Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

for

Highly Efficient Perovskite Solar Cells Based on a Nanostructured WO_3-TiO_2 Core-Shell Electron Transporting Material

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1. Experimental Section

1.1 Deposition of monoclinic WO_3 nanoparticles (NPs) film using electrospray

The WO_3 film of nanoparticles (NPs) was deposited onto the cleaned fluorine-doped tin oxide (FTO) substrates using the electrospraying method at atmospheric pressure.[S1,S2] The sprayed solution was made by dissolving 1.25 g of tungstic acid (H_2WO_4) and 0.5 g poly(vinyl alcohol) (PVA) in 10 mL of 5 wt% hydrogen peroxide (H_2O_2) as reported elsewhere. [S3] FTO substrates were cleaned using isopropyl alcohol (IPA), ethanol, acetone and water, respectively. The cleaning process was repeated three times to obtain the well cleaned substrates. The precursor solution was sprayed with a flow rate of 0.003 mL/min, through a small stainless steel nozzle using a syringe pump (KD200, KD Scientific Inc., U.S.A.). To obtain the stable cone-jet mode high voltage of about 5 kV was applied between the nozzle tip and the substrate with the help of a dc power supply (Korea switching, Inc., Korea), by keeping a fixed distance of 4.2 cm between these two. In order to completely evaporate the solvent inside the film, substrate was heated upto 160°C before spraying; using a hot plate and solution was sprayed for 80 minutes. The resulting WO_3 films composed of nanoparticles were the annealed in air at 500°C for 1 h.

1.2 Hydrothermal growth of monoclinic WO_3 nanorods (NRs) arrays

In order to accomplish the hydrothermal reaction, the growth solution was prepared as mentioned below and reported elsewhere. [S3] Citric acid (0.96 g) and tungstic acid (0.125 g) were dissolved into the 50 mL of DI water and stirred continuously for about three days in order to obtain the homogeneous solution. The FTO substrates having the electrospray-deposited monoclinic WO_3 NPs film were transferred to an autoclave which contained the above mentioned growth solution with pH of 2.5, adjusted by using a 0.5M NaOH solution. The autoclave was sealed and growth temperature was maintained at 180°C for 12 hours to complete the growth of nanorods. The samples were then taken out and thoroughly washed in DI water, acetone and ethanol to remove the residual salts and finally dried in air at 50°C. The resulting WO_3 nanorod arrays were annealed in air at 500 °C for 1 h.

1.3 Hydrothermal growth of monoclinic WO_3 nanosheets (NSs) arrays

For hydrothermal growth of WO_3 nanosheet arrays, the growth solution was prepared using 0.7 g of oxalic acid and 0.1 g of tungstic acid were dissolved into 50 mL of deionized water followed by a continuously stirring for more than two days in order to prepare the clear and homogeneous solution. The pH of 1.5 of the growth solution was adjusted using a 6 M HCL solution and finally the FTO substrates coated with the electrospray-deposited WO_3 seed layers were placed into the an autoclave having the above mentioned clear solution. The autoclave was heated to 180°C for a full day to grow the WO_3 nanosheet arrays. These were then washed, dried and annealed in air at 500 °C for 1 h.

1.4 Perovskite solar cells fabrication

The perovskite solar cells were fabricated with the help of a sequential deposition method reported elsewhere. [S4] Firstly, a very thin and compact layer of monoclinic WO_3 (act as blocking layer) was prepared using spin coating (2000 rpm for 30 sec) a solution which was made by dissolving 1.25 g H_2WO_4 and 0.5 g PVA in 10 mL of 35 wt% H_2O_2 on FTO glass, followed by annealing at 500 °C for 1 h in air. $TiCl_4$ treatment was applied to the WO_3 nanostructures in some cases to form a very thin layer of TiO_2. To do so, the as-prepared WO_3 nanostructures were immersed in 40 mM aqueous $TiCl_4$ solution at 70°C for 1 h, then rinsed with water and ethanol and sintered at 500 °C for 30 min. After that 1 M PbI_2 solution was dissolved in DMF while stirring overnight, with constant temperature of 70°C. Then the PbI_2 solution was spin coated for 5 s at a speed of 6000 rpm onto the as-prepared WO_3 nanostructures with different morphologies (electrosprayed NP film, vertically grown NRs arrays and NSs arrays) and optionally formed TiO_2 shell and baked at 70°C for 30 minutes until it dried completely. Samples were subsequently dipped into a solution of CH_3NH_3I in IPA with concentration of 10 mg/mL for roughly 20 minutes, followed by rinsing in IPA and finally drying at 70°C for 30 minutes. The HTL was prepared by spin coating the spiro-OMeTAD Hole (80 mg of 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene, 8.4 μl of 4-tert-butylpyridine, and 51.6 μl of bis (trifluoromethane) sulfonamide lithium salt (Li-TFSI) solution (154 mg/ml in acetonitrile), all mixture was dissolved in 1 ml chlorobenzene) solution for 30 s at 3000 rpm. Finally, 90 nm of silver was evaporated on top as the back contact.

1.5 Characterization

The nanostructured WO_3 films and fabricated perovskite solar cells were examined using field emission scanning electron microscopy (FE-SEM, Nova 320), which is coupled with an

X-ray energy dispersive spectrometer (EDXS) DX-4 to confirm the elemental composition of nanostructures. The crystallinity and the presence of conformal coating of TiO_2 on the WO_3 surface were confirmed using TEM images (HRTEM, JEM-3000F, JEOL). The elemental analysis of TiO_2 coated WO_3 nanostructures was performed using high resolution X-ray photoelectron spectroscopy (XPS, Theta Probe XPS Instrument, Thermo Fisher Scientific Co.) with step size 0.1 eV. The crystal structure was obtained using an X-ray diffractometer (XRD; D8 DISCOVER). The current-voltage characteristics of solar cells were achieved with the help of a using a solar simulator (Newport) under steady illumination AM1.5 spectral filter, and the intensity was adjusted to provide 1 sun (100 mW cm^{-2}). A forward scan was used with a rate of 1 V/s. The external quantum efficiency (EQE) spectra was measured with the help of EQE measurement system (PV Measurements Inc). Transport properties of solar cells were obtained using transient photocurrent decay and transient photovoltage decay. Diffusion coefficient and time constant for recombination (τ_R) of photo-generated electrons were measured by transient photocurrent-voltage spectroscopy setup, described elsewhere. [S5]

Supplementry References

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S5. H. S. Kim, J. W. Lee, N. Yantara, P. P. Boix, S. A. Kulkarni, S. Mhaisalkar, M. Grätzel and N. G. Park, *Nano Lett.,* 2013, **13**, 2412–2417.

Supplementary Figures

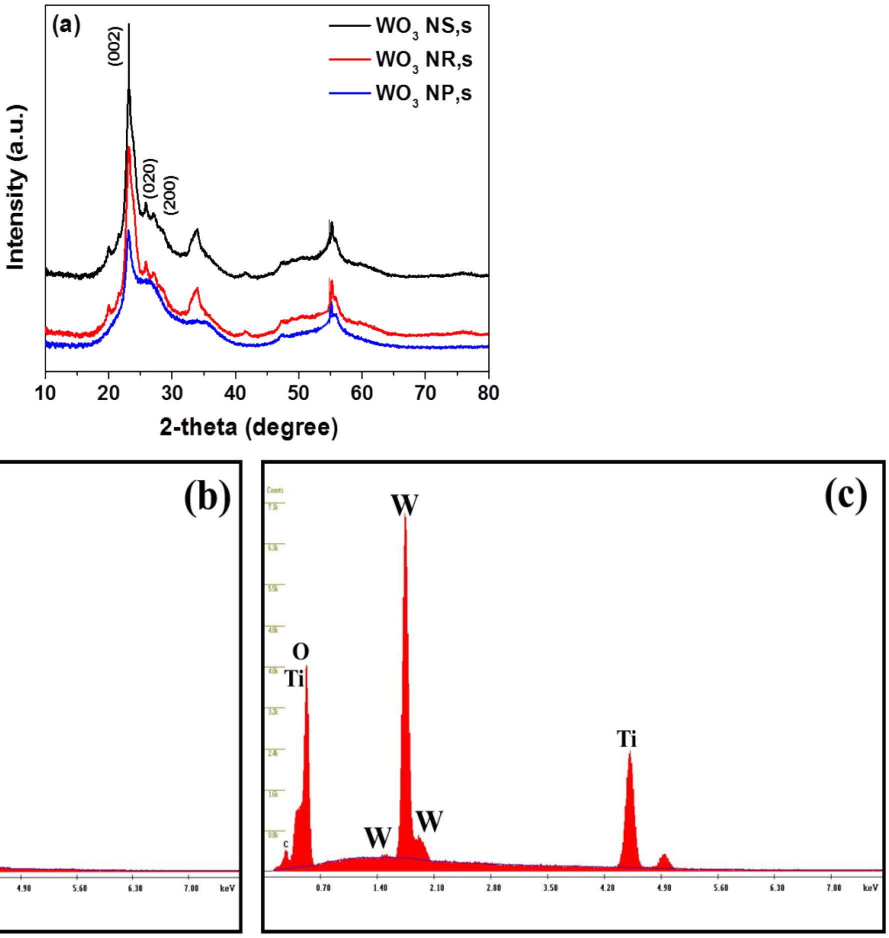

Figure. S1 (a) Comparison of XRD spectra of monoclinic WO_3 NPs, NRs and NSs, EDS spectra of WO_3 NSs before (b), and after (b) $TiCl_4$ treatment confirming the coexistence of W, O and Ti for TiO_2 coated WO_3 NS,s arrays.

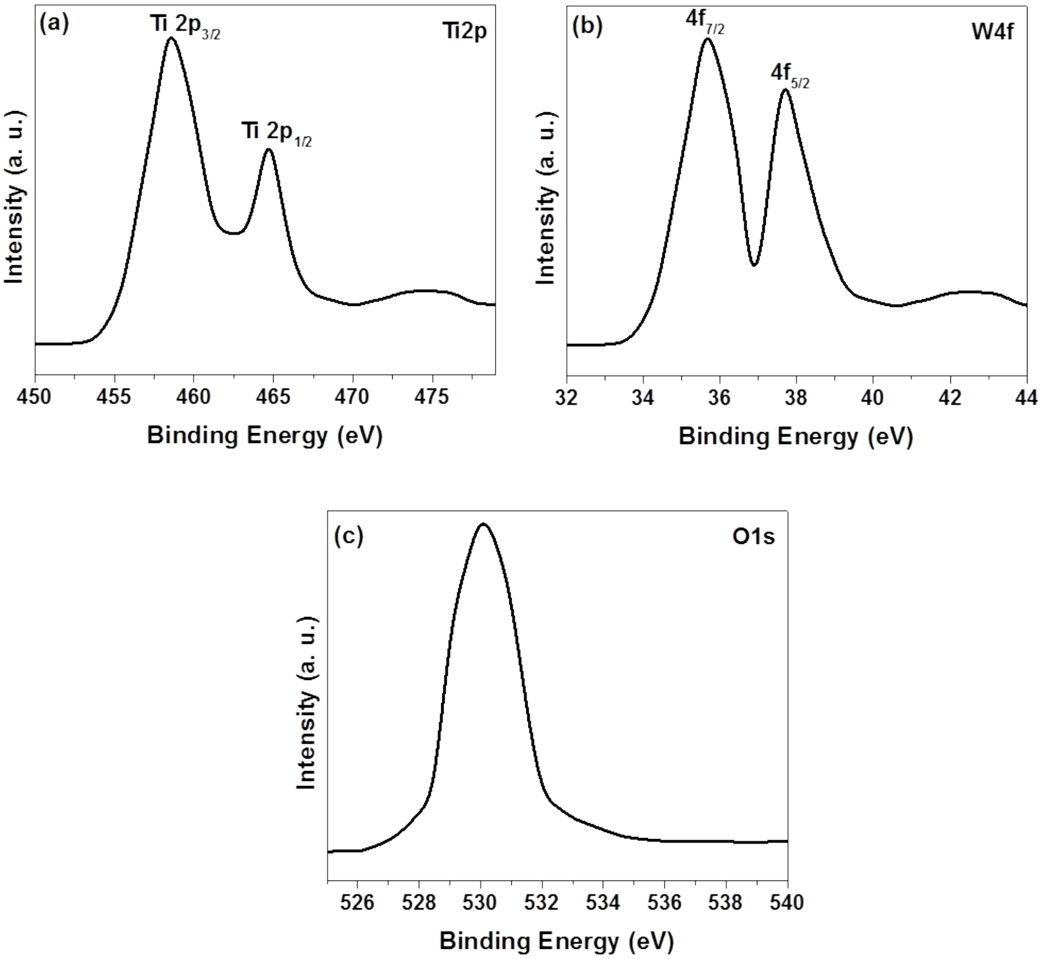

Figure. S2 XPS spectra of (a) Ti2p, (b) W4f, and (c) O1s obtained from $TiCl_4$ treated WO_3 NSs arrays confirming the existence of TiO_2 over the surface of pure WO_3 NSs arrays.