Flame-made Tungsten Trioxide Loaded Zinc Oxide Nanoparticles in Hybrid Photovoltaic Application†

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ABSTRACT

WO₃-loaded ZnO nanoparticles containing 0, 0.25, 0.50, 0.75, 1.0 and 3.0 mol% of WO₃ were synthesized by Flame Spray Pyrolysis (FSP) from zinc naphthenate and tungsten ethoxide precursors under 5/5 (precursor/oxygen) flame condition. The crystalline phase, morphology and size of pure ZnO and WO₃-loaded ZnO prepared by FSP were observed by XRD, BET, TEM and SEM. Moreover, these nanoparticles were successfully applied in hybrid photovoltaic devices as an electron acceptor. Theses devices were fabricated using conjugated polymers Poly(3-hexylthiophene) (P3HT) as an electron donor and poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT: PSS) as an electrode improver. Exciton dissociation of P3HT/ZnO hybrid photovoltaic that was deposited on an ITO substrate with PEDOT:PSS layer and capped with Al as a metal back electrode, was shown in figure below. The current-voltage characteristic of these devices showed that WO₃ could increase the number of photons actually converted to charge carriers that affect the power conversion efficiency. These results concluded that an appropriate amount of WO₃ loading could enhance the hybrid photovoltaic efficiency. Especially, the hybrid ZnO/P3HT photovoltaic device with 0.50 mol% WO₃-loadeded ZnO as an electron acceptor exhibited maximum power conversion efficiency (η) of 0.411%.

Keywords: ZnO, flame spray pyrolysis, WO₃, hybrid photovoltaic

1. INTRODUCTION

It is expected that the global energy demand will double within the next 50 years. Fossil fuels, however, are running out and held responsible for the increased concentration of CO₂ in the earth’s atmosphere. One of the interesting renewable energy technologies is photovoltaic, the technology that directly convert daylight into electricity.

Hybrid bunk-heterojunction is one of photovoltaic types that combines the advantages of inorganic and organic materials.
It could generate the prospect of cheaper production using large area devices and the use of flexible substrates as organic photovoltaic and it has high charge-carrier mobility from the inorganic component. In this research, ZnO nanocrystalline loading with various concentration of WO$_3$, inorganic material, can be introduced as the n-type semiconductor in hybrid bulk-heterojunction photovoltaic as it is a cheap and environmentally friendly material. This material can be synthesized in high purity and crystallinity by FSP. ZnO has high electron mobility, even when measured on films consisting of assembled ZnO nanoparticles [1,2]

Our hybrid photovoltaic devices were fabricated using ZnO nanoparticles as an electron acceptor and conjugated polymers P3HT as an electron donor. P3HT always be chosen as an electron donor in bulk heterojunction because of its high carrier mobility [3-4]. The excitons of these devices, created after the light absorption of P3HT, had to diffuse towards this charge-transfer interface for charge generation to occur. The diffusion length of the excitons, however, was typically 10 nm or less. This means that for efficient charge generation after absorption of light, each exciton had to find a donor-acceptor interface within a few nm, otherwise it will be lost without charge generation. Therefore, the hybrid bulk heterojunction devices are much more sensitive to the nanoscale morphology in the blend.

2. MATERIALS AND METHODS

2.1 Particle Synthesis

Zinc naphthenate (Aldrich, 8 wt% Zn) and tungsten ethoxide (Alfa Aesar, 5% w/v in ethanol 99.8%) were used as zinc and tungsten precursors respectively. The precursors were dissolved in absolute ethanol (Scharlau) to obtain a 0.5 M precursor solution for the synthesis via FSP experiments. Figure 1 shows the experimental setup for the synthesis of the flame-made unloaded ZnO and WO$_3$-loaded ZnO nanoparticles containing 0.25, 0.50, 0.75, 1.0 and 3.0 mol% WO$_3$ by FSP. In a typical run, the precursor was fed into a FSP reactor by a syringe pump with a rate of 5 ml/min and dispersed of 5 l/min O$_2$. This flame condition was depicted as 5/5 flame. The gas flow rates of methane and O$_2$ supporting flamelets were 1.19, and 2.46 l/min, respectively. The pressure drop at the capillary tip was kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle tip. The liquid precursor mixtures were rapidly dispersed by a gas stream and ignited by a premixed methane/oxygen flame. The flame height was 11 cm and showed an orange-yellowish flame appearance as shown in the inset. After evaporation and combustion of precursor droplets, particles were formed by nucleation, condensation, coagulation, coalescence and WO$_3$ deposited on ZnO support. Finally, the nanoparticles were collected on glass microfibre filters (Whatmann GF/A, 25.7 cm in diameter) with the aid of a vacuum pump.

Figure 1. Sketch of the flame spray pyrolysis unit.
2.2 ZnO/P3HT Solution Preparation

The 30 mg of ZnO nanoparticles and WO$_3$-loaded ZnO with different WO$_3$ concentrations including 0.25, 0.50, 0.75, 1.0 and 3.0 mol% were dispersed in 1 mL of methanol (Aldrich, 99.5%) and chlorobenzene (Sigma-Aldrich, 99.99%) solution in the ratio of 15:85 by volume. These suspensions were stirred for 2 days before filtering through 1.0 μm filter. The 30 mg of P3HT were dissolved in 1 mL of chlorobenzene for 8 h before filtering through 0.45 μm filter. Each ZnO solution sample was mixed with P3HT solution. These solutions were calculated using 26 vol% ZnO. This value was reported as the optimum ratio for this photovoltaic type [5].

2.3 Hybrid Photovoltaic Fabrication

Poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) (Baytron P, 99.99%) (PEDOT: PSS: DI water ratio of 1:1) was deposited on ITO glasses by spin coating at 4,000 rpm for 40 sec. These samples were dried at 80°C for 15 min. Then, the ZnO/P3HT solution was spin coated onto the PEDOT: PSS layer at 1500 rpm. After that lithium fluoride (LiF) (Aldrich, 99.99%) and aluminum (Al) (Sigma-Aldrich, 99.99%) electrodes were evaporated on the samples in a Denton DV 502 vacuum chamber at approximately 3-4 Å and 100 nm thick, respectively.

Finally, the devices were annealed in a dry nitrogen glovebox using direct contact with a hot plate at 150°C for 3 min. Schematic cross-sectional view of hybrid bulk heterojunction photovoltaic device structure is shown in Figure 2.

Exciton dissociation of P3HT/ZnO hybrid bulk-heterojunction that was deposited on an ITO substrate with PEDOT:PSS layer and capped with Al as a metal back electrode, was shown in Figure 3.

![Figure 2. Cross-sectional view of hybrid bulk heterojunction photovoltaic structure.](image)

![Figure 3. Exciton dissociation of P3HT/ZnO hybrid bulk-heterojunction [4,6].](image)
2.4 Measurement Conditions

Since the photovoltaic efficiency is temperature excitation therefore spectrum, illumination intensity dependence and test conditions were designed to obtain meaningful and comparable values. Standard test conditions include measurement at 25°C under 100 mW/cm² of Air Mass (AM) 1.5 irradiation (Oriel). The AM 1.5 is the spectrum of the 1 sun equivalent, which can be considered to be a blackbody radiation at 5,800 K, attenuated for scattering and absorption in the atmosphere. The system’s solar mismatch factor of 10% was determined using a calibrated standard diode. Current-voltage characteristics were collected using Keithley 236 source-measurement unit.

3. RESULTS AND DISCUSSION

3.1 Particle Characteristics

XRD was performed to confirm the phase and crystallinity of the nanopowders. Figure 4 shows the XRD patterns the flame-made (5/5) pure ZnO and WO₃-loaded ZnO nanoparticles containing 0.25, 0.50, 0.75, 1.0 and 3 mol% WO₃. It was found that all samples were highly crystalline, and all peaks can be confirmed to be the hexagonal structure of ZnO, which match well with the JCPDS file No. 89-0510 [7]. Amorphous phase of ZnO and WO₃ peaks were not found in these patterns. It can be assumed that concentrations of WO₃ were too low and the sizes of WO₃ particles too small, which affected the WO₃ peaks appearance. The intensity and sharpness of all diffraction patterns were not changed, indicating that the ZnO crystallinity did not change before or after doping with WO₃.

The specific surface areas (SSA_BET) from BET method of pure ZnO and WO₃-loaded ZnO nanoparticles containing 0.25, 0.50, 0.75, 1.0 and 3 mol% WO₃ were 114, 104, 99.2, 115, 121 and 119 respectively. The BET-particle diameter (d_BET) can be calculated using the formula as follows:

\[
d_{\text{BET}} = \frac{6}{(\rho_{\text{ZnO}} \times \text{SSA}_{\text{BET}} \times \text{wt}\% \text{ ZnO} + \rho_{\text{WO}_3} \times \text{SSA}_{\text{BET}} \times \text{wt}\% \text{ WO}_3)}
\]

From equation 1 [8], \(d_{\text{BET}}\) is the particle diameter, \(\rho_{\text{ZnO}}\) and \(\rho_{\text{WO}_3}\) are the weight density of the ZnO (5.680 g/cm³) and WO₃ (7.268 g/cm³), respectively. Figure 5 shows the comparison of SSA_BET and \(d_{\text{BET}}\) of the

Figure 4. XRD patterns of the flame-made (5/5) pure ZnO and WO₃-loaded ZnO nanoparticles with different WO₃ concentrations.
pure ZnO and WO$_3$-loaded ZnO nanoparticles with different amount of WO$_3$. It was found that the calculated particle sizes of all samples were in the same range of 9-10 nm, indicating that the low WO$_3$ load did not affect the particle size of ZnO.

Figure 6 show the TEM bright-field images of samples (A) the pure ZnO and (B) 3.0 mol% WO$_3$-loaded ZnO. The flame-made (5/5) pure ZnO nanoparticles in Figure 6(A) and WO$_3$-loaded ZnO nanoparticles in Figure 6(B) can be observed as particles having the clear spheroidal, hexagonal and rod-like morphologies. The particles sizes were found to be almost in the same range in both figures, which are in good agreement with the BET data. The

![Figure 5](image5.png)

**Figure 5.** The specific surface area ($SSA_{BET}$) and BET-particle diameter ($d_{BET}$) of the flame-made (5/5) pure ZnO and WO$_3$-loaded ZnO nanoparticles with different WO$_3$ concentration.

![Figure 6](image6.png)

**Figure 6.** TEM bright-field images of the flame-made (5/5) (A) pure ZnO and (B) 3 mol% WO$_3$-loaded ZnO nanoparticles.

The crystallite sizes of ZnO spheroidal particles and hexagonal were found to be in the range of 5-25 nm. The ZnO rod-like particles were found to be ranging from 5-10 nm in width and 10-25 nm in length. Figure 7 shows SEM image of 3.0 mol% WO$_3$-loaded ZnO nanoparticles. The EDS spectrum in the inset shows
elemental compositions for the region indicated by the white arrow. The W element was found about 0.66 at.% in this region. This result confirmed the existence of W.

3.2 Hybrid Photovoltaic Characteristics

The comparison of current-voltage (I-V) characteristic of hybrid WO$_3$-loaded ZnO/P3HT photovoltaic with difference WO$_3$ concentration was shown in Figure 8. It was found that I$_{SC}$ of all hybrid photovoltaic devices using WO$_3$-loaded ZnO as an electron acceptor were higher than that of hybrid photovoltaic device using pure ZnO. Moreover, the areas under curves in the fourth quadrant of 0.25-3.0 mol% WO$_3$-loaded ZnO/P3HT photovoltaic devices were bigger than that of pure ZnO/P3HT photovoltaic device. Especially, 0.50 mol% WO$_3$-loaded ZnO/P3HT photovoltaic device showed the biggest area under curve in the fourth quadrant. As we know, the more area under

![Figure 7](image1.jpg)

Figure 7. SEM image of the flame-made (5/5) 3.0 mol% WO$_3$-loaded ZnO nanoparticles. Inset shows EDS spectrum for the region indicated by the white arrow.

![Figure 8](image2.png)

Figure 8. The comparison of current-voltage (I-V) characteristic of hybrid WO$_3$-loaded ZnO/P3HT photovoltaic with difference amount of WO$_3$ concentration.
curve is, the higher power conversion efficiency will get. Therefore, the optimum amount of WO$_3$ doping in hybrid WO$_3$-loaded ZnO/P3HT photovoltaic was 0.50 mol%.

The characteristic parameters of hybrid WO$_3$-loaded ZnO/P3HT photovoltaic with different WO$_3$ concentration were concluded in Table 1. It was found that the highest $V_{oc}$ was shown by hybrid photovoltaic that used 0.25 mol% WO$_3$-loaded ZnO as an electron acceptor, while the highest $I_{sc}$ was shown by hybrid photovoltaic that used 0.50 mol% WO$_3$-loaded ZnO as an electron acceptor. This suggests that there is an effect due to the WO$_3$ which improves the number of photons that are actually converted to charge carriers. The fill factors (FF) of all devices were in the same range of 0.40-0.47. Moreover, hybrid 0.50 mol% WO$_3$-loaded ZnO/P3HT photovoltaic was the best device that got the highest power conversion efficiency ($\eta$) of 0.411%. This power conversion efficiency value is comparable with Janssen’s value of 0.9% [5].

<table>
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<th>Mol % of WO$_3$-loaded ZnO</th>
<th>$V_{oc}$ (V)</th>
<th>$I$ at $V=0V$ (mA)</th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>$V_{m\cdot I_m}$ (mW)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
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<td>0</td>
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<td>0.324</td>
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<tr>
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<tr>
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<td>0.381</td>
<td>1.24</td>
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4. CONCLUSIONS

The pure ZnO and WO$_3$-loaded ZnO nanoparticles containing 0.25, 0.50, 0.75, 1.0 and 3.0 mol% WO$_3$ were successfully synthesized by FSP from zinc naphthenate and tungsten ethoxide precursors under 5/5 (precursor/oxygen) flame condition.

These nanoparticles were successfully applied in hybrid photovoltaic devices as an electron acceptor. The current-voltage characteristic of these devices showed that WO$_3$ could increase the number of photons actually converted to charge carriers which affect the power conversion efficiency. These results could be concluded that an appropriate amount of WO$_3$ doping could enhance the hybrid photovoltaic efficiency. Especially, hybrid ZnO/P3HT photovoltaic device with 0.50 mol% WO$_3$-loaded ZnO as an electron acceptor exhibited maximum power conversion efficiency of 0.411%.

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