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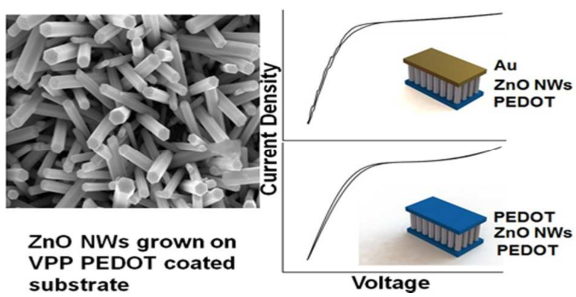
ZnO NWs were directly grown on Vapour phase polymerised (VPP) PEDOT. I-V measurement of ZnO grown on PEDOT shows an ohmic contact whereas with a PEDOT electrode sandwiched on top of ZnO NWs gives a schottky contact.



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New Junction materials by the direct growth of ZnO NWs on Organic Semiconductors

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Ordered hetero-junctions using one dimensional inorganic nanostructures is currently widely studied to develop devices such as high efficiency photovoltaic devices, light emitting diodes, catalysts, supercapacitors, lithium ion batteries and nanogenerators. High quality schottky contacts can be obtained by spin coating of conducting polymer dispersions/solutions onto inorganic nanostructures; however the interaction of polar surfaces of the nanostructures with chemically active materials in the spin coating solution makes the junctions less reliable. In this present work, we show that we can fabricate high quality junctions by either directly growing the nanostructures onto the vapour phase polymerised (VPP) poly (3,4-ethylenedioxythiophene) (PEDOT) substrates or sandwiching VPP polymerised substrates, thus avoiding any unwanted interaction with the acidic additives from the polymer solution at the organic/inorganic interfaces. I-V measurements prove that the direct growth of ZnO NWs on PEDOT coated substrates creates an ohmic contact, whereas the PEDOT layer on top surface creates a schottky contact due to the dipole moment with the polar ends.

Zinc oxide (ZnO) is a well-known wide band gap *n*-type semiconductor (3.37eV at RT) with large exciton binding energy of 60 meV compared to other wide band gap semiconductors.[1-4] The impressive properties exhibited by ZnO nanowires (ZnO NWs) such as coupling of semiconducting-piezoelectric properties, strong UV emission and readiness to form a wide variety of nanostructures made them feature as one of the important semiconductors for fabricating functional devices.[3-5] In organic photovoltaic devices, the heterojunctions created by mixing donor and acceptor molecules were hampered by the "random walk" of the holes and electrons in the absence of proper contacts.[6, 7] To tackle this problem ZnO NWs were used as a channel for better charge transport medium for electrons.[6, 8] The heart of these kinds of solid state semiconductor devices is the metal-semiconductor contacts which can control the electron flow directions in and out of the devices.[9] The first metal-ZnO contact was observed by Mead (1966)[9] and it was believed that the noble metals (Au,Pt and Pd) forms a schottky barrier and the lower work function metal (Ag, Al) and alloys forms an ohmic contact with ZnO.[10] It was found that this classification was overly simplified because the non-reproducible results.[10] Metal deposition methods, surface contamination, interface native defects, chemical bonding can affect the barrier height and change an expected schottky contact into ohmic or vice versa especially on nanostructures.[9] Chatman et al[11] reported selective schottky /ohmic contact formation in accordance with electrodeposition potential of ZnO on Pt or Au electrodes. On similar lines there are reports available for the formation of high quality schottky barriers as high as 0.92 eV with Ag by the virtue of silver oxide formation at the interface.[12]

A tunable diode based on organic- inorganic interface was reported by Lonergan[13] using *p*-type organic polymer poly(pyrrole) and inorganic *n*-type InP, unlike the metal contacts these contacts exhibited better slope parameter indicating Fermi level pinning. Inspired by this study, there have been a few attempts to produce high quality schottky barrier with other widely studied metal oxides such as ZnO by coating dispersions/solutions of conducting polymers. A schottky contact was fabricated on ZnO (0001) single crystal by spin coating a PEDOT: poly (styrenesulfonate) (PSS) and an energy band diagram was proposed by Nakano et al.[14] On a correspondence to this, Lin[15] suggested that more than the dipole interaction between acidic PSS and ZnO polar plane (0001), the chemical reaction should be accounted, which changes the vaccum level shift direction in the energy band diagram. Gunji et al[16] found that spin coating of PEDOT:PSS on epitaxially grown ZnO NWs (with O-polar terminating layer) will lead to etching of NWs as deep as 120 nm. It was found that due to strong thermo-mechanical interaction with PEDOT:PSS and ZnO NWs surfaces, NWs can get exfoliated from the growth substrate.[17] To avoid the use of highly acidic solution (pH of PEDOT:PSS is 1-3 at 25 ^{0}C) on a material which is not stable below a pH of 4.5, we propose solvent free techniques such as oxidative chemical vapour deposition or vapour phase polymerisation

Vapour phase polymerisation (VPP) has attracted significant interest as a flexible technique to obtain high quality conducting polymer thin films on a variety of substrates without any compatibility issues.18 In this method the oxidant is applied to the substrate using wet chemical method and monomer is delivered in the vapour phase avoiding the complications and compromises for processability as in the case of PEDOT:PSS.[18] A modified base inhibited VPP of PEDOT was demonstrated to produce conductivity as high as 1000 S/cm, whereas PEDOT:PSS spin coated layers exhibits 10 S/cm.[19] VPP polymerized PEDOT has shown good conductivity, chemical and mechanical stability and demonstrated as a replacement material for Pt in fuel cell application.[20] Herein, we demonstrate the possibility of using VPP PEDOT on a variety of substrates as a support for the growth of ZnO NWs via low temperature aqueous techniques. To demonstrate that the presented technique is compatible with flexible substrates, polyethersulfone (PES) was chosen as substrate material.

PES in DMF was electrospun to obtain uniform flawless electrospun membranes with a mean diameter of 583 ± 124 nm. PEDOT was polymerized via VPP on 2-D and 3-D PES substrates. The success of PEDOT functionalization was confirmed by the characteristic Raman peaks of PEDOT observed on the functionalized substrate (see supporting information S1). The SEM images shows a thin uniform PEDOT layer on 2-D PES and 3-D PES substrates (see fig 1.a & 1.c). ZnO NWs were synthesized using a low temperature seed mediated growth method21 on functionalized PEDOT substrates and seed density was optimized in terms of iterations of seed coating and dipping time to achieve complete surface coverage and vertically oriented NWs (see fig 1.b &1.d). The SEM images of the bare PES substrates and confirmation of the synthesis of ZnO NWs by EDX on FTO can be found in supporting information S2 and S3. The synthesized NWs are single crystalline, having a length of ~1500 nm in the (0001) direction with inter plane space separation of 0.26 nm (see supporting information S4).[21] The corresponding SAED pattern indicates a wurtzite crystalline structure (see supporting information S5). The sheet resistance of PEDOT coated 2-D PES is 94 Ω/square and increases to 125 Ω/square after the growth of ZnO NWs due to the highly alkaline growth medium. However, the retained conductivity suggests that the ZnO NW growth doesn't affect the PEDOT on the PES substrate.[20, 22] To our knowledge this is the first report to demonstrate that n-type ZnO NWs can be grown directly on a p-type polymer (PEDOT) without compromising the stability of ZnO NW's or the conductivity of the polymer.

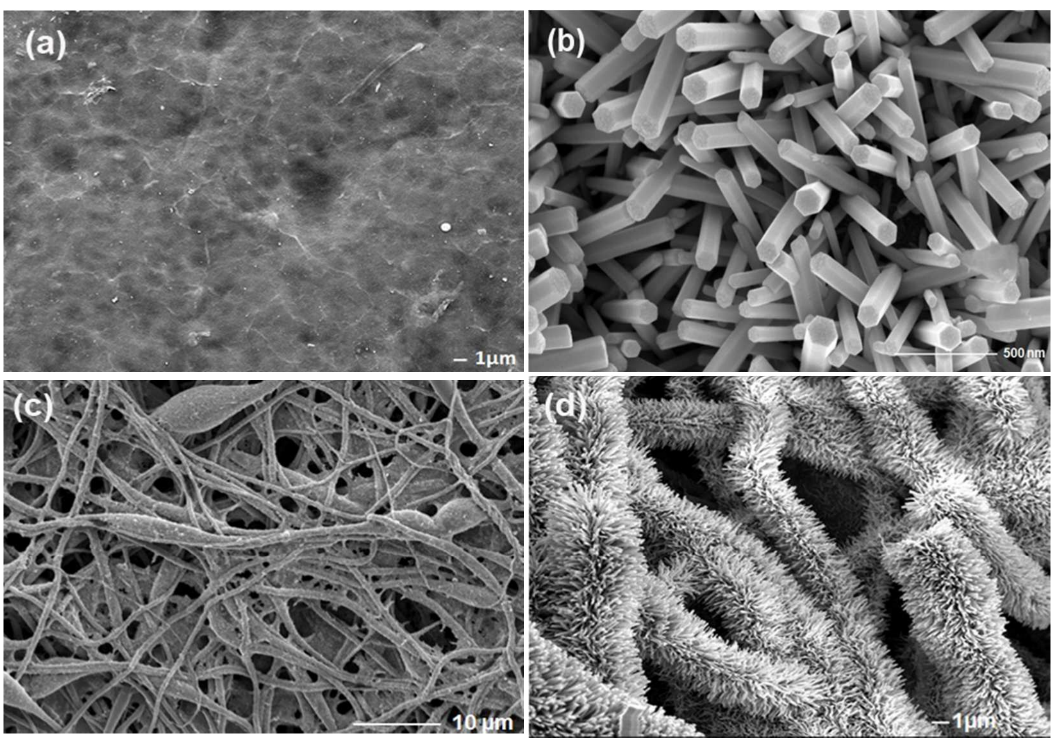

Fig 1 SEM image of (a) PEDOT coated 2D-PES, (b) ZnO NWs grown on PEDOT coated 2D-PES (c), PEDOT coated 3D-PES and (d) ZnO NWs grown on PEDOT coated 3D-PES.

The growth of inorganic semiconductors is not limited to ZnO NWs alone; we have synthesized CuO nanowalls onto PEDOT coated substrates. The corresponding SEM images are given in supporting information S6, suggesting that the method can be extended to other metal oxide nanowires which can be synthesized using low temperature seed mediated aqueous routes. To understand the junction properties of newly synthesized heterojunctions, I-V characteristics were measured using a potentiostat. All electrodes were fabricated on glass in order to increase the robustness and to avoid any vibrational perturbation and all the measurement were done inside a Faraday`s cage.

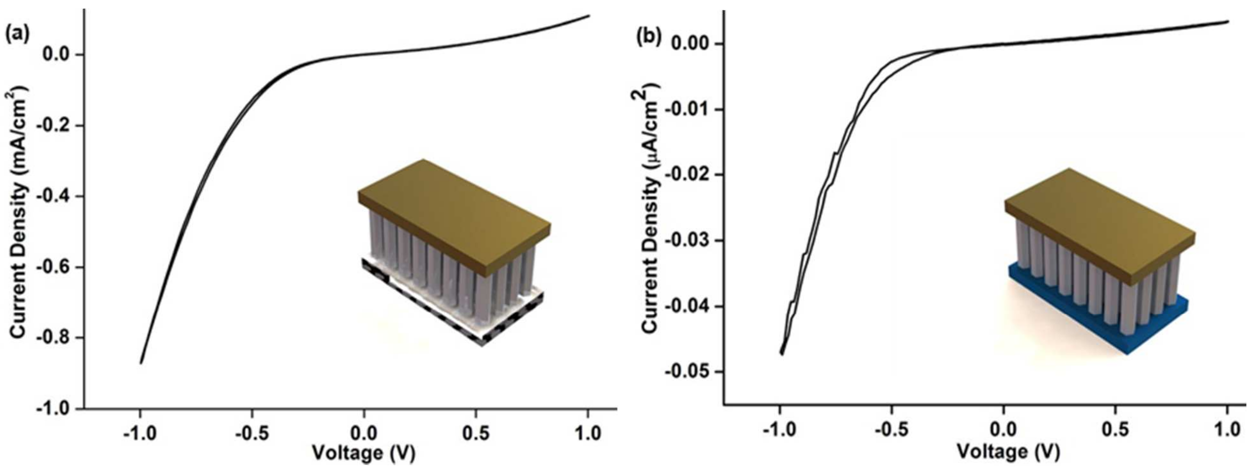

Fig 2 I-V curves obtained for (a) ITO+ZnO-Au and (b) PEDOT+ZnO-Au, +sign denotes on which electrode ZnO NWS were grown.

ZnO NWs produced an ohmic contact with ITO and a schottky contact with Au as reported in the literature.[23] To our surprise, ZnO NWs grown on VPP PEDOT substrate behaves exactly similar to ITO, whereas Nakano et al[14] and all other reports suggesting a schottky contact. In the case of PEDOT:PSS there was a debate on whether the chemical reaction between PSS and polar ZnO or dipole interaction induces the high schottky barrier.[15] But there was no indication of formation of an ohmic contact and moreover it was against the Schottky-Mott limit prediction ($\phi B=\phi PEDOT-\chi ZnO$, 5.0- 4.1 = 0.7 eV).[14] However, there are numerous reports available where ZnO NWs exhibiting a different junction property with a given metal than fabricated with VPP PEDOT coated top electrode and I-V characteristics were measured.

By considering only the shape of the I-V curves, it is obvious that all four combinations show a rectification with a plateau before it extends to reverse leakage current. In other words all the four combinations have a top schottky contact. This may seem like an impossible proposal, but there are several examples in the literature that demonstrate that Au can act both as an ohmic and Schottky contact.[25] In a recently demonstrated device (piezoelectric nanogenerator) gold was used to sandwich the ZnO NWs to form one side ohmic and other side schottky contacts. But it is imagined that when a piezopotential is induced across the interface it may lead to a linear tilt of the bands and the Fermi level along the direction of the ZnO NWs.[25] Since there was no force applied a similar kind of band bending can be ruled out. The Schottky barrier formation on the top contact with VPP PEDOT substrate is presumably due to the dipole interaction between the polar end of the NWs (0001) with PTSa (p-toluenesulfonic acid) dopant in the PEDOT. However this kind of interaction is absent when ZnO NWs were directly grown on VPP coated PEDOT (not in contact with polar end).[26] The ZnO NWs were grown through seed mediated synthesis. Greene et al[26] found that acetate derived seeds shows (0002) plane reflection in XRD analysis and shows texturing along the c-axis. It was postulated that (0001) plane with high energy may adsorb molecules to compensate the high energy and may not be polar. And c-axis texturing is not due to the polarity of the seeds because as the thickness of seed layer increases the selectivity is lost.[26] Moreover seeds derived from sources other than acetate demonstrate different properties.[21] In this case, seeds were deposited onto the VPP PEDOT coated substrates prior to the aqueous chemical growth. Thus the ZnO surface which has got in the intimate contact with VPP PEDOT may not be polar moreover the p-n junction created could create some pacification of free electrons from ZnO. The surface states present in the contact area can behave similar to hydrogen adsorption to a schottky barrier, where the electrons are depleted from the interface.[9, 10] This reduces the barrier height and converts the schottky barrier to an ohmic contact in case of direct growth. On the other hand, when VPP PEDOT was in contact with the polar end of the NW, the dipole moment increases the barrier and forms a schottky barrier.

The symmetrical junctions with other materials were fabricated and tested for their I-V characterstics. Au+ZnO-Au (Fig 3(b)) behaved similar to PEDOT+ZnO-PEDOT with high rectification current whereas ITO+ZnO-ITO shown ohmic contact on both the sides. We have extended the method to other organic semiconductor such as polybithiophene. Polythiophene (PBTh) was vapour phase polymerized onto the FTO and ZnO NWs were grown using seed mediated method. I-V characteristics of PBTh+ZnO-Au heterostructures were found similar to PEDOT+ZnO-Au (supporting information S7). The conductivity of VPP PBTh was low and the symmetrical junction measurements were similar to PEDOT+ZnO-PEDOT junctions with small current. I-V characteristics of the CuO nanowalls grown on PEDOT also showed an ohmic contact (supporting information S8).[27]

The absence of dipole interaction and the formation of p-n junction is not a sufficient condition to reduce a barrier height of 0.7 eV. To understand the change of PEDOT before and after the growth of the ZnO NWs, PEDOT coated glass slide was treated in an exactly similar alkaline medium without ZnO precursors. The work function and UV spectra were recorded as shown in the Fig 4 (a) and (b).

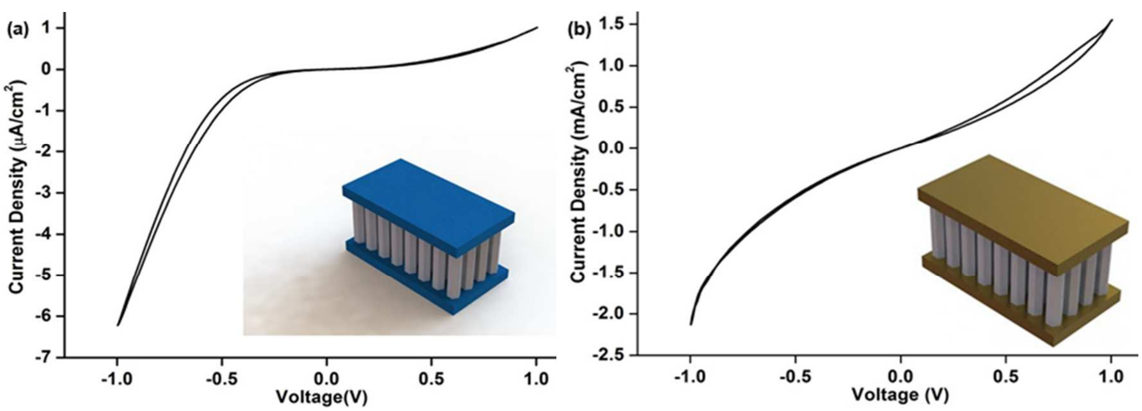

Fig 3 I-V characteristics of (a) PEDOT+ZnO-PEDOT and (b) Au+ZnO-Au.

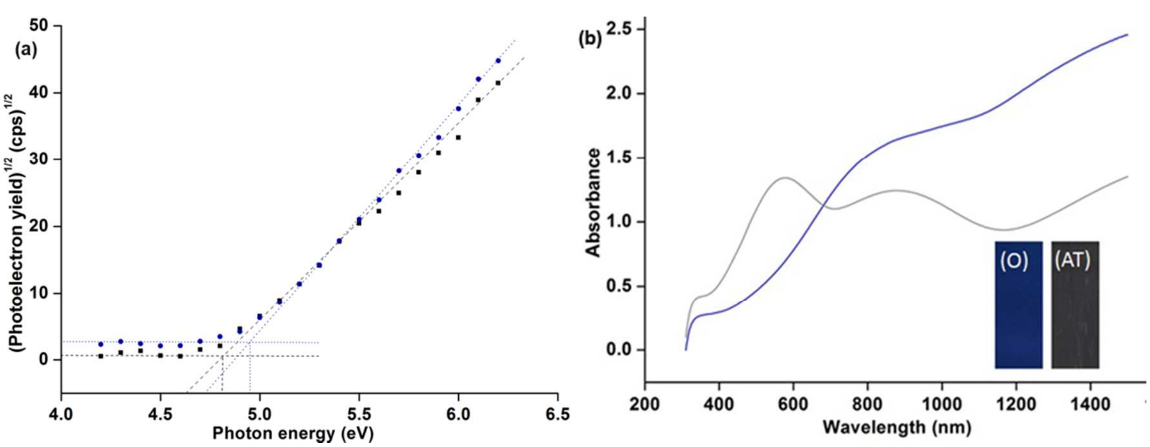

Fig 4 (a) UPS spectrum of VPP PEDOT (light blue line) and alkaline treated (AT) VPP PEDOT (dark blue line) and (b) UV spectra of VPP PEDOT and AT VPP PEDOT, inset the pictures of the respective VPP PEDOT (marked as O) and AT VPP PEDOT (marked as AT)

The work functions of VPP PEDOT and Alkaline Treated VPP PEDOT (AT VPP PEDOT, more neutral PEDOT) were found to be 4.93 and 4.81 respectively. A reduction in the work function could lower the barrier height, but the observed change was not sufficient to prompt a change to an ohmic contact. The alkaline treatment has changed the light blue colour of PEDOT to dark blue and there is also a striking difference in their corresponding UV spectra. In AT VPP PEDOT, a new absorption peak appeared at ~570 nm which corresponds to π-π* transition. Surprisingly both the VPP PEDOT and AT VPP PEDOT has about the same amount of polarons (~890 nm), however there was reduction in the amount of bipolarons (~1260 nm) in the latter.[28] During the ZnO growth PEDOT has been treated with NaOH and hexamethyl teteramine which reduces the PEDOT by adding electrons to the delocalized π orbital on the polymer chains and thereby reduce the level of p-doping. The significant decrease in bi-polarons and development of π-π* transition from neutral segments is a well-known result of alkaline treatment.[22] A relation was derived between the conductivity and doping level of the PEDOT (Supporting information S9 to S12). The as made VPP PEDOT is considered to have a doping level more than 25 %, whereas the alkaline treatment has reduced the doping level to less than 10% (Supporting information S12).[29] The reduction of doping in the AT VPP PEDOT creates less bipolarons, and thus less charge carriers.[28] To confirm this understanding we have carried out the conductivity measurement using four point probe. The VPP PEDOT and AT VPP PEDOT exhibited a conductivity of 708 and 3.66 S cm^{-1} respectively, which means that the amount of the charge carriers is much less in the latter. The work function measurement does not reflect the huge change in the number of carriers, because the technique only analyzing the energy of the most easily ionizable electron, which in both VPP PEDOT and AT VPP PEDOT comes from the same (more or less filled) π orbital. This suggests that the reduction of bipolarons i.e. the added electrons to the PEDOT during ZnO NWs synthesis reduces the barrier height, which makes the PEDOT-ZnO junction an ohmic contact.

Vertically oriented one dimensional nanostructure arrays on conductive substrates are considered as promising candidates for building energy storage devices such as lithium ion batteries and supercapacitors.[30] Advantages of such electrodes are highly regarded due to the ability to provide room for individual nanostructures in participating in chemical reaction, more forgiving during straining (cycling/ Li insertion) and less complex fabrication techniques.[30, 31] However the unavailability of simple synthetic methods to fabricate ordered high quality nanoarrays of metal oxides on flexible conductive substrates has been prevented the exploitation of three dimensional spaces (weight and volume) in charge storage devices.[30] To show that the combination of VPP and seed mediated growth method can unveil a range of potential electrode materials; we have tested the electrochemical performance of the fabricated electrode in 1 M NaCl solution. The enormous increase in surface area in PEDOT coated 3-D PES compares to their 2-D counterpart was reflected in the electrochemical storage ability (shown in Fig 5). It was found that the capacitance was increased from 4.4 nF to 355.9 nF by changing

into three dimensional electrode.[32] ZnO act as a non-faradaic material and exhibits no redox reaction in NaCl electrolyte, hence only a small increase in capacitance is observed in both PEDOT coated 2-D and 3-D PES was due to the higher surface area contributed by the ZnO NWs.

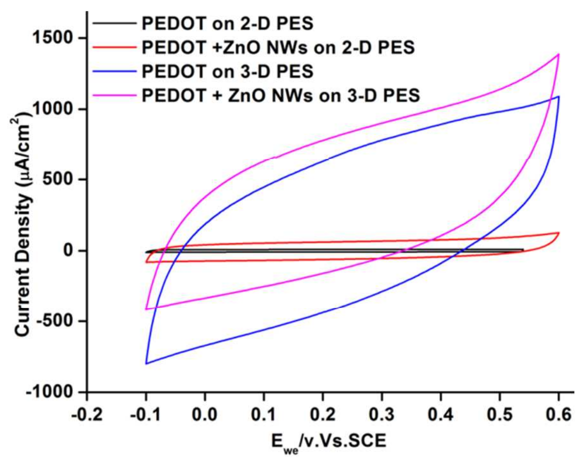

Fig 5 The cyclic voltammogram of PEDOT coated 2-D and 3-D PES with and without ZnO NWS in 1 M NaCl solution with a scan rate of 2 mV/s under N_2 atmosphere.

There are quite a few studies proposing the growth of C materials, MnO_2 nanostructures on ZnO NWs to improve its faradaic contribution,[33] however, our current interest was in establishing the combination of VPP and seed mediated growth methods to produce potential candidates for energy storage applications. The currently available reports in three dimensional flexible electrodes widely used sputtering of noble metals such as gold even with a conductive carbon fibre base, which not only reduce the interest in commercial applications but also increase the complexity of electrode fabrication.[34, 35]

Conclusions

In summary, in this work we have shown that we could directly grow metal oxide nanostructures on organic semiconductors thus avoiding unwanted chemical interaction at the interface. The direct growth method provides ohmic contact with ZnO and CuO nanostructure when they were grown on VPP PEDOT/PBTh. The fabricated ohmic contacts using direct growth on VPP p- type semiconductors are interesting candidates for supercapacitors, lithium ion batteries and inverted solar cells. A high quality schottky barrier could be tailored by sandwiching a VPP PEDOT electrode on top of the ZnO NWs grown on VPP PEDOT electrode. It is the first time observation where a single material can be tuned to ohmic/schottky contact on the basis of the polar interactions of the nanostructures and engineering of the doping level of a conducting polymer.

Notes and references

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