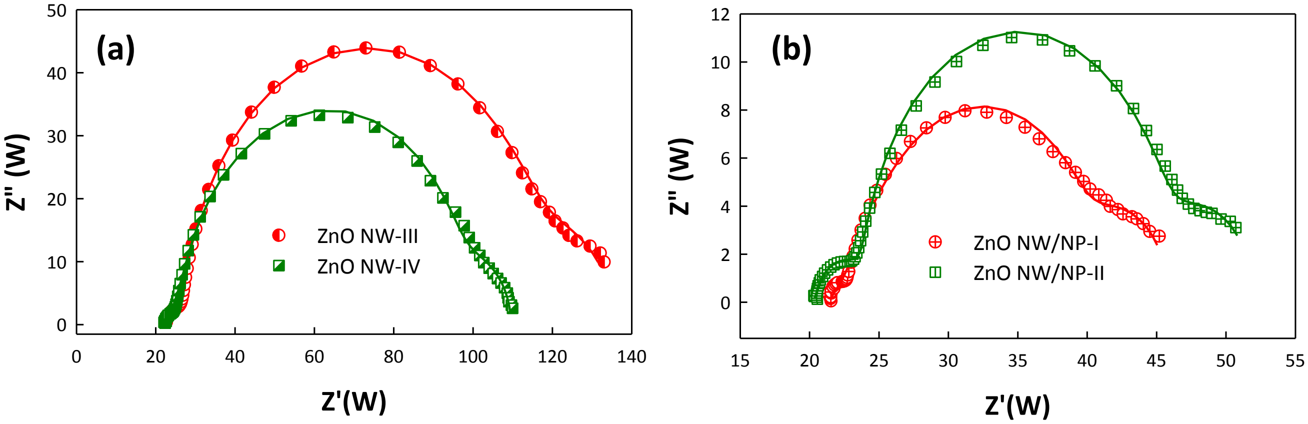

Fig. S1 Nyquist plots of (a) ZnO NW-III (CFI, 24 h) and ZnO NW-IV (NH_3-assisted CFI, 24 h) DSSCs; (b) ZnO NW/NP-I (NPs, 8 h) and ZnO NW/NP (NPs, 20 h) DSSCs.

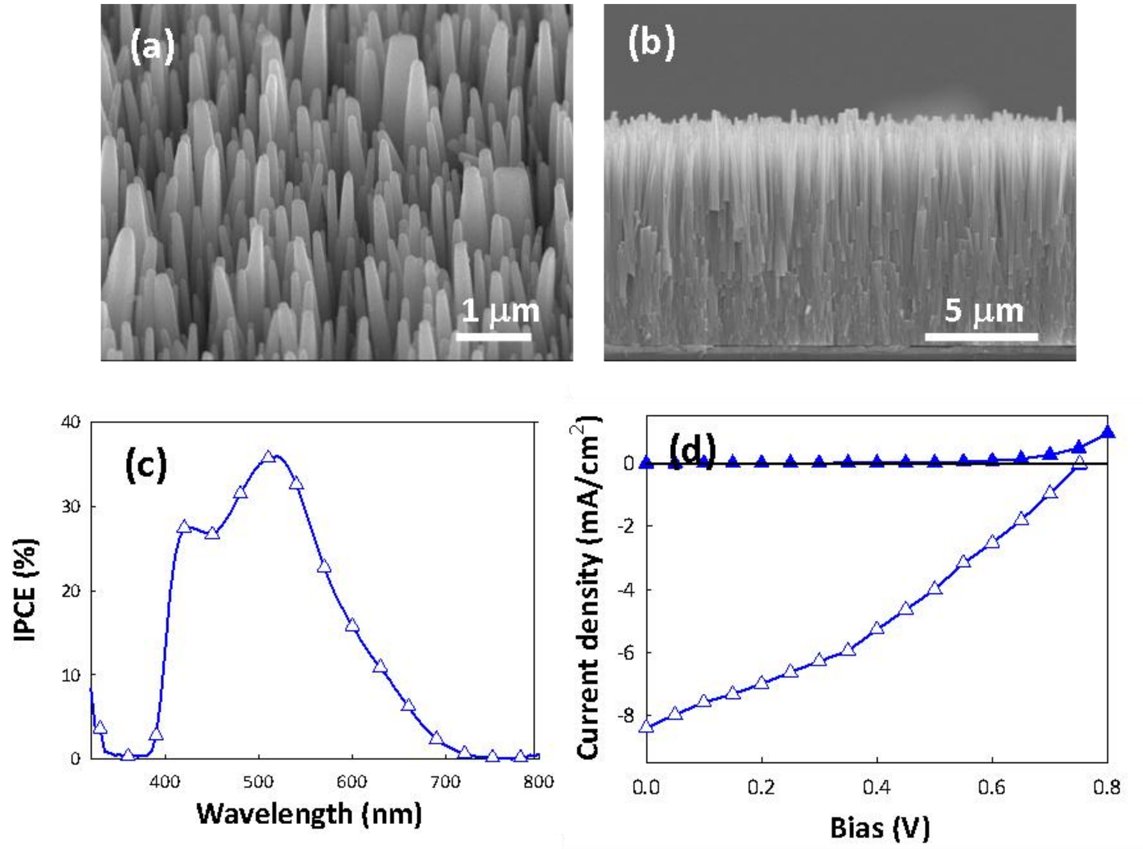

Fig. S2 (a) tilt-view and (b) cross-sectional SEM images of ZnO-NWs prepared by using batch process with adding ammonium (batch-NH_3). (c) IPCE and (d) J-V characteristic of N719 dye sensitized solar cells by this photoanode

Table S2 The performance and electron transport properties of DSSCs with batch-NH_3 photoanode

R_{ct} (Ω)	C_μ (μF)	τ_d (ms)	τ_n (ms)	D_n (cm^2/s)	L_n (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
36	569	0.35	20.66	3.61×10^{-3}	86	8.40	0.75	0.34	2.11

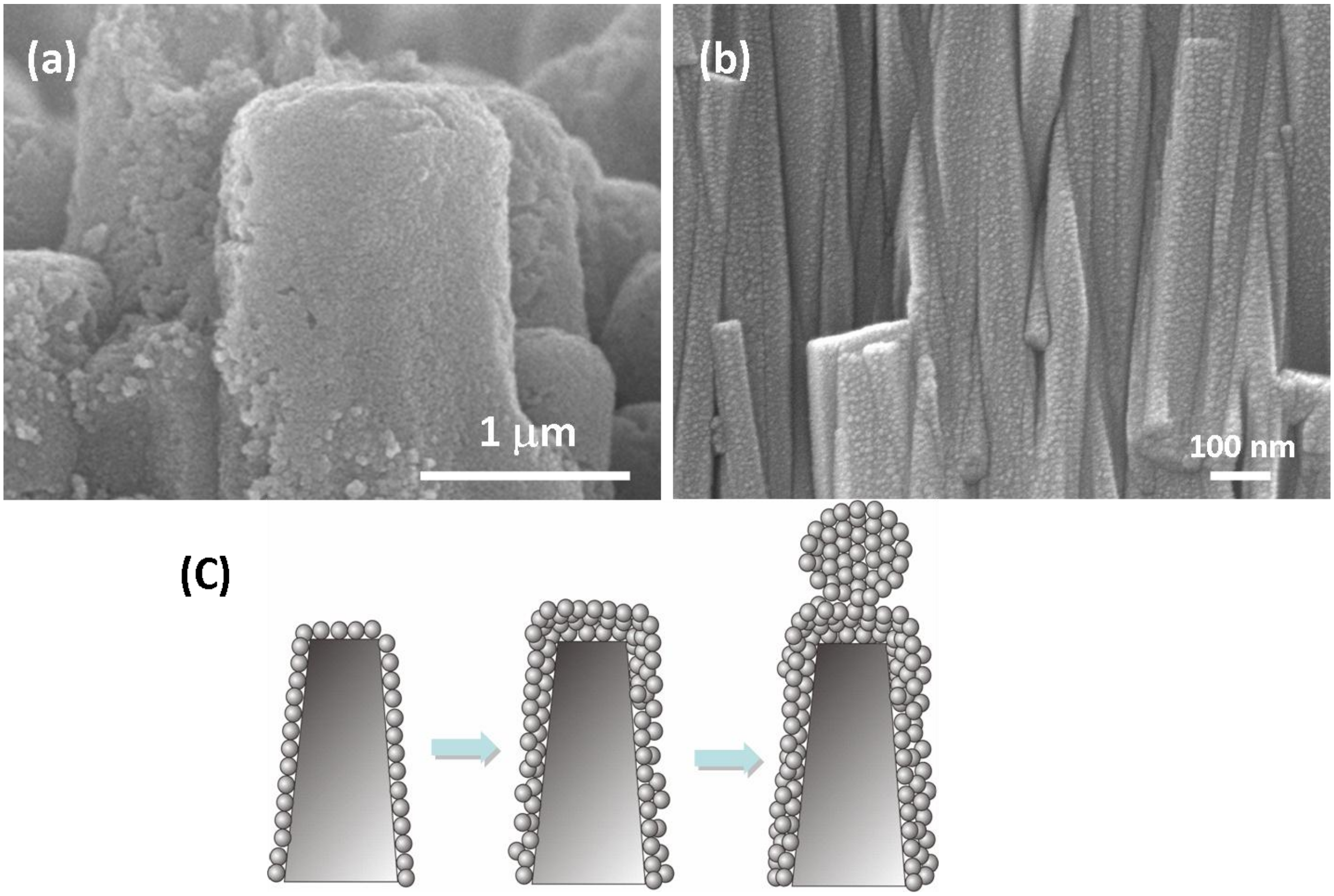

Fig. S3 Enlarging cross-section scanning electron microscopy images of (a) top and (b) bottom part of ZnO NWs/NPs composite photoanode. (c) The schematic figure for the formation of ZnO NW/NP and ZnO microclusters.

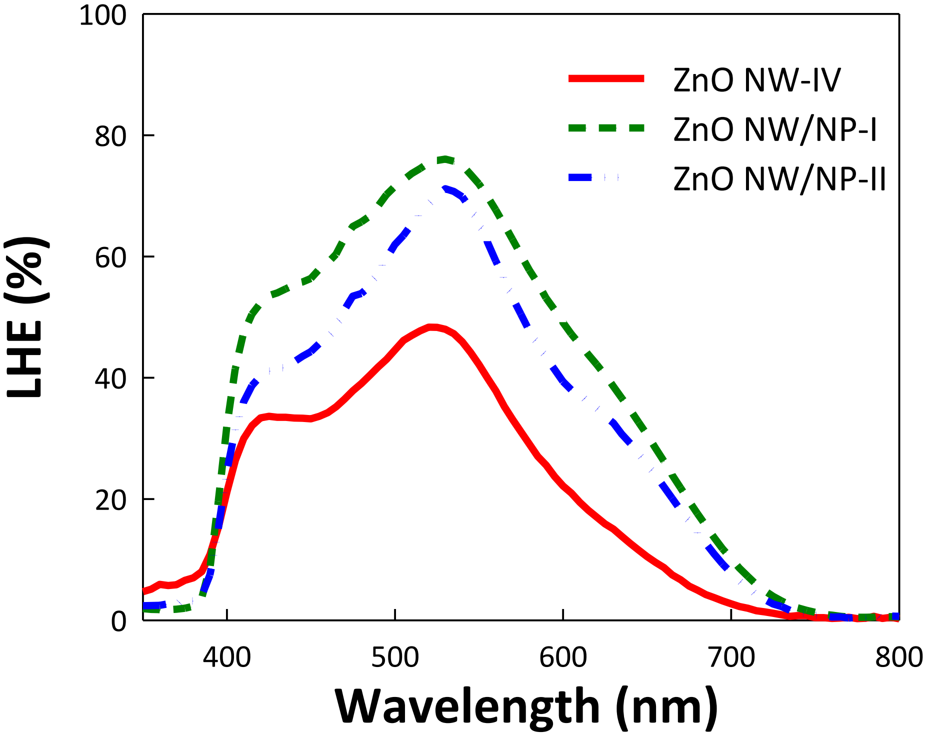

Fig. S4 Light harvesting efficiency (LHE) of ZnO NW-IV, ZnO NW/NP-I and ZnO NW/NP-II