Organic solvent wetting properties of UV and plasma treated ZnO nanorods - printed electronics approach

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ABSTRACT

Due to low manufacturing costs, printed organic solar cells are on the short-list of renewable and environmentally-friendly energy production technologies of the future. However, electrode materials and each photoactive layer require different techniques and approaches. Printing technologies have attracted considerable attention for organic electronics due to their potentially high volume and low cost processing. A case in point is the interface between the substrate and solution (ink) drop, which is a particularly critical issue for printing quality. In addition, methods such as UV, oxygen and argon plasma treatments have proven suitable to increasing the hydrophilicity of treated surfaces. Among several methods of measuring the ink-substrate interface, the simplest and most reliable is the contact angle method. In terms of nanoscale device applications, zinc oxide (ZnO) has gained popularity, owing to its physical and chemical properties. In particular, there is a growing interest in exploiting the unique properties that the so-called nanorod structure exhibits for future 1-dimensional opto-electronic devices. Applications, such as photodiodes, thin-film transistors, sensors and photo anodes in photovoltaic cells have already been demonstrated. This paper presents the wettability properties of ZnO nanorods treated with UV illumination, oxygen and argon plasma for various periods of time. Since this work concentrates on solar cell applications, four of the most common solutions used in organic solar cell manufacture were tested: P3HT:PCBM DCB, P3HT:PCBM CHB, PEDOT:PSS and water. The achieved results prove that different treatments change the contact angle differently. Moreover, solvent behaviour varied uniquely with the applied treatment.

Keywords: Wettability, Printing, inkjet, R2R, contact angle, solar cells, OSC, organic, plasma, treatment, UV, ZnO, nanorods, nanostructures

1. INTRODUCTION

A variety of techniques have been developed to improve the cost-efficiency of solar cells, which is important for the strive towards carbon-free technologies.[1,2] A concrete example is mass production of organic-based photovoltaic (PV) cells processed at low temperature using roll-to-roll (R2R) and inkjet printing.[3,4] Additionally, printing allows deposition of active materials on specific areas of the substrate, contrary to, e.g., spin coating.[5] Organic solar cells (OSCs), due to their low manufacturing costs, may well become the technology of choice for renewable and environmentally-friendly energy production in future.[6] Intensive research is being carried out to study photoactive materials to increase their power output and exploit their comparative advantages.[7] A popular candidate is zinc oxide, owing to its physical and chemical properties for nanoscale device applications. In particular, there is growing interest in electrochemically deposited (ECD) ZnO nanorods (NRs), exploiting the unique properties that the nanorod structure exhibits for 1-dimensional opto-electronic devices. An added advantage of such ZnO NRs is the controlled large-scale synthesis of nanostructures, which increases the surface-to-volume ratio and enhances carrier lifetime, while providing higher excitation and dissociation site densities

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than etched ZnO nanorods.[8] Its functionality as improving the solar cell performance by increasing the optical path has also been demonstrated.[9] Applications, such as photodiodes, thin-film transistors, sensors and photo anodes in photovoltaic cells have already been demonstrated.[10–12] Also photoactive layer or electrode materials are being explored using different approaches. For instance, the interface between the substrate and solution (ink) drop is heavily studied, as it is considered the most critical factor in achieving high printing quality.[13,14] So far, UV, oxygen and argon plasma treatments have been shown to improve the hydrophilicity of treated surfaces and, thus, printing properties.[15–17]

This paper presents the wettability properties of ZnO nanorods treated with UV illumination, oxygen and argon plasma for various periods of time. To characterise the ink-substrate interface, this study employs the contact angle method. Although recent research has illustrated the usability of pre-treatment methods for water solutions,[18] a more in-depth investigation is necessary to understand the behaviour of solvents, particularly organic solvents with different substrates. Since this work concentrates on solar cell applications, four of the most common solutions used in organic solar cell manufacture were tested here: P3HT:PCBM dissolved in 1,2-dichlorobenzene, P3HT:PCBM dissolved in chlorobenzene, PEDOT:PSS and water. Moreover, to characterize the morphology of the ZnO NRs layer, a series of measurements were performed using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

The results achieved in this paper confirm that different treatment methods have a different effect on the wettability of the substrate. Furthermore, solvent selection plays an important role in the printing process by influencing the interface between ink and substrate. This study provides a step toward better understanding of the ink/ZnO NR interface and the fabrication of more efficient solar cells made of a hybrid of inorganic and organic materials.

2. METHODS

2.1 ZnO growth and characterization

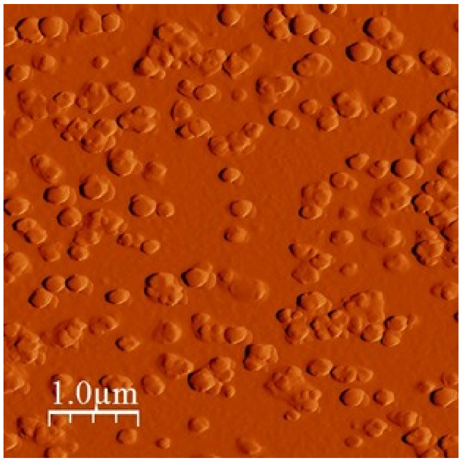
ZnO nanorods were electrochemically deposited from zinc nitrate ($Zn(NO_3)_2$) on ITO-covered glass substrates (TFD, resistivity 20 $\Omega/\square$). These NRs were grown using a galvanostatic deposition method adapted from Seipel.[19] Deposition was set for a period of about 300 seconds, with an applied current density of -450 $\mu A \cdot cm^{-2}$ (cathodic current). Growth parameters were computer controlled and monitored using a potentiostat/galvanostat PAR 270. For all experiments, 50 mM of aqueous zinc nitrate (sigma Aldrich, 99.999%) was used as precursor. The ZnO film was grown in an undivided three-electrode cell arrangement, with pre-cleaned ITO as the working electrode, 1 cm^2 platinum foil as the counter and a standard calomel electrode (SCE) as the reference electrode. In our setup, the working and counter electrodes were placed 2 cm apart. The solution was maintained at 80°C during synthesis. The measured pH of the solution was 5.3. Next, the surface morphology and crystal properties of the thus grown ZnO film were characterised under a Scanning Electron Microscope (Carl Zeiss Evo MA10 SEM) and Atomic Force Microscope (Veeco Dimension 3100).

2.2 Surface Treatments

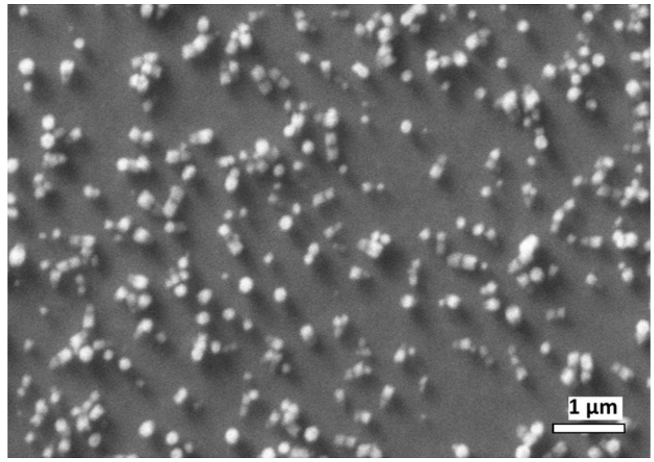
Sample surfaces were treated by UV, argon (Ar) plasma, oxygen (O_2) plasma, and a mixture of UV and Ar plasma. Three ZnO NR covered ITO samples were prepared for each method and treated for 1, 2 or 3 minutes. The corresponding UV wavelength was 254 nm (Jetlight UVO cleaner 42-220), and the O_2 and Argon plasma were generated at Plasma-Preen II 862 (frequency 2.4 GHz and power 60 W). Lastly, the UV+Ar Plasma treatment was carried out in two steps: first the samples were treated with UV illumination for 2 min and then with argon plasma for 1, 2 and 3 minutes. A sample covered with untreated ZnO NR was used as reference. A Drop Shape Analyser Kruss DSA100 was used to measure and extract the surface contact angle. Four solutions were prepared for this test: DI water, Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), poly(3-hexylthiophene):Phenyl-C61-butyric acid methyl ester (P3HT:PCBM) dissolved in chlorobenzene (CHB) and P3HT:PCBM dissolved in 1,2-dichlorobenzene (DCB) at 30 mg/ml wt. All materials were supplied by Sigma-Aldrich. In these measurements, performed at room temperature, the surface contact angle of droplets at two different locations on the same sample were averaged out and standard deviations were calculated.

3. RESULTS

Morphology characterizations by AFM and SEM are presented in Fig. 1. As seen, ZnO nanorods were typically 150 nm in height and 100 nm in diameter. Fig. 2 presents water droplet at treated and untreated ZnO NR surface.

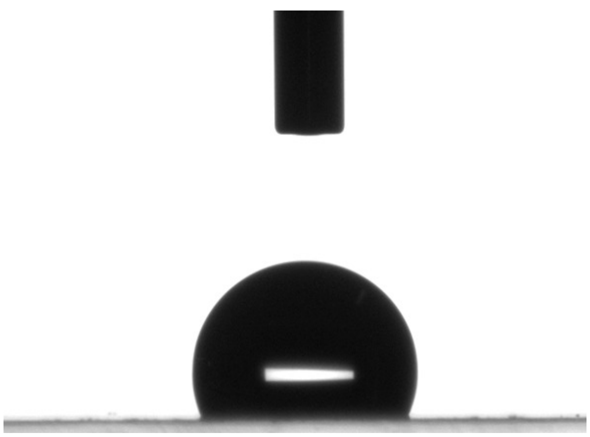


(a) AFM image of ZnO NR deposited at ITO substrate



(b) SEM image of ZnO NR deposited at ITO substrate

Figure 1. Morphology characterization of ZnO NR deposited with ECD method at ITO substrate



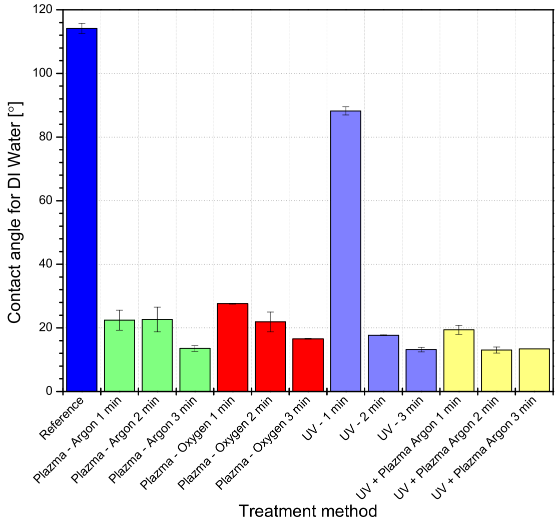
(a) Water droplet at untreated ZnO NR substrate - large contact angle

(b) Water droplet at ZnO NR substrate treated with argon plasma for 3 minutes - small contact angle

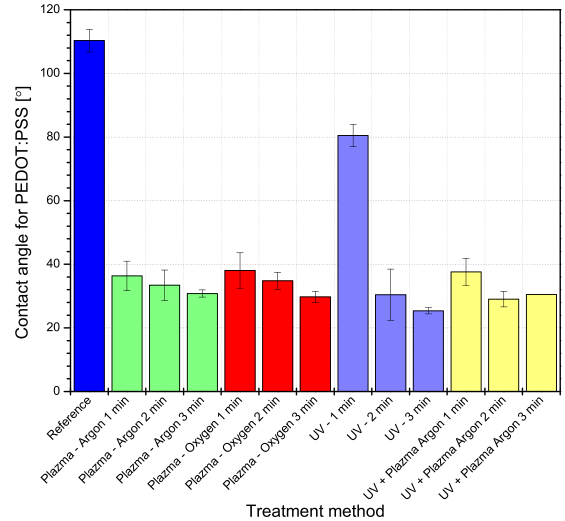
Figure 2. Depicted example of surface treatment influence on the contact angle

Fig. 3 and Fig. 4 show the measured contact angle for each treatment, along with the corresponding treatment time for all solutions. As can be seen, the largest contact angle was in fact the reference (untreated). The difference between treated samples and the reference is especially distinguishable in water-based solutions, i.e., DI water and PEDOT:PSS, where the contact angle was 110° for untreated samples and significantly lower for treated samples. All treatments reduced the contact angle to around 20° for DI water and 30° for PEDOT:PSS. In addition, there was a visible time-dependable trend; thus, a longer treatment invariably produced a lower contact angle value. It is worth noting that UV treatment is more time-dependant than plasma treatment and has less influence on contact angle. Results from the UV+Plasma treatment do not differ from those achieved with plasma treatment only.

DHB and CHB based inks interact differently with ZnO NRs than with water solutions, forming drops with a low contact angle of approximately 17°, even without treatment. Although treatment reduces the contact angle by approximately 5° and is time-dependable, the change is not as substantial as in water-based solutions.

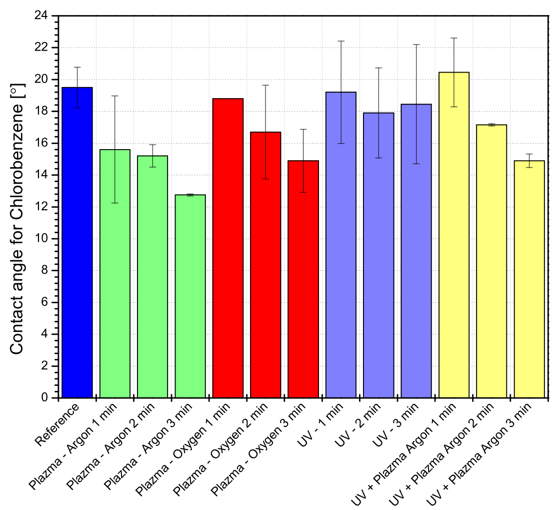


(a) DI Water contact angle results

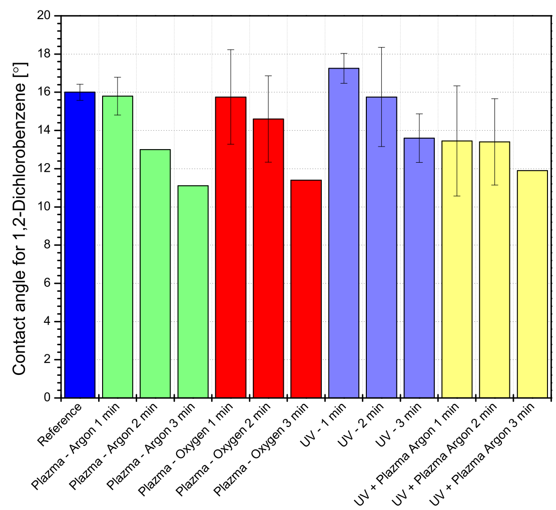


(b) PEDOT:PSS PH500 contact angle measurements results

Figure 3. The contact angle measurements of water-based solvents for different ZnO NR treatments



(a) Contact angle for P3HT:PCBM disolved in chlorobenzene



(b) Contact angle for P3HT:PCBM disolved in 1,2-dichlorobenzene

Figure 4. The contact angle measurements for P3HT:PCBM materials dissolved in organic solvents for different ZnO NR treatments

4. DISCUSSION

In pre-treated samples, contact angles were significantly reduced for water-based solutions. This implies that their surface properties have undergone modifications, making them more hydrophilic. Some of the underlying mechanisms have been demonstrated by previous studies. For UV irradiation, for example, electron-hole pairs are generated within the ZnO surface, and some of the holes react with the lattice oxygen to form surface oxygen vacancies. Meanwhile, water and oxygen may compete to dissociatively adsorb on them. As the defective sites are kinetically more favourable for hydroxyl adsorption than oxygen adsorption, surface hydrophilicity is improved.[20,21] In plasma treatments, ZnO NR films are etched anisotropically, which generates more hydrophilic rough surfaces.[18,22] The impact of the treatment duration is more prominent in UV that in plasma treatment. However, its actual effect on the contact angle even after 3 minutes is lower compared to the plasma treated, which is probably due to the differences in energy delivered during the treatment and the subsequent alteration of the surface. A comparison between the used gases - argon and oxygen for plasma treatment showed no significant difference in measured contact angle, making gas selection a non-critical issue for the plasma process.

Differences in measured contact angles observed with DHB and CHB were less significant than those for water. Since these changes are mostly affected by the surface tension of organic solvents, which is lower than that of water-based solutions, pre-treatment has less effect on contact angle. Additionally, the results for DCB and CHB are almost identical, because their surface tension values are similar, approximately 33 $mN{\cdot}m^{-1}$. Moreover, as the error bar is significantly large in some cases (Fig. 4), it is difficult to deduce the exact cause for the change in contact angle. ITO surface morphology characterization in particular depicted uneven distributions of NRs in different sample areas, which may have influenced the results by increasing the standard deviation. A more detailed studies on NR size and areal density distribution will be presented elsewhere.

5. CONCLUSIONS

In this paper, we have investigated the effects of standard surface treatments, including UV, O_2 plasma, Ar plasma on ZnO nanorods films. By inspecting the contact angle of droplets, we studied the wettability of the thus treated surfaces. Our results indicate that UV and plasma treatment of ZnO nanorods could significantly improve surface hydrophilicity for water solutions. In contrast, the change was less significant for organic solvents. One of the reasons for this difference is the low surface tension of organic solvents compared to water-based solutions. Nevertheless, for organic solvents and ZnO NR, the mechanisms of wetting need to be studied further to define all physical and chemical properties that differ from the well-known principles of water-based solutions. This research provides a step toward better understanding of the ink/ZnO NR interface, which is essential for inkjet and R2R printing process of organic solar cells.

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