Supplementary Information

Transport of photogenerated charges and photoelectric properties in two types of heterostructures with different ZnO microstructures †

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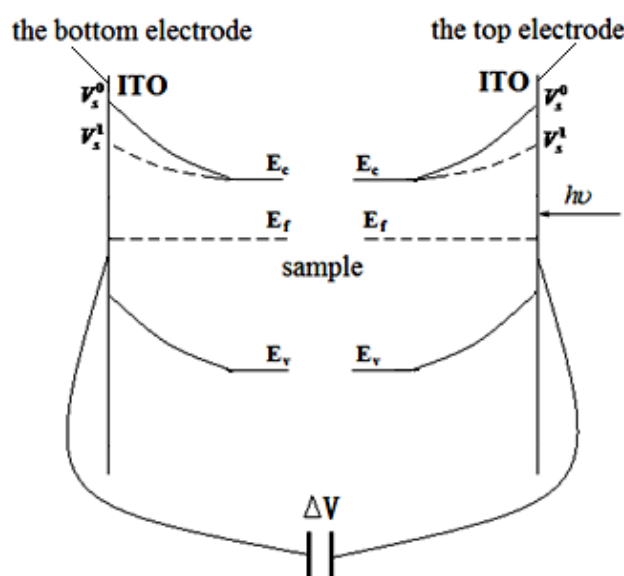*E-mail: lxy081276@126.com*

Supplementary Figures

Fig. SI1 The schematic diagram of sandwich structure consisting of ITO (indium tin oxide) and sample in the steady state and electric field induced-surface photovoltage spectroscopy. (E_c : the bottom of conduction band; E_v : the top of valence band; E_f : the Fermi energy level; ΔV : the difference of different surface potential; V_s^0 : the surface potential before illumination; V_s^1 : the surface potential after illumination; V_s^0 , $V_s^1 > 0$; $h\upsilon$: the incident photon energy).
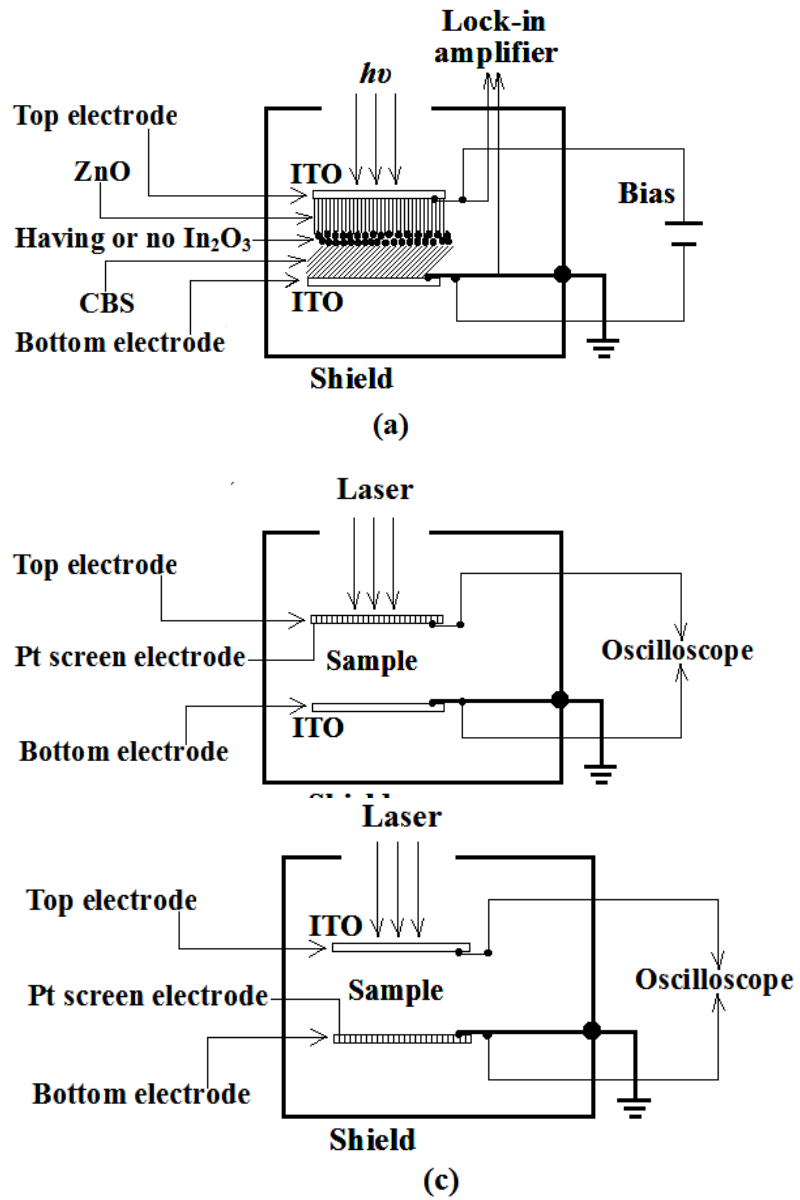
Fig. SI2 The schematic diagrams of sandwich structure for (a) SPS, EFISPS, (b) and (c) TSP measurements with the direction of illumination (*hv*: the incident photon energy).
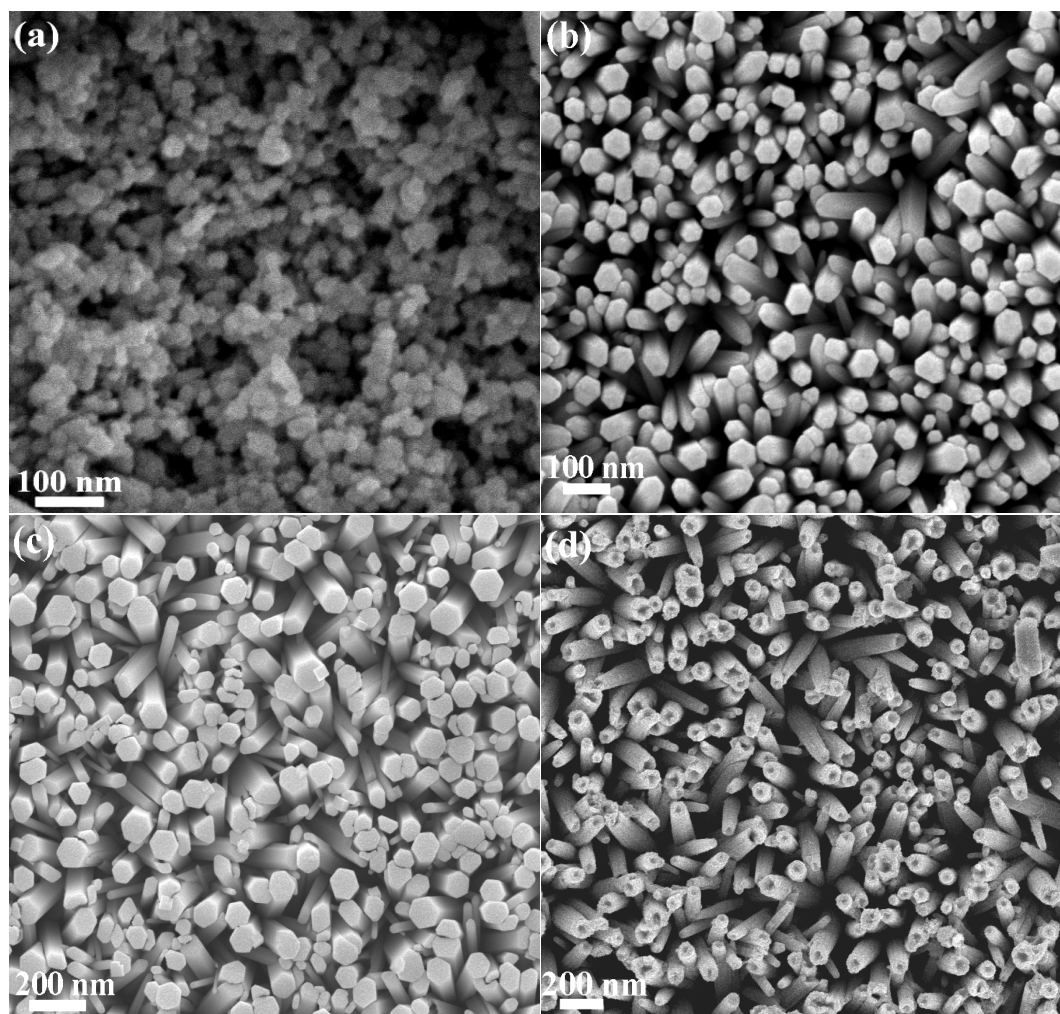
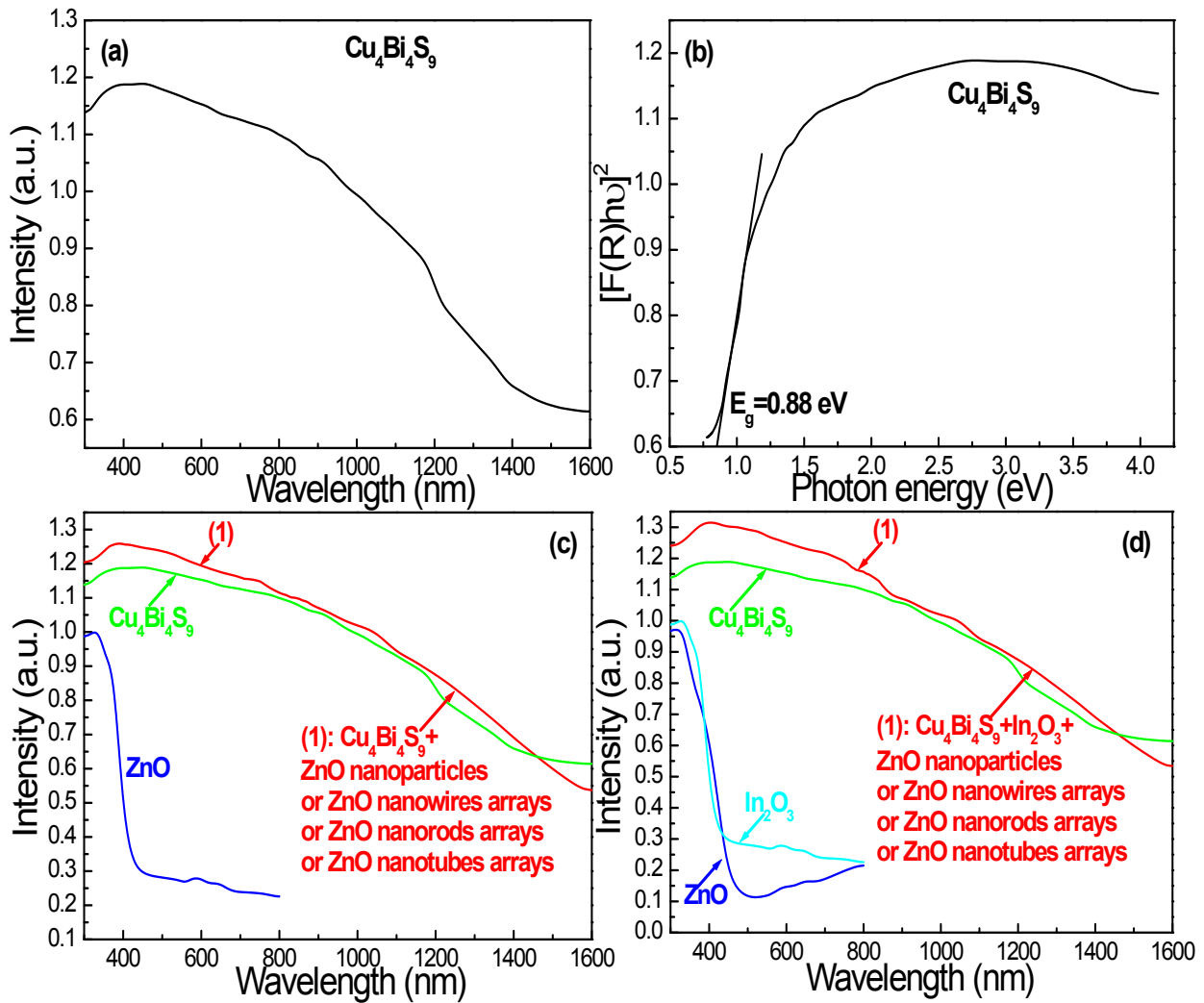**Fig. SI3** SEM images of ZnO (a) nanoparticles, (b) nanowires arrays, (c) nanorods arrays and (d) nanotubes arrays.

Fig. SI4 UV-Vis spectra of (a) $Cu_4Bi_4S_9$, (b) $Cu_4Bi_4S_9$, (c) $Cu_4Bi_4S_9$, ZnO, ZnO/$Cu_4Bi_4S_9$ (only showing one nanostructure of ZnO), (d) $Cu_4Bi_4S_9$, In_2O_3, ZnO, ZnO/In_2O_3/$Cu_4Bi_4S_9$ (only showing one nanostructure of ZnO).
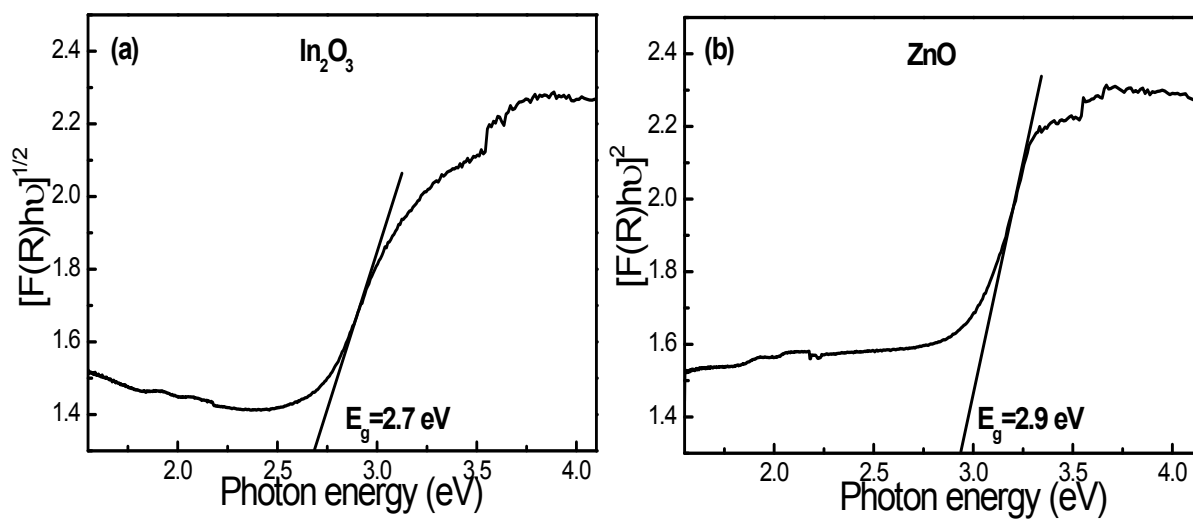
Fig. SI5 The plots of F(R)hv against the photo energy about (a) In$_2$O$_3$ and (b) ZnO with different nanostructures, respectively.

vacuum   vacuum

unoccupied levels

the energy band of CBS

E^0_{unoc}

the overlapped zone

E^0_{unoc}

the energy band
of CBS

the energy band of oxides

unoccupied levels

the energy band
of oxides

density of states

Electron Energy: eV (AVSV)   0.0

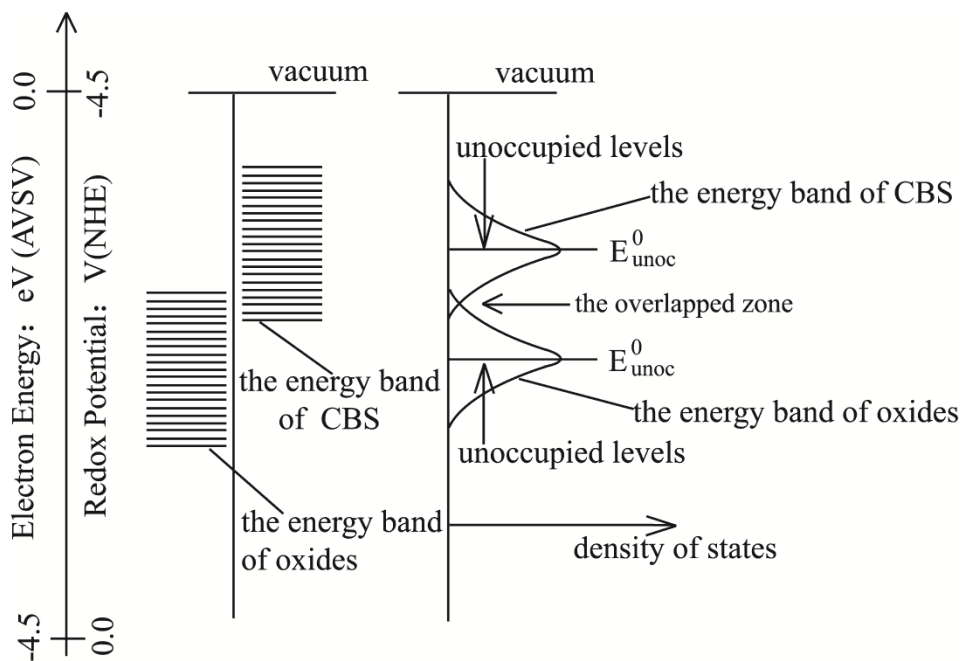Redox Potential: V(NHE)   -4.5

-4.5

0.0

Fig. SI6 The transport mechanism of photogenerated charges under zero and positive bias in four sensitized electrodes (E_c: the bottom of conduction band; E_v: the top of valence band; E_f: the Fermi energy level; ΔEc: the difference of conduction band edges at the interface; ΔEv: the difference of valence band edges at the interface; *NHE*: the normal hydrogen electrode; *AVS*: the absolute vacuum energy scale; *hv*: the energy of photon).