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Plasmonic enhancement of aqueous processed organic photovoltaics†

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Sodium tungsten bronze (Na_xWO_3) is a promising alternative plasmonic material to nanoparticulate gold due to its strong plasmonic resonances in both the visible and near-infrared (NIR) regions. Additional benefits include its simple production either as a bulk or a nanoparticle material at a relatively low cost. In this work, plasmonic Na_xWO_3 nanoparticles were introduced and mixed into the nanoparticulate zinc oxide electron transport layer of a water processed poly(3-hexylthiophene):phenyl-C₆₁-butyric acid methyl ester (P3HT:PC₆₁BM) nanoparticle (NP) based organic photovoltaic device (NP-OPV). The power conversion efficiency of NP-OPV devices with Na_xWO_3 NPs added was found to improve by around 35% compared to the control devices, attributed to improved light absorption, resulting in an enhanced short circuit current and fill factor.

1 Introduction

To meet the environmental, socio-economic and ethical sustainability demands of a future energy system necessarily requires that this energy system be renewable and sustainable.^{1,2} Within this framework, solar energy (compared to other sources of renewable energy) offers a cost effective, non-polluting, sustainable, silent solution that has the capacity to supply efficient power at large scale.³ Over the past few decades, organic photovoltaics (OPVs), based on the bulk-heterojunction (BHJ) structure, have been developed into a promising technology due to their intrinsically low manufacturing cost and eco-friendly fabrication process through roll-to-roll printing techniques.^{4,5} Additionally, several life cycle cost analysis reports have confirmed the ability of OPV technology to contribute cost-effectively to the global energy supply.^{6,7}

The main drawback of current BHJ-OPV technology is the synthesis of the photo-active layer from hazardous chlorinated and/or aromatic solvents such as chloroform (CF), chlorobenzene (CB) and dichlorobenzene (DCB). In response to these concerns, researchers have been working on non-toxic or 'green' solvent ink formations for OPV application.^{8–11} Non-toxic solvents, in particular, aqueous nanoparticulate organic

photovoltaics (NP-OPV) have been investigated in our group since last ten years and the device efficiency has steadily increased from 1.4% to 3.3%.^{12–15} Other research groups using different donor-acceptor materials have reported NP-OPV device performance in the range of 1.9% to 3.8%.^{16,17} More recently, the efficiency of aqueous NP-OPV devices has reached 7.5% through the use of removable surfactants.¹⁸

Nevertheless, aqueous processed OPVs are still much less efficient than those of conventional BHJ OPVs. Previous work to improve device efficiency has focussed on investigating the donor-acceptor mixed NP domain morphology and its associated photo-physics.¹⁹ This research identified the origin of the poor performance of these NP-OPV devices to be: (1) the presence of excess surfactant in the photoactive layer; (2) poor wetting of aqueous nanoparticle inks resulting in low film quality in the photoactive layer; (3) improper distribution of the donor and acceptor material domains in the photoactive layer, leading to poor charge generation.^{18,20}

A number of studies have already been undertaken to address these issues. For instance, removing the excess of surfactant from the NP ink and forming better quality of films by optimising the dialysis strategy and utilising the thermal treatment has been reported.^{18,21} In addition, a new rapid evaporation technique was introduced by Marks *et al.* to form highly intermixed donor-acceptor film morphology.²² However, the issue of poor charge generation in NP-OPV devices has yet to be addressed and requires, through careful nanoscale engineering, the development of new NP-OPV structures that are able to enhance charge generation and extraction.

Due to the low carrier mobility of conducting polymers²³ and short exciton lifetime,²⁴ the optimal thickness of the active layer of BHJ-OPVs is limited to 100 nm or less.^{25–27} Hence, this thin

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active layer limits the light absorption and consequently affects the photo-conversion efficiency. The introduction of plasmonic NPs into BHJ-OPVs is commonly used to improve their light absorption and charge generation by enhancing the light scattering either within the active layer or at the active layer/electrode interface, which in turn increases the length of the optical path thus improving light absorption in the photoactive layer.^{28–32} Moreover, plasmonic nanoparticles can be made into a suspension that is compatible with the solution processing techniques used for BHJ-OPV fabrication.^{33–35} To date, a number of different plasmonic nanoparticles, such as Au, Ag, graphene oxide with Au spheres, *etc.*, have been reported as plasmonic nanoparticles for BHJ-OPVs.^{36–38}

Recent work has assessed the feasibility of Na_xWO_3 as an alternative plasmonic material since it exhibits strong plasmonic resonances compared to Au and offers simple nanofabrication at low cost.^{39,40} In this work, plasmonic structured NP-OPV devices have been fabricated to study the light–matter interaction in the nanoscale region between metal oxide plasmonic nanoparticle and water processed photo-active layer. A combination of microscopic and film physical/chemical spectroscopic techniques have been used to elucidate the multilayer film morphology of Na_xWO_3 NP-OPV devices and the effect of plasmonic nanoparticles on their performance.

2 Experimental details

2.1 Synthesis of Na_xWO_3 nanoparticles

Na_xWO_3 nanoparticles were prepared using a modification of furnace-assisted method of Straumanis,⁴¹ as described previously.⁴² Briefly, powders of sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, VWR, >99%), tungsten(vi) oxide (WO_3 , Sigma-Aldrich, 99.9%) and tungsten (Aldrich, ≥99.9%) were mixed proportionally to target $x = 0.81$. The powders were crushed and mixed using mortar and pestle, pressed under ≈ 20 MPa into a pellet, then heated in a vertical tube furnace at 875 °C for 3 min under flowing N_2 . The sample was then milled in a high-energy ball mill for 1 h, with a 1 : 5 charge ratio of 2–5 mm steel balls. X-ray diffraction (XRD) patterns of the Na_xWO_3 nanoparticles were collected using a Philips X'Pert MPD XRD fitted with a Cu $\text{K}\alpha$ anode. Patterns were collected across $5^\circ \leq 2\theta \leq 90^\circ$ in 0.013° steps, with a total acquisition time of ≈ 60 min. From the Rietveld analysis of the patterns, the sample purity was determined using the method of Hill and Howard,⁴³ and the Na content of the Na_xWO_3 phase was found using the relationship of Brown and Banks.⁴⁴

2.2 P3HT:PC₆₁BM photoactive nanoparticle synthesis

Poly(3-hexylthiophene) (P3HT) (M_n 20 kDa) and PC₆₁BM were synthesised in house (Centre for Organic Electronics, University of Newcastle, Australia) according to literature.^{45,46} Sodium dodecyl sulphate (SDS) with 98% purity was purchased from Sigma-Aldrich. PEDOT:PSS (AI4083) was purchased from Heraeus, Germany and filtered through a 0.45 μm PVDF filter before use. 15 mg of P3HT polymer donor material and 15 mg of PC₆₁BM fullerene acceptor material were mixed in 560 μl of anhydrous chloroform and stirred at 500 rpm, 35 °C for 25 min

on a hotplate to form organic phase. The aqueous phase was prepared by mixing 33 mg of sodium dodecyl sulphate (SDS) surfactant in 2800 μl of filtered Milli-Q water using stirring condition of 500 rpm for 25 min at room temperature. After that the organic and aqueous phases were mixed to form a macro-emulsion and then generate a miniemulsion using Hielscher UP400S (ultra-horn sonication) at 50% amplitude for 2 minutes with a surrounding ice bath in place (to dissipate produced heat during sonication). The miniemulsion was then transferred immediately into the pre-set hotplate (stirrer at 1200 rpm, 60 °C) for overnight to evaporate the chloroform from the emulsion droplets to form the nanoparticle dispersion. Next, the dispersion was placed by pipette into the Hettich Zentrifugen Rotina 420 centrifugal dialysis to remove excess surfactant as well as concentrate the nanoparticle inks following the same procedure reported in our previous work to get an ink solid loading of 6 wt%.¹⁵

2.3 Microscopy

For scanning electron microscopy (SEM) analysis, Na_xWO_3 nanoparticles were mixed with ZnO in ethanol and SEM samples were prepared by spin coating of 70 μl of the mixture onto glass substrates at 5000 rpm for 1 min. Another sample of mixture of Na_xWO_3 nanoparticles and ZnO on aluminium sheet was prepared by drop cast of solution to collect the energy dispersive spectrometer (EDS) data. A Zeiss Sigma VP Field Emission SEM (FESEM) was used under 15 kV beam, using back scattering electron detector and magnification ranges of 5k–50k \times . High-magnification transmission electron microscopy (TEM) (JEOL JEM-2100 LaB6) instrument also was used to observe the morphology of the ZnO and Na_xWO_3 NP mixture as well as to collect the local EDS element mapping to validate that the mixture contains both ZnO and Na_xWO_3 nanoparticles. The acceleration voltage was 200 kV. The TEM sample also prepared by drop cast process on lacey Cu grid and dried the solution in ambient environment. The drop casting of nanoparticles on lacey Cu grid run 2–3 times to confirm enough nanoparticles on grid.

Atomic force microscopy (AFM) images were collected using an Asylum Research Cypher in AC mode. Soft tapping mode Tap150Al-G AFM tips were supplied by Budget Sensors with resonant frequency of 150 kHz and force constant: 5 N m⁻¹. Bare ZnO and mixture of Na_xWO_3 plasmonic nanoparticles with ZnO nanoparticle films were coated onto glass substrates for AFM analysis.

2.4 Spectroscopy

To measure the UV-vis spectrum, an ultraviolet-visible absorption spectrophotometer (UV Vis, Varian Cary 6000i) with an integrating sphere was used in the wavelength range of 200–1200 nm in 1 nm step, with a deuterium plasma lamp for the 200–350 nm range, and a tungsten halogen lamp used for the 350–1200 nm range. For photoluminescence (PL) measurements, Shimadzu RF-6000 spectrofluorophotometer with a beam to sample angle of 65°, $\lambda_{\text{exc}} = 550$ nm, $\lambda_{\text{em}} = 400$ –900 nm, excitation bandwidth of 5 nm and emission bandwidth of 10 nm was used. A 420 nm high-pass cut-off filter was placed in the path of the beam before the sample. All samples for UV Vis and PL were kept as the same structure of NP-OPV devices (without Al layer).



2.5 Device fabrication

To fabricate the NP-OPV devices, pre-cleaned (by water, acetone and isopropanol for 10 minutes) patterned Indium Tin Oxide (ITO) substrates were treated by UV-ozone cleaner for 20 minutes. PEDOT:PSS (AI4083) films of 33 ± 6 nm thickness were spin coated onto ITO at 5000 rpm (1 min) and then dried on a hotplate at 150°C , 20 min. After that, the PEDOT:PSS coated ITO substrates were treated 10 min into the UV-ozone cleaner. Then, P3HT:PC₆₁BM NP ink (35 μl) was spin-coated at 2000 rpm for 1 min and baked for 5 min at 110°C . The thickness of the photoactive layer was 103 ± 7 nm. Then, ZnO/ZnO : Na_xWO₃ films were deposited at 5000 rpm for 1 min and dried at 110°C for 5 min in nitrogen glove box. The thickness of ZnO/ZnO : Na_xWO₃ layers were measured with an average thickness of 15 ± 6 nm. Finally, Al (thickness: 100 nm) electrodes were deposited under vacuum conditions (10^{-6} torr) *via* thermal evaporation using an Angstrom Amod deposition system.

2.6 Device characterisation

The current density-voltage (*J-V*) measurements of fabricated NP-OPV devices were conducted using a Newport Class A solar simulator with an AM 1.5 spectrum filter. The light intensity was measured to be 100 mW cm^{-2} by a silicon reference solar cell (FHG-ISE) and the *J-V* data were recorded with a Keithley 2400 Source Meter. The NP-OPV devices were masked during testing under AM 1.5 conditions where the masked area was 4 mm^2 . For the device performance, it is reported as the average value \pm standard deviation which were calculated from 12 devices based on two substrates with the value for the best devices in the bracket.

3 Results and discussion

3.1 Characterisation of Na_xWO₃ and ZnO : Na_xWO₃ mixed nanoparticles

The light absorption spectra of Na_xWO₃ nanoparticles coated on a quartz substrate is presented in Fig. 1a. There are two

distinct visible and near infrared absorption features arising from the Na_xWO₃ plasmonic material, at ~ 630 nm and ~ 1045 nm, corresponding to the excitation of localised surface plasmonic resonances (LSPR) of Na_xWO₃.⁴⁷ The strong but narrow absorption peak at ~ 230 nm in the ultraviolet (UV) range is attributed to the inter-band transition of Na_xWO₃ plasmonic nanoparticle.³⁹ The transmission electron microscopy (TEM) image shown in Fig. 1b indicates that the size of nanoparticles is of the order of tens of nanometres. Fig. 1c shows an XRD pattern of the Na_xWO₃ nanoparticles after ball-milling. Overall, the refined model is a good fit to the measured data. From quantitative phase analysis, the sample was found to be ≈ 99 mol% Na_xWO₃, and ≈ 1 mol% W and Fe impurity. From the refinement of the Na_xWO₃ lattice parameter, $a = 3.8508(1) \text{ \AA}$, the Na content was found to be $x = 0.81$.

The back-scattered SEM image of a drop-cast ZnO : Na_xWO₃ mixture on aluminium sheet is shown in Fig. 2a, with the Na_xWO₃ nanoparticles clearly visible (marked by arrow sign and circle) as bright objects with respect to background. The EDS spectra (Fig. 2b) clearly show that tungsten is present in the mixture, along with zinc, oxygen and aluminium; consistent with well-mixed ZnO and Na_xWO₃ plasmonic nanoparticles deposited on an aluminium substrate. The small peaks at about 6.39 keV correspond to the K α peak of iron; consistent with the low levels of iron impurity identified in the XRD analysis. Moreover, the Zn L α and Na K α peaks are overlapped as observed in Fig. 2b, therefore the obtained elemental composition of 31% around 1 keV would be the summation of both elements. However, clear EDS peaks of Zn K α and W M indicate presence of both Zn and Na in NaWO₃. High-magnification transmission electron microscopy (TEM) imaging and corresponding Zn and W element EDS mappings of the ZnO : Na_xWO₃ mixture are shown in Fig. 2c-e. The images show a nanoparticulate aggregate within the ZnO : Na_xWO₃ mixture, with a Na_xWO₃ (Fig. 2e) core region surrounded by a ZnO coating (Fig. 2d).

3.2 Performance of plasmonic NP-OPV devices

The architecture of the control NP-OPV device (ITO/PEDOT:PSS/ NP-P3HT:PC₆₁BM/ZnO/Al) the plasmonic NP-OPV device (ITO/

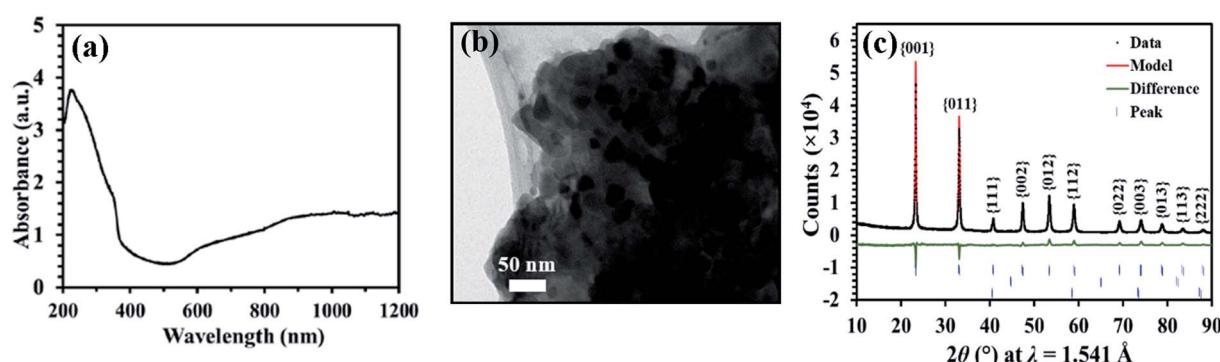


Fig. 1 (a) UV-vis spectrum of Na_xWO₃ nanoparticle film. (b) The TEM image of Na_xWO₃ nanoparticle with 50 nm scale bar. (c) XRD pattern and Rietveld refinement of Na_xWO₃ nanoparticles. The black dots show the data, the red line shows the Rietveld model, and the green line is the difference between the two. Peaks of Na_xWO₃ are indexed according to the *Pm3m* structure of Straumanis.⁴¹ The blue dashes indicate the peaks included in the model, from top to bottom corresponding to Na_xWO₃,⁴⁴ BCC Fe and BCC W.



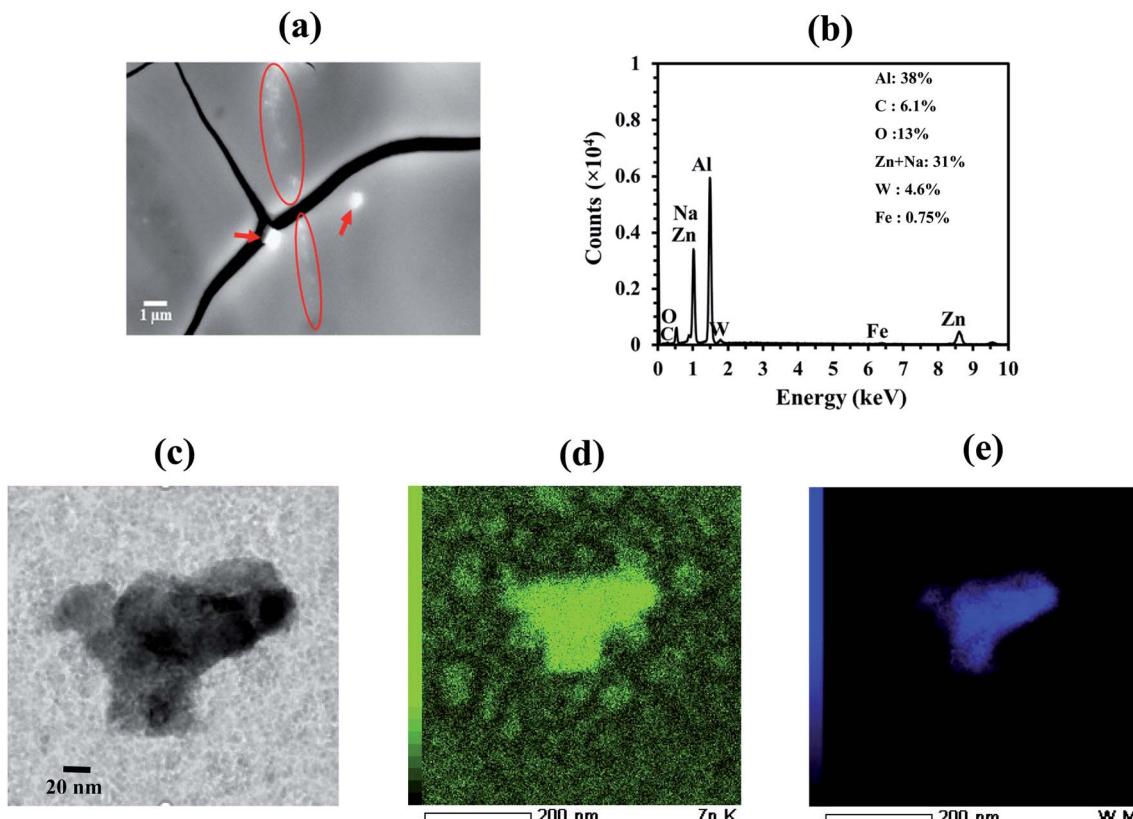


Fig. 2 (a) Backscattering detector scanning electron microscopy (BSD-SEM) image of $\text{ZnO} : \text{Na}_x\text{WO}_3$ mixture nanoparticles where $\text{ZnO} : \text{Na}_x\text{WO}_3$ solution drop casted on Al sheet substrate. The Na_xWO_3 nanoparticles mixed with ZnO clearly observed in the SEM image those were marked by red arrows and circles. (b) Energy dispersive X-ray spectrum (EDS) of the SEM scanned area indicates the composition of Na, Zn, O and W which confirms the proper mixing of Na_xWO_3 nanoparticles into the ZnO . (c) High-magnification transmission electron microscopy (TEM) image of the drop cast $\text{ZnO} : \text{Na}_x\text{WO}_3$ mixture nanoparticles was presented along with EDS mapping of (d) Zn and (e) W elements.

PEDOT:PSS/NP-P3HT:PC₆₁BM/ Na_xWO_3 : ZnO/Al) is shown in Fig. 3a and b, respectively. The Na_xWO_3 : ZnO weight ratios (dispersed in ethanol) were 0, 0.35, 0.40, 0.45, 0.50.

The performance of the ITO/PEDOT:PSS/NP-P3HT:PC₆₁BM/ Na_xWO_3 : ZnO/Al OPV devices (device A to E) for the five different Na_xWO_3 : ZnO ratios are presented in Fig. 4a-f with the device performance statistics summarised in Table 1. By systematically varying the Na_xWO_3 : ZnO weight concentration ratios in the suspension based on Table 1 (device A to E), the corresponding device PCEs (Fig. 4a) improved from $1.25 \pm 0.09\%$ (1.32%) (device A Na_xWO_3 : ZnO = 0) to $1.42 \pm 0.05\%$ (1.58%) in NP-OPV (device B Na_xWO_3 : ZnO = 0.35) before maximising at $1.60 \pm 0.09\%$ (1.78%) (device C Na_xWO_3 : ZnO = 0.4). The improvements (corresponding to a $\sim 17\%$ and $\sim 35\%$ increase in PCE for device B and C, respectively) originate primarily from an increased FF (Fig. 4c) and J_{SC} (Fig. 4d). In particular, for device B, the FF and J_{SC} increase from 0.48 to 0.51 and J_{SC} from 6.64 mA cm^{-2} to 7.20 mA cm^{-2} , respectively, whereas for device C, the FF and J_{SC} increase from 0.48 to 0.53 and 6.64 mA cm^{-2} to 7.47 mA cm^{-2} correspondingly. It should

0.09% (1.32%) (device A Na_xWO_3 : ZnO = 0) to $1.42 \pm 0.05\%$ (1.58%) in NP-OPV (device B Na_xWO_3 : ZnO = 0.35) before maximising at $1.60 \pm 0.09\%$ (1.78%) (device C Na_xWO_3 : ZnO = 0.4). The improvements (corresponding to a $\sim 17\%$ and $\sim 35\%$ increase in PCE for device B and C, respectively) originate primarily from an increased FF (Fig. 4c) and J_{SC} (Fig. 4d). In particular, for device B, the FF and J_{SC} increase from 0.48 to 0.51 and J_{SC} from 6.64 mA cm^{-2} to 7.20 mA cm^{-2} , respectively, whereas for device C, the FF and J_{SC} increase from 0.48 to 0.53 and 6.64 mA cm^{-2} to 7.47 mA cm^{-2} correspondingly. It should

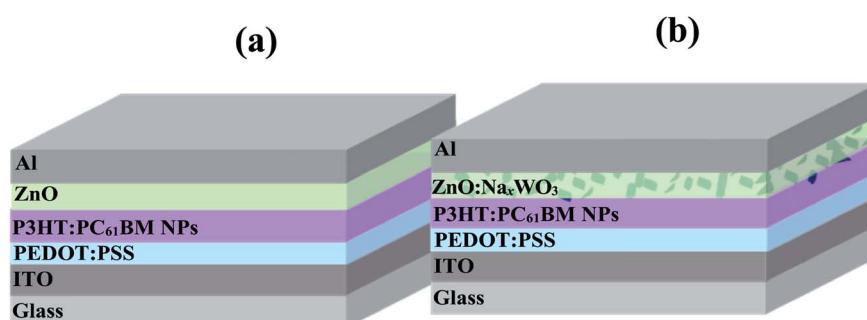


Fig. 3 Schematic diagrams of the device architecture (a) control NP-OPV device and (b) Na_xWO_3 plasmonic NP-OPV device.



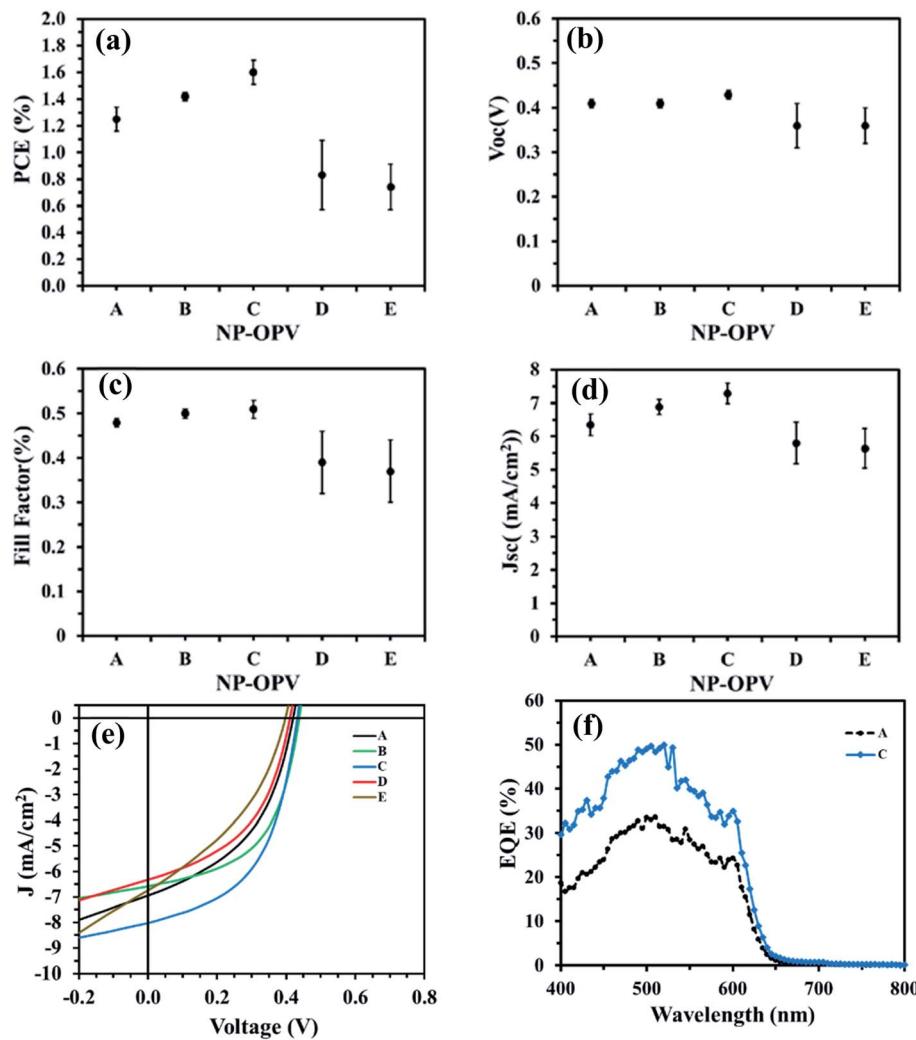


Fig. 4 (a) Average power conversion efficiency, (b) average open circuit voltage (V_{OC}), (c) average fill factor (FF), (d) average short circuit current density (J_{SC}) and (e) current density–voltage (J – V) curves of NP-OPV devices with (NP-OPV devices from B to E) and without (NP-OPV device A) Na_xWO_3 nanoparticles. (f) The external quantum efficiency of the best Na_xWO_3 NP-OPV device C compared with the control NP-OPV device A.

Table 1 Performance of NP-OPV devices with varied weight concentrations of Na_xWO_3 nanoparticles mixed in ZnO (from B–E) compare to without (A) Na_xWO_3 nanoparticles. The average values \pm standard deviations that are calculated from 12 devices with the values for the best devices in the bracket

Name of NP-OPV	Weight concentration (mg ml ⁻¹)		PCE (%)	V_{OC} (V)	FF (%)	J_{SC} (mA cm ⁻²)
	Na_xWO_3	ZnO				
A	0	10	1.25 ± 0.09 (1.32)	0.41 ± 0.01 (0.41)	0.47 ± 0.02 (0.48)	6.47 ± 0.48 (6.64)
B	3.5	6.5	1.42 ± 0.05 (1.58)	0.42 ± 0.01 (0.43)	0.50 ± 0.02 (0.51)	6.80 ± 0.16 (7.20)
C	4	6	1.60 ± 0.09 (1.78)	0.43 ± 0.01 (0.45)	0.51 ± 0.02 (0.53)	7.29 ± 0.31 (7.47)
D	4.5	5.5	0.83 ± 0.26 (1.22)	0.36 ± 0.05 (0.41)	0.39 ± 0.07 (0.47)	5.80 ± 0.63 (6.33)
E	5	5	0.74 ± 0.17 (0.93)	0.36 ± 0.04 (0.39)	0.37 ± 0.07 (0.40)	5.64 ± 0.59 (5.95)



be noted that, for device A (control), the 10 mg ml^{-1} of ZnO weight concentration has been optimized to achieve the best OPV device performance.⁴⁸ Therefore, any device performance enhancement cannot be due to the change of ZnO weight concentrations.

Further increases of the $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratio had a negative effect on NP-OPV performance; for device D ($\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.45$) and device E ($\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.5$) the PCE dropped to $0.83 \pm 0.26\%$ (1.22%) and $0.74 \pm 0.17\%$ (0.93%), respectively. Devices A to C show no noticeable changes in the trend of V_{OC} as presented in Fig. 4b. By contrast, for $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratios above 0.4, the PCE starts to decrease as shown in Fig. 4a, due to decreases across V_{OC} , FF and J_{SC} (Fig. 4b-d). The external quantum efficiency (EQE) spectra of best NP-OPV device (device C) in comparison with the control NP-OPV (device A) device are presented in Fig. 4f. Device C exhibits higher EQE compared to device A across the entire spectral range; consistent with the J_{SC} data.

3.3 Effect of Na_xWO_3 on device performance

To investigate the origin of device performance enhancement of Na_xWO_3 nanoparticle embedded aqueous NP-OPV devices, microscopy and spectroscopy have been used to examine the film quality and the morphological distribution of the plasmonic NP in the overall electron transport layer (ETL). The back scattering SEM images of bare ZnO and $\text{Na}_x\text{WO}_3 : \text{ZnO}$ films are shown in Fig. 5, with the bright particles (with respect to the background) corresponding to Na_xWO_3 nanoparticles. Fig. 5a reveal a very smooth bare ZnO film whereas Fig. 5b and c show that for $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratios of 0.35 and 0.4, the surface contains an increasing number of Na_xWO_3 NPs that are evenly

distributed within the ZnO film. For $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratios of 0.45 (Fig. 5d) and 0.5 (Fig. 5e), Na_xWO_3 NPs aggregates (marked as red arrow signs) start to appear in the SEM images. The presence of aggregated Na_xWO_3 nanoparticles in the ZnO ETL would have a detrimental effect on the morphology of the ZnO ETL and, consequently, on the film quality of the subsequently deposited aluminium electrode. As such, the observation of Na_xWO_3 NP aggregates at $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratios above 0.4 is entirely consistent with the decreased device performance observed for devices with higher Na_xWO_3 loadings.

Atomic force microscopy (AFM) has also been used to examine the morphology of a control ZnO film (Fig. 6a), and $\text{Na}_x\text{WO}_3 : \text{ZnO}$ films with weight ratios of 0.4 (Fig. 6b) and 0.5 (Fig. 6c). In addition, to compare the effect of optimal ($\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.4$) and highest Na_xWO_3 NP concentration ($\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.5$) of Na_xWO_3 on ZnO film, the 3D views of the films are illustrated in Fig. 6d-f. The morphology of bare ZnO film (Fig. 6a) is very smooth, consistent with the SEM image (Fig. 5a) and the surface root-mean-square (RMS) roughness is very small ($0.5 \pm 0.1 \text{ nm}$). By comparison, the roughness of the $\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.4$ film increases to $2.5 \pm 2.1 \text{ nm}$. However, the distribution of Na_xWO_3 nanoparticles in the $\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.4$ film (Fig. 6b-e) is uniform, with well separated NPs showing no significant aggregation in the 3D image (Fig. 6e); consistent with the corresponding SEM image (Fig. 5c). By contrast, the surface of $\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.5$ film is rougher ($\text{RMS } 5.5 \pm 3.4 \text{ nm}$) with more densely packed Na_xWO_3 nanoparticles and larger aggregates observed in 3D view (Fig. 6f); consistent with the observation in Fig. 5e. Typical surface height profiles for the three films are presented in Fig. 6g-i, with

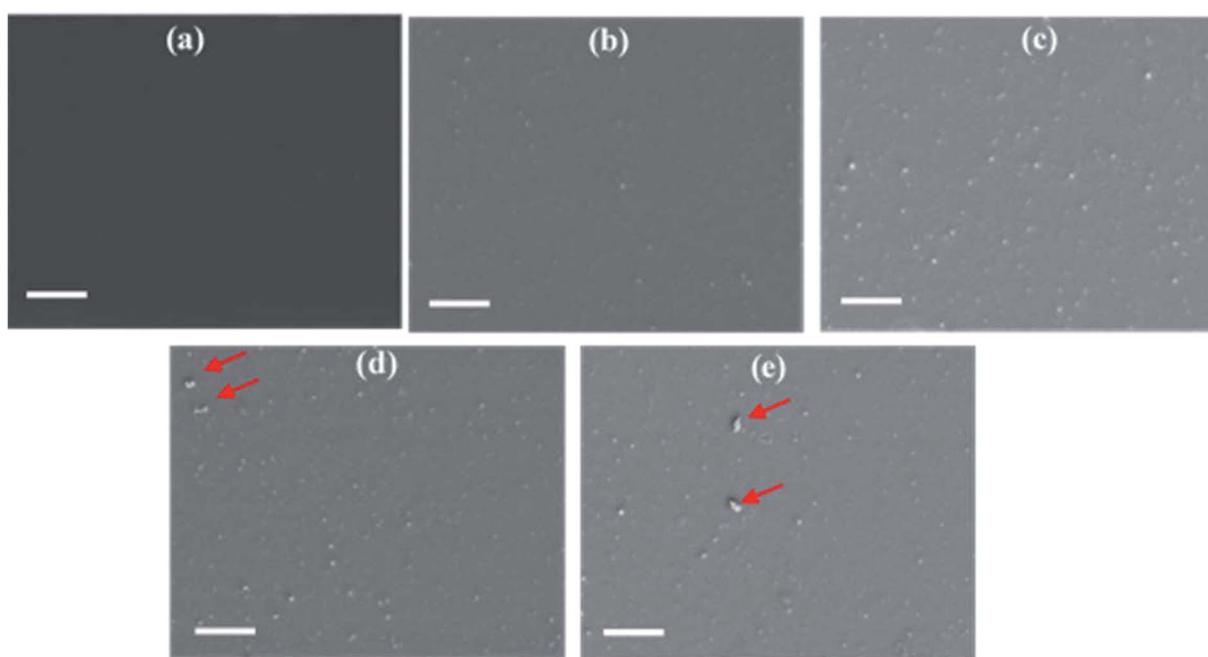


Fig. 5 SEM images of mixture of films (prepared on glass substrates) with (a) 0 mg ml^{-1} , (b) 3.5 mg ml^{-1} , (c) 4 mg ml^{-1} , (d) 4.5 mg ml^{-1} and (e) 5 mg ml^{-1} weight concentration of Na_xWO_3 in ZnO. All of the SEM images are collected using back scattering electron detector. The scale bar is $10 \mu\text{m}$.



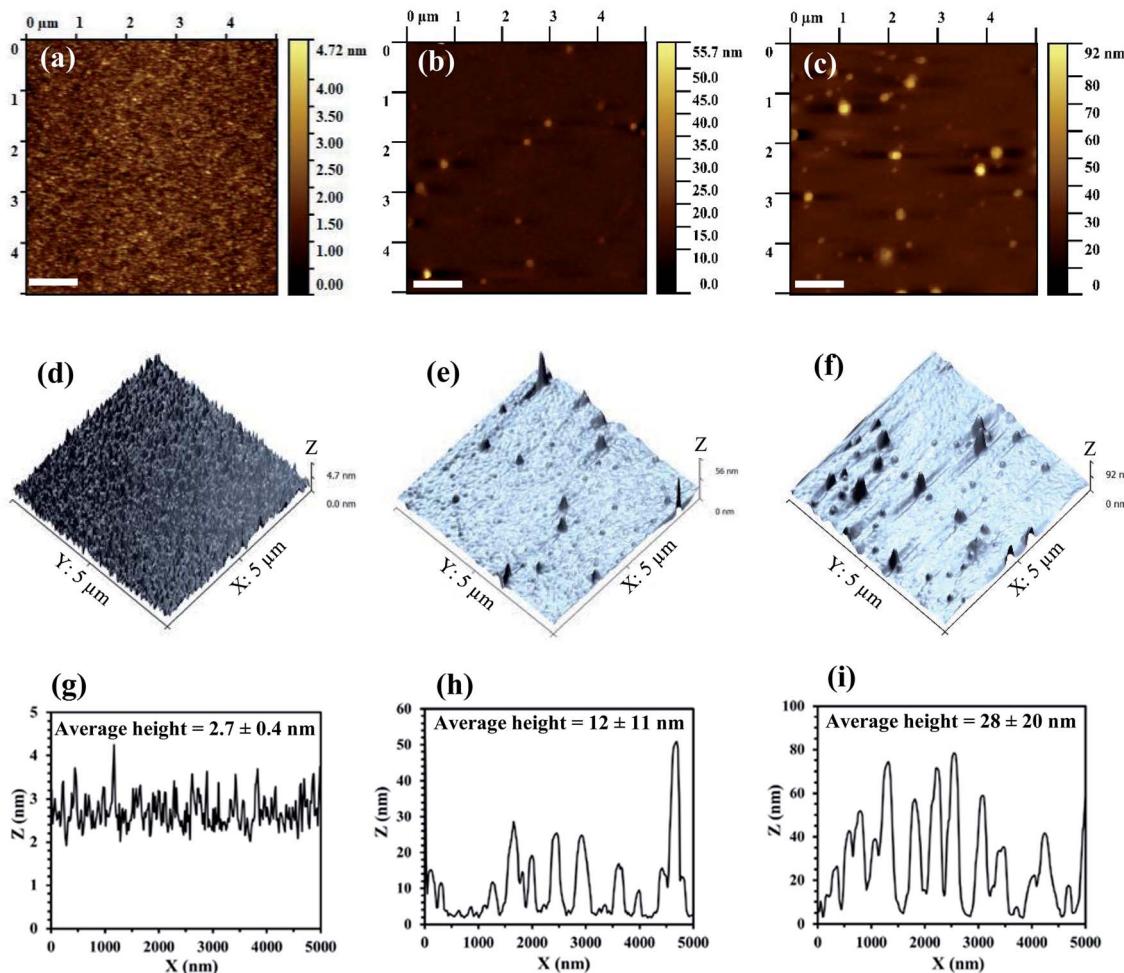


Fig. 6 (a)–(c) Show the AFM images ($5 \mu\text{m} \times 5 \mu\text{m}$) of ZnO films with $\text{Na}_x\text{WO}_3 : \text{ZnO}$ concentration ratios of 0, 0.4 and 0.5, respectively. (d)–(f) Show the corresponding 3D images of (a)–(c). (g)–(i) Typical surface height profiles of the Na_xWO_3 nanoparticles observed in (a)–(c) with respect to the X-axis.

average NPs heights of $2.7 \pm 0.4 \text{ nm}$, $12 \pm 11 \text{ nm}$ and $28 \pm 20 \text{ nm}$ for the $\text{Na}_x\text{WO}_3 : \text{ZnO} = 0$, 0.4 and 0.5 films, respectively. The AFM data supports the SEM observation that for $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratios above 0.4, the Na_xWO_3 plasmonic nanoparticles start to aggregate and form larger surface structures with dimensions that are large enough to completely penetrate into the aqueous photoactive layer and degrade of device performance. In addition, the increased roughness at ZnO/Al interface can also deteriorate electron transport within NP-OPV device again leading to lower device performance. Therefore, the device performance starts to drop at $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratios above 0.4. The AFM morphology of the $\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.35$ and $\text{Na}_x\text{WO}_3 : \text{ZnO} = 0.45$ samples provide further support for this observation (Fig. S1, ESI†).

The UV-vis absorption spectra of the ZnO and the optimal $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratio (0.4) films on quartz substrates are presented in Fig. 7a. It clearly shows the light absorption arising from the Na_xWO_3 NPs across the visible to near infrared regions compared to the ZnO only film and matches the light absorption spectra of the pure Na_xWO_3 film shown in Fig. 1a. The UV-

vis data confirms that the $\text{Na}_x\text{WO}_3 : \text{ZnO}$ film consists of well-mixed Na_xWO_3 nanoparticles within the ZnO layer; consistent with the EDS data in Fig. 2. The absorption spectra of the PEDOT:PSS/NP-P3HT:PC₆₁BM/ZnO multilayer films with and without Na_xWO_3 nanoparticles are presented in Fig. 7b, where the light absorption in the near infrared range (650–800 nm) is presented as an inset. Sample A to E follow the same $\text{Na}_x\text{WO}_3 : \text{ZnO}$ ratios described in Table 1. The effect of the Na_xWO_3 plasmonic enhancement on the light absorption is most clearly visible for samples B and C. As the weight concentration of Na_xWO_3 NPs in the ZnO film is increased, the light absorbance of sample B and C across the visible region is enhanced by around 9% and 15%, respectively, compared to the control sample A. This increased light absorption explains the enhanced photocurrent in the plasmonic nanoparticle embedded NP-OPV devices of B and C over the control NP-OPV device. The higher scattering background in the near infrared range of 650 to 800 nm (inset) for samples B and C is also consistent with a plasmonic enhancement due to light scattering. Furthermore, the overall light absorption of the



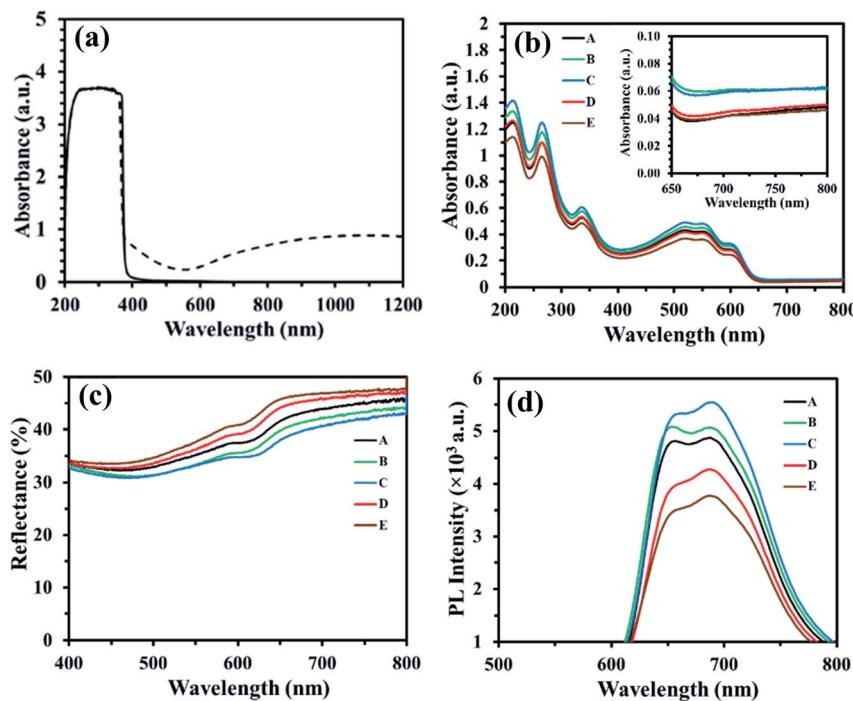


Fig. 7 Light absorbance spectra of (a) ZnO : Na_xWO₃ film (dash line) and ZnO film (solid line). (b) The light absorbance spectrum of PEDOT:PSS/P3HT:PC₆₁BM NP/ZnO films A to E, the inset figure expands and highlights the light absorbance spectra in the higher wavelength of visible region. (c) The total light reflectance (specular and diffuse reflectance) spectra and (d) photoluminescence (PL) spectra of the PEDOT:PSS/P3HT:PC₆₁BM NP/ZnO films for the control multilayer sample A and PEDOT:PSS/P3HT:PC₆₁BM NP/ZnO : Na_xWO₃ samples B to E.

plasmonic nanoparticle embedded films for sample D and E decreases by around 1% (sample D) and 11% (sample E) as the Na_xWO₃ : ZnO ratio increases to 0.45 and 0.5, respectively, again in good agreement with the variation of the photocurrent density.

To further probe the effect of the higher Na_xWO₃ weight concentrations on light absorption, the total (specular plus diffuse) light reflectance spectrum of PEDOT:PSS/NP-P3HT:PC₆₁BM/ZnO : Na_xWO₃ multilayer films were collected and are presented in Fig. 7c. Samples D and E exhibit higher reflectivity across the entire 400–800 nm spectral range, consistent with decreased light absorption^{32,49} arising from the increased aggregation of the Na_xWO₃ NPs observed for these

samples; resulting in a reduced plasmonic enhancement of their surrounding electric field.⁵⁰ Moreover, as the aggregated NPs are large enough (peak heights > 50 nm observed in Fig. 6i) to penetrate the active layer, it is likely that the morphology of the water processed P3HT:PC₆₁BM nanoparticle based photoactive layer is also degraded; decreasing the light absorption capacity of these multilayer films D and E. By contrast, the spectrum-wide lower reflectivity of the lower Na_xWO₃ : ZnO ratio samples (B and C) is consistent with increased light absorption arising from the plasmonic enhancement of the Na_xWO₃ NPs.

The photoluminescence (PL) spectra of the PEDOT:PSS/NP-P3HT:PC₆₁BM/ZnO (Na_xWO₃) multilayer films are presented in

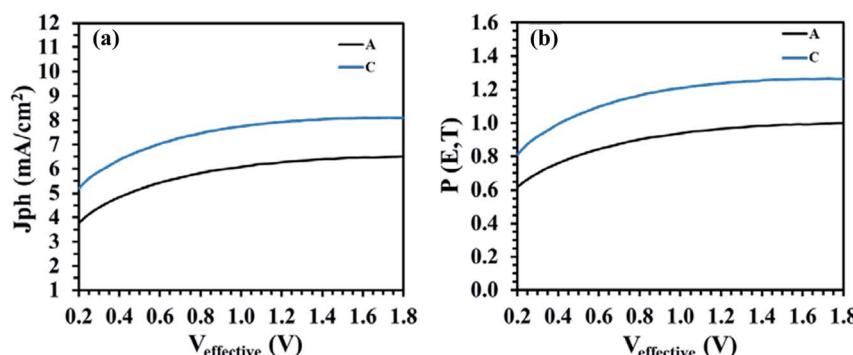


Fig. 8 (a) J_{ph} vs. V_{eff} curves and (b) $P[E, T]$ vs. V_{eff} curves of the NP-OPV devices with (NP-OPV device C) and without (NP-OPV device A) Na_xWO₃ plasmonic nanoparticles.

Table 2 A summary of reported organic photovoltaic devices with different plasmonic materials or nanostructures. The bracket values refer to the control device without plasmonic nanostructure

Plasmonic structure	Location of plasmonic structure	Proposed mechanism	PCE (%)	J_{SC} (mA cm ⁻²)	Enhancement (%)	
					PCE	J_{SC}
Au nano-rods ³²	ETL	Scattering	8.01 (7.43)	17.17 (16.27)	7.8	5.5
Fe ₃ O ₄ NPs ³³	Photoactive layer	Scattering	2.22 (1.09)	8.62 (7.74)	104	11
Au–Ag nano-cube ³⁵	HTL	Electric field and scattering	3.10 (2.85)	8.70 (8.40)	8.8	3.6
Au NPs ³⁶	HTL	LSPR	4.19 (3.48)	10.18 (8.95)	20	14
Au spheres and Au rods ³⁷	HTL	Scattering and LSPR	4.28 (3.46)	11.49 (9.28)	24	24
Au spheres and GO composites ³⁸	HTL	Near field effect	3.98 (3.25)	10.44 (9.37)	22	11
Au nano-arrows ⁵⁶	ETL	Scattering and LSPR	7.82 (6.14)	17.40 (14.70)	27	18
Au NPs–TiO ₂ composite ⁵⁷	ETL	Scattering and LSPR	4.20 (3.73)	10.15 (9.38)	13	8.2
Au/Ag NPs ⁵⁸	Active layer	LSPR	4.85 (4.44)	12.21 (11.17)	9.2	9.3
Ag NPs ⁵⁹	Active layer	LSPR	3.92 (3.19)	10.41 (8.67)	23	20
Ag NPs–SiO ₂ ⁶⁰	Active layer	LSPR	3.96 (3.44)	9.50 (8.37)	15	14
Au NPs–SiO ₂ ⁶¹	Active layer	LSPR	2.17 (1.95)	9.19 (7.23)	11	27
Au NRs ⁶²	Active layer	LSPR	3.58 (3.17)	8.73 (7.97)	13	9.5
Na _x WO ₃ [this work]	ETL	Scattering and LSPR	1.78 (1.32)	7.47 (6.64)	35	13

Fig. 7d in order to investigate the effect of Na_xWO₃ nanoparticles on exciton generation. The incorporation of the Na_xWO₃ plasmonic NPs leads to broader PL spectra and an increase of the PL intensity by ~8% for the multilayer film B and by ~13% for the multilayer film C compared to the control multilayer film A. The broadening and enhancement of the PL intensity can be attributed to the fact that the LSPR excitation and light scattering of the Na_xWO₃ plasmonic nanoparticles inside the device increase the degree of light collection, thereby, leading to an enhanced light excitation generation rate.⁵¹ Moreover, the enhanced PL intensity arises from the strong coupling between the excitonic state of the polymer and the plasmonic field of the Na_xWO₃ nanoparticles, which is due to the oscillation of the surface plasmonic dipole electric field and excitons.⁵² Thus, it can be concluded that the incorporation of Na_xWO₃ nanoparticles significantly enhances the exciton generation, rate as observed in multilayer films B and C. However, further increasing the Na_xWO₃ nanoparticles weight concentration in the ZnO results in the aggregation of nanoparticles, as is evident in the SEM images of multilayer films D and E (Fig. 5d and e). As a result, the electric field intensity starts to decay with the increase of nanoparticle aggregate size, leading to a reduction in the LSPR excitation effect of the plasmonic materials, as well a decrease in the PL intensity of the

multilayer film, as shown in Fig. 7d, which is consistent with the UV-vis spectra of the corresponding multilayer films D and E.

To further validate the effect of Na_xWO₃ nanoparticles on the exciton generation and dissociation of the NP-OPV devices, the maximum exciton generation rate (G_{max}) and the exciton dissociation probability ($P[E, T]$) are considered for the hero NP-OPV device C with respect to control NP-OPV device A, following a previously reported method.^{32,53,54} The dependence of the photocurrent density (J_{ph}) on the effective voltage (V_{eff}) is shown in Fig. 8a for NP-OPV device A and NP-OPV device C. Herein, J_{ph} is calculated by the following formula:

$$J_{ph} = J_L - J_D \quad (1)$$

where, J_L is the current densities under light and J_D is the current densities under dark.

V_{eff} is described by the following equation:

$$V_{eff} = V_0 - V_a \quad (2)$$

where, V_0 is the voltage when photocurrent density (J_{ph}) equals to zero and V_a is the applied voltage. As illustrated in Fig. 8a, J_{ph} increases with increasing of V_{eff} and then approaches a saturation limit at high effective voltages. The value of the saturation photocurrent density J_{sat} ³⁵ is independent of the bias and



temperature and can be derived from Fig. 8a directly. Assuming that all the photo-generated excitons are dissociated and contribute to the current at high V_{eff} , G_{max} can also be calculated from:

$$J_{\text{sat}} = qG_{\text{max}}L \quad (3)$$

where, q is the electronic charge and L is the thickness of the active layer (here, $L = 103$ nm). The resulting G_{max} values for the control NP-OPV device A and the plasmonic NP-OPV device C were $5.12 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$ ($J_{\text{sat}} = 8.10 \text{ mA cm}^{-2}$) and $4.15 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$ ($J_{\text{sat}} = 6.52 \text{ mA cm}^{-2}$), respectively. The impressive enhancement ($\sim 21.5\%$) in G_{max} strongly suggests that the presence of the Na_xWO_3 nanoparticles in NP-OPV device C amplifies the exciton generation rate in the photoactive layer. As the maximum exciton generation rate (G_{max}) is related to the maximum absorption of incident light,^{53,55} the enhancement G_{max} implies increased light absorption in NP-OPV device C due to the plasmonic nanoparticles, which in good agreement with the observed increased light absorption of around 15% in the corresponding absorbance spectra (Fig. 7b). In addition, to measure the effective charge separation, the exciton dissociation probability, $P[E, T]$ was also calculated and is presented with respect to the effective voltage (V_{eff}) in Fig. 8b. To calculate the exciton dissociation probability $P[E, T]$ under the short-circuit condition ($V_a = 0$) the following equation is used:

$$J_{\text{ph}} = qG_{\text{max}}P[E, T] \quad (4)$$

The corresponding values of $P[E, T]$ at any effective voltage (V_{eff}) can be attained from the plot of the normalized photocurrent density $J_{\text{ph}}/J_{\text{sat}}$. The calculated J_{ph} values at $V_a = 0$ were 4.88 mA cm^{-2} and 6.40 mA cm^{-2} resulting in $P(E, T)$ of around 75% and 80%, for the control (NP-OPV device A) and best Na_xWO_3 (NP-OPV device C) devices, respectively. These results demonstrate that the presence of the Na_xWO_3 nanoparticles in the NP-OPV structure directly increases the dissociation of excitons into free carriers.

For the best of our knowledge, our work is the first study using plasmonic nanoparticles, in particular, a plasmonic material other than Au or Ag nanostructures, in aqueous processed OPV devices. We put a summary of literature in Table 2 that shows different types of plasmonic nanostructures used in bulk heterojunction (BHJ) OPV devices and compare them with our aqueous processed OPV work. The enhancement due to the plasmonic nanostructure observed in this work is comparable to those studies. It also should be noted that the previous studies in our group have showed that the aqueous processed OPV devices behave very differently from the conventional BHJ OPV devices.^{12–15} This work points a future direction to further explore Na_xWO_3 nanoparticles in the OPV applications.

4 Conclusions

Low cost Na_xWO_3 plasmonic nanoparticles have been added to the architecture of water processed NP-OPVs and an improved device performance is found. By carefully controlling the mixing

ratio of the absolute weight concentration of Na_xWO_3 (4 mg ml^{-1}) and ZnO in the cathodic interfacial layer, the light absorbance of the NP-OPV device can be improved about 15% which leads to an enhanced EQE. The J_{SC} of the best NP-OPV device is found to be amplified about 12.5% and ultimately, the PCE of the corresponding NP-OPV device was boosted from 1.32% ($1.25 \pm 0.09\%$) (control NP-OPV device without Na_xWO_3) to 1.8% ($1.60 \pm 0.09\%$) (with Na_xWO_3), about a 35% enhancement. Further investigation of the maximum exciton generation rate and probability of exciton dissociation of this hero NP-OPV device showed that these parameters increased by around 21.5% and 6.6% correspondingly, confirming the effect of Na_xWO_3 nanoparticles on enhancing the performance of NP-OPV device. In addition, recorded PL data is consistent with the calculated maximum exciton generation rate at the optimized mixing ratio of ZnO : Na_xWO_3 used in the NP-OPV devices. The overall results indicate that enhancement in light absorption of the water processed photoactive layer by scattering and LSPR effects increases the exciton generation rate and probability of exciton dissociation which play the most important roles in the charge generation of the water processed NP-OPV device. However, our current study so far can rule out the possibility that the device performance improvement is due to morphological difference(s) in the photoactive layer, and/or, the interfacial layer between the photoactive layer and the Na_xWO_3 embedded ZnO buffer layer. Since this is the first study on Na_xWO_3 based aqueous processed OPVs, further work to clarify the plasmonic effect is warranted.

Conflicts of interest

There are no conflicts to declare.

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