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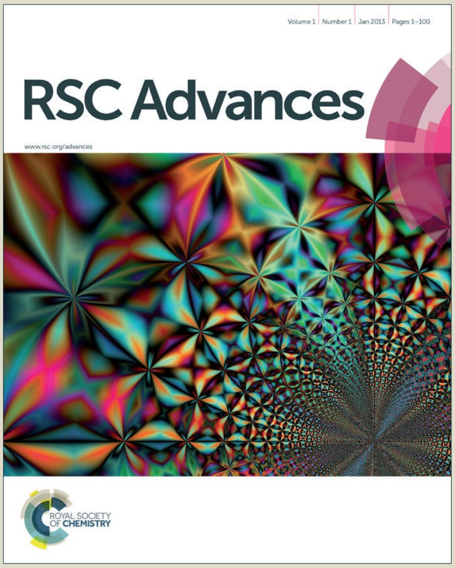

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Directing the Growth of ZnO Nano Structures on Flexible Substrates Using Low Temperature Aqueous Synthesis

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This paper reports a detailed discussion on the aqueous chemical growth of ZnO nanowires (NWs) on 2-D and 3-D polyethersulfone. Substrate surface chemistry and substrate placement in the growth solution is found to affect the morphology of the grown nanostructures and indeed the growth direction of the NWs. We report for the first time a-axis ZnO NWs using a low temperature synthesis method. The electrochemical behaviour regarding water oxidation showed significant differences depending on the growth directions but this difference was eliminated after annealing, both in dark and under illumination.

Introduction

Vertically oriented zinc oxide nanowire (ZnO NW) arrays are utilised in a wide variety of electronic and photonic devices. Integrating semiconducting NW arrays to flexible and wearable organic substrates opens up exciting possibilities for new devices. Synthetic techniques such as vapour –liquid –solid process, chemical vapour deposition and thermal evaporation used high temperature processing which limit the choice of substrates to only inorganic ones.[1-3]

The first ZnO NW obtained through a solution route was reported in 1981 by forced hydrolysis and these hydrothermal studies also produced other interesting morphologies of ZnO crystals.[4, 5] In Chemical Bath Deposition (CBD), a thin film of metal oxide is generated on a substrate by controlled precipitation by the virtue of condensation or hydrolysis of the metal ion or metal complex. Most of these studies used an alkaline hydrolysis around the isoelectric point of ZnO (9.5) but the morphology of the films was subject to optimisation for each application due to the dependence on the substrate.[6, 7]

Hexamethyltetramine (HMTA) and $Zn(NO_3)_2$ were used as precursors by Andres et al and they reported rod shaped ZnO precipitates.[8] The reaction was modified and engineered by Vayssieres and well-defined ZnO NW arrays were fabricated on a variety of crystalline substrates including FTO glass and Si wafers.[9] Thus synthesised NW arrays exhibited good crystallinity, better control of morphology and better adhesion to the substrates. The concept developed was called purpose-built materials and the method became known as the low temperature aqueous chemical growth method (ACG).[9, 10] ACG involves hydrolysis-condensation of metal ions at a given pH and ionic strength on a substrate in a closed bottle at a temperature below 100 ^{0}C.[9] The interfacial tension and thermodynamic nucleation on a heterogeneous surface (substrate) was used as a guiding principle for this synthesis.[10] Compared to the other synthetic methods such as hydrothermal, sol-gel process and template based synthesis which involves hazardous pressure vessels, organic solvents and harsh etching processes, ACG is safe, simple and uses water as solvent.[10]

1-D aligned nanostructures growth using the ACG method consists of two steps (1) heterogeneous nucleation and (2) controlled aqueous hydrolysis and deposition of metal oxide.[10] The first step is more complex and crucial involving control of interfacial surface energy/tension and kinetics. Interfacial energy between crystals and substrate is comparatively smaller than crystals in the solution due to the instability of colloidal solution with bigger particle size. Once the heterogeneous nuclei are formed on the substrate the crystal growth takes place along the preferred direction as long as the controlled supply of necessary ions are maintained.[11, 12] To obtain a greater understanding of the surface energy dynamics of water/oxide interface, different groups tried to bypass the higher activation energy requiring step by depositing Au and Ag on the substrate prior to the ZnO NW growth. Greene et al proposed a two-step process called low temperature seed mediated synthesis.[13,] Seed mediated synthesis involved depositing 50-200 nm ZnO crystal seeds prior to growth. ZnO seeds are fabricated by either thermal decomposition of zinc acetate precursor (350 ^{0}C) or zinc oxide colloid synthesised by Pacholski method (annealing at 150 ^{0}C).[13, 15] The two step seed mediated growth technique, including the Pacholski method, has gained a lot of interest in the scientific community due to the easy integration with low temperature substrates including polymer, polymer fibres, and paper substrates.[1, 3] Zinc acetate derived seeds are proven to form ZnO islands with their (0001) planes parallel to the

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Electronic Supplementary Information (ESI) available: [Effect of plasma treatment on ZnO NWs grown on PES substrates and Nanowalls water oxidation behaviour]. See DOI: 10.1039/x0xx00000x substrate surface. The alignment of this Zn terminated positively charged planes are reported to form on any flat substrate regardless of crystallinity and substrate chemistry.[1, 16] The density of NWs and aspect ratios of NWs were controlled by precursor concentration ($Zn(NO_3)_2$ and HMTA, growth temperature and growth times.[1] There has been a huge interest in the study of different morphologies of ZnO nanostructures, with adjusting the growth habitat through electrostatic interactions using both inorganic/organic molecules.[17-19] However the effect of substrate chemistry in the seed mediated synthesis is still not well understood.

In this report, the influence of seed density, surface treatment of the substrate and substrate position in growth solution were investigated to understand and optimize the ZnO growth via ACG. Both unannealed and annealed NWs were used as catalysts for water oxidation experiments both in dark and under illumination and the results were compared.

Experimental

ZnO NWs on 2-D and 3-D polyethersulfone (PES) was synthesised as reported by Greene et al.[13] Seed solution was prepared by following the Pacholski method.[15] 0.01 M Zinc acetate dihydrate (Alfa-Aesar) was hydrolysed by the slow addition of 0.03 M NaOH at 60 ^{0}C for 2 hour. Both solutions are prepared in methanol. The prepared seed solution was found to be stable for weeks. Seed solution was spin-coated onto 2-D PES and annealed for 20 minutes at 100 ^{0}C (instead of 150 ^{0}C as suggested by Greene et al[13]). The spin-coating parameters used were 1500 rpm for 30 s. For 3-D PES a dip-coating procedure was adopted. Seed deposition was optimized to obtain complete coverage. ACG growth was conducted using equimolar (0.025 M) $Zn(NO_3)_2$ 6 H_2O and HMTA (both from Sigma Aldrich) in the aqueous medium at 95 ^{0}C in a conventional lab oven.[11] The samples were washed with distilled water and dried at 100 ^{0}C. PES flexible films were found highly hydrophobic and various chemical treatments were adopted to engineer the wettability of the surface. Ammonium persulfate oxidation is a commonly used technique to change the wetting properties of electrospun PES membrane in the literature.[20] In an oxidation step 25 cm^2 of 2-D and 3-D PES was initially wetted in isopropyl alcohol and then washed in distilled water. Then pre-wetted PES substrate was treated with 3 w/v % ammonium persulfate solution at 70 ^{0}C for 15 min. After the reaction, the substrate was dried in vacuum at 70 ^{0}C for 40 min. The contact angle was assessed by OCA contact angle measuring system. In another surface treatment attempt, maleic anhydride was plasma polymerised onto PES substrate. The plasma polymerisation technique was as described by Ademovic et al.[21] Seed solution was deposited onto treated PES as previously described followed by ACG growth. The morphology of the NWs was studied using a field emission scanning electron microscope (JEOL 7001 A FEG SEM), while growth orientation and crystallinity were analysed using a transmission electron microscope (Technai T 20 TEM). The samples for SEM were coated with Pt nanoparticles about 1-3 nm thick. NWs from the substrate were detached using ultrasonication into ethanol and drop casted on a holy carbon coated Cu grid for TEM analysis. X-ray diffraction and electron diffraction studies were used to examine the crystallinity and growth direction of the NWs. The substrate placement in the growth solution was varied and the corresponding nanostructures morphology was assessed.

Water oxidation experiments were performed using standard 3 electrode set up. Saturated Calomel Electrode and Ti mesh were used as reference and counter electrode, respectively. 0.01 M KOH solution was used as an electrolyte. The NWs or nanowalls were deposited on FTO glass and the working area was 1 cm^2. Cyclic Voltammetry was used to study the reaction both in dark condition and under illumination. The light source was Leica KL2500 LCD. The results from unannealed and annealed (500 ºC for 1 hour) electrodes were compared.

Results and Discussion

Effect of seed density

ZnO NWs fabrication on flexible substrates has been reported and well documented in the literature.[22, 23] Even though the preparation of ZnO seed solution and growth method was thought identical, the number of seed layer depositions, growth time, growth temperature was different in various reports. For example, Greene et al[13] used an annealing temperature of 150 ^{0}C and growth time of 6 hours on Si wafer whereas Chang[23] used an annealing temperature of 300 ^{0}C and growth time 6 hours on polyimide nanofibres. Moreover throughout this report a conscious attempt was made to keep the temperature below 100 ^{0}C to reduce the impact of thermal treatment on functionalised substrates. In the literature, growth temperature was varied from 70 to 95 ^{0}C on different substrates and reports which indicates that the higher temperature will lead to a change in morphology and aspect ratio of the NWs.[1] These differences indicate that the aqueous chemical growth method should be optimized for 2-D PES and 3-D PES. Seed solution was prepared according to the Pacholski method and spin coated to 2-D PES, and each seed deposition step was followed by annealing for 20 minutes at 100 ^{0}C. Aqueous growth temperature and time was fixed arbitrarily to 90 ^{0}C and 6 hours. Seed deposition cycles were increased from 1 to 6 cycles. It was observed that the 1-3 layers of seed deposition does not create complete coverage and the NWs are not aligned vertically (Fig 1 (a) and 1 (b)).

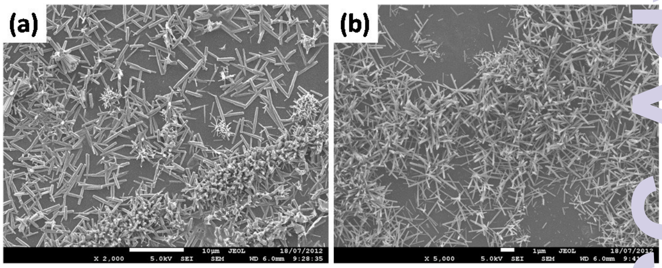

Fig 1 (a) NWs grown after 1 seed layer coating (b) NWs grown after 3 seed layer coating

The coverage of NWs on the substrate was increased or multilayer formation was observed if the seed solution deposition was repeated more than five times (Fig 2 (a) and 2 (b)).

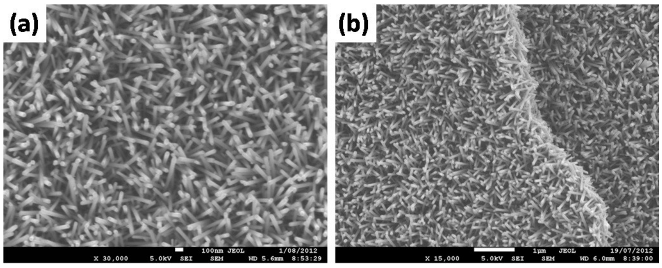

Fig 2 (a) NWs grown after 5 seed layer coating (b) NWs grown 6 seed layer coating

Seed solution was dip coated onto 3-D PES for 1 minute followed by a 20 minute annealing step. This cycle was repeated 5 times. Multiple immersions produced uneven growth on 3-D PES whereas single immersion and annealing produced evenly grown bottlebrush structure (Fig 3 (a) and 3(b)), respectively.

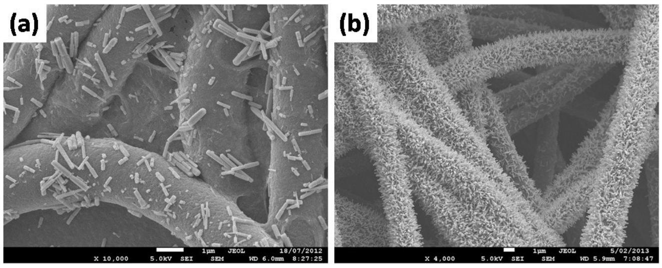

Fig 3 (a) NWs grown after 5 seed deposition (b) NWs grown after 1 seed layer deposition

The effect of seed density was different between the 2-D PES and 3-D PES. For 2-D PES more than 5 cycles of seed layer deposition (spin-coating), was needed for the complete coverage of the NWs on the substrate. However, for 3-D PES, only after 1 seed layer deposition (dip-coating) the grown NWs completely covered the substrate surface. Higher number of cycles contributed adverse effect on the NWs growth. XRD was performed on the NWs (Fig S3) and shows the expected pattern as in previous reports.[16]

Effect of surface treatment

There are reports suggesting that chemical bath deposition and biomimetic film growth depends on the surface functional groups.[5, 24] But in both cases, the nucleation process was one of the decisive steps, which can be avoided by pre-deposition of seed layers to the substrate. Greene et al[14] observed that thermal decomposition of zinc nitrate hexahydrate or zinc acetylacetonate does not produce aligned ZnO NWs unlike zinc acetates. Even though the role of acetate on ZnO seed layers was quite surprising the exact reason was unknown.[14] During the colloidal synthesis of zinc oxide quantum dots, zinc acetate precursor was found to have superior stability.[15] In order to understand the effect of surface functional groups on nanostructure growth, two different surface treatments were attempted. Maleic anhydride was plasma polymerised on the surface of the 2-D and 3-D PES to create –COOH functional groups and the water contact angle was found to be reduced from 75 to 45^0 (Fig 4 (a) and (b)).[21] It was well documented that –COOH groups can be used to create patterns chemically for ZnO NWs grown by the chemical bath deposition but the possibility of obtaining the same by seed mediated method was ruled out because of the prior nucleation.[25] To understand the effect of –COOH groups on seed mediated synthesis, an attempt was made to coat the seed solution on plasma coated 2-D PES and grow NWs on them. Even after 5 times seed deposition, NW coverage and vertical alignment was poor on 2-D PES (Fig 4 (c)). ZnO NWs were reported to grow on FTO without seed layer.[11]

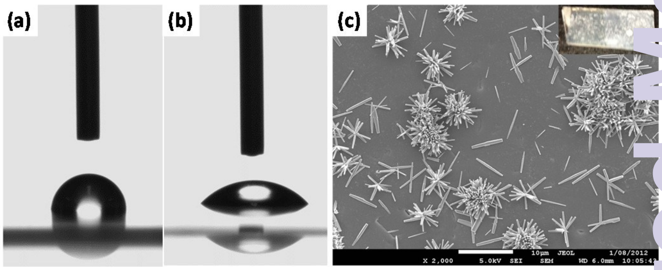

Fig 4 (a) Water contact angle before plasma treatment (b) after treatment on 2-D PES. (c) NWs grown on the plasma treated 2-D PES after 5 layer of seed deposition (Inset ZnO NWs grown on FTO glass where the left hand side was plasma treated).

To study the effect of surface –COOH group on a hetero-epitaxial substrate, one half of a FTO glass was treated with plasma and the other half untreated was used as the substrate. The seed layer was deposited five times and aqueous chemical growth was carried out. There was a clear colour difference observed between neat FTO glass and FTO with plasma coating indicating less density of NWs on the plasma coated area (inset of Fig 4 (C)).

NW formation confirms that the aqueous growth was taking place even though there were –COOH groups on the surface. SEM images of five times seed layer deposited 2-D and 3-D PES on plasma treated substrates shows that seed deposition was uneven and there was precipitation of ZnO particles unlike the untreated PES (Fig S1 (a), (b), (c) and (d)).

The appearance of seed agglomerates in the SEM of plasma coated substrates confirms that differences in the resulting morphology are due to differences in the seed deposition. It was not clear whether the change in morphology is due to the change in the wetting properties or due to the presence of surface functional groups. In order to confirm whether the surface functional groups or decrease in the contact angle induce the change in morphology, another surface treatment was attempted. Ammonium persulfate (APS) oxidation was used to reduce the hydrophobicity of the electrospun PES (according to Yoon et al[20]). PES flexible substrates were APS treated and the contact angle was lowered from 75 to 54^0 (for

2-D PES) and no change in the IR spectra was observed. The surface –OH groups were expected to be too few to be seen in the IR spectrum. An indirect evidence on surface implantation of –OH groups on polymer surface during APS oxidation was given by Bamford and Al-Lamee using their surface grafting experiments.[26] Seed depositions were done 5 times (for all, treated and bare), and after each seed deposition there was annealing step for 20 minutes at 100 °C. The resulting nanowall morphology was studied using SEM (Fig 5 (a) and (b)).

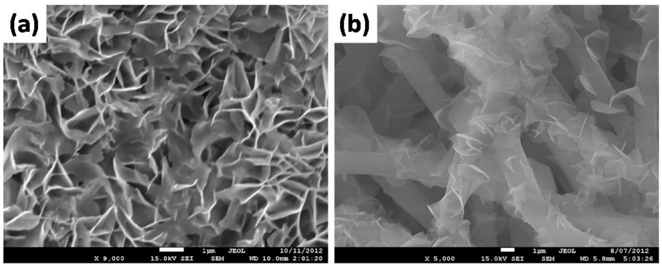

Fig 5 (a) Nanowalls grown on APS treated 2-D PES (b) Nanowalls with occasional NWs on APS treated 3-D PES.

Since the wetting properties of the plasma treated and APS treated PES were nearly the same, the resulting morphology could only be due to the effect of surface functional groups. In the case of unmodified substrate, the seeds were aligned parallel to the substrate, with the preferred (0001) planes.[16] During the growth $Zn(OH)_2$ growth units will attach to the polar surfaces following the fast dehydration reaction.[27] The new growth unit will attach to the polar surface and the growth take place along the highest growth rate (0001) direction. In the case of carboxylic acid functionalised surfaces, the polar surfaces of the seeds are already attached to the surfaces, which make them unavailable for the incoming growth units. $Zn(OH)_2$ growth units attached to the crystal surface should undergo fast dehydration reaction to produce ZnO units, this reaction will be impeded by the competing acid-base reaction. Moreover ZnO seeds are reported to get corroded at this kind of acidic environment.[25] Hence there is no nanowire/nanowall formation. However in the case of hydroxyl groups the nonpolar surfaces are available for the growth and the reaction proceeds through the second highest growth direction of the crystal facets namely $(2\bar{1}\bar{1}0)$.[19, 28] To the best of our knowledge this is the first report suggesting that the functional groups on the substrate can drastically control the morphology of nanostructures in the seed mediated ACG.

Effect of substrate position in growth solution

Vertically aligned NWs were thus far reported for the aqueous chemical growth method when the seed deposited substrate was immersed face down (seed coated side facing down in the growth solution). Due to surface tension most of the substrates easily floats on the growth solution. Face down position of the substrate avoids unwanted precipitates to fall onto the substrate which could initiate a secondary growth.[1] During growth it was assumed that ZnO nuclei was initially formed at the air-solution–substrate three phase boundaries and later migrated onto the substrate.[1] The evidence of nuclei formation at three phase boundary came much later by Wang et al.[29] In our study, the substrate was immersed in the growth solution and the whole reaction was conducted in a laboratory pyrex glass bottle fitted with a screw cap. In order to find out the ideal substrate position in the growth solution a set of experiments was conducted in which the substrate was kept in three different positions as described in Fig 6. The SEM of resulting morphology are given below.

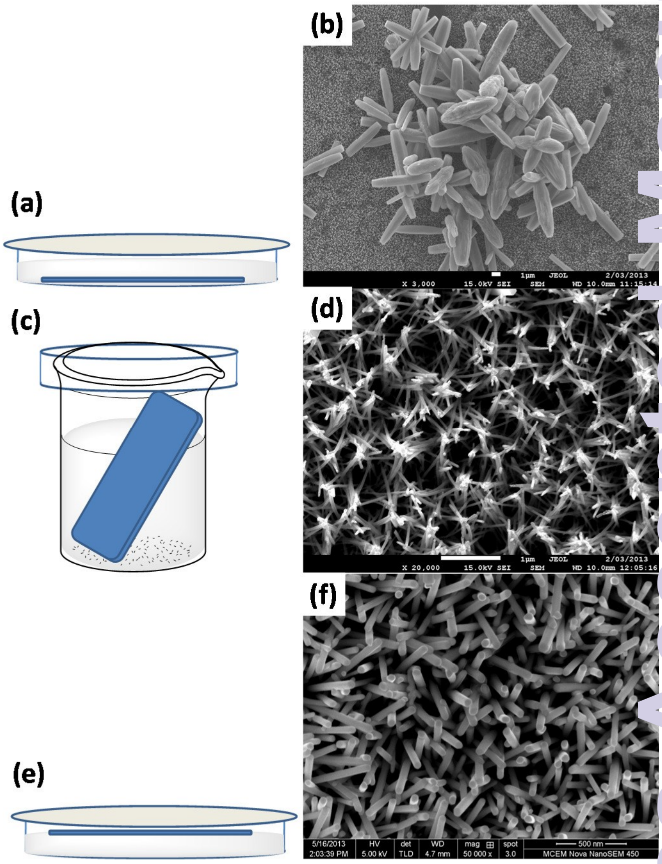

Fig 6 (a) Five times seed coated substrate kept *facing up* into the growth solution (b) Corresponding SEM image from experiment (a) (c) Five times seed coated substrate kept *at a ~45° angle* in the growth solution, face up (d) Corresponding SEM image from experiment (c) (e) Five times seed coated substrate kept floating and *facing down* into the growth solution (f) Corresponding SEM image from experiment (e).

It can be seen that the position of the substrate has a crucial influence on the NWs obtained. The ***reasons*** for these differences are not clear and will need a much more in-depth study than possible in this report.

A very interesting observation was that the lengths of the NWs obtained using the methods described in fig 6 (c) and (e) were different even though the precursor concentration, time and temperature were the same. To understand the difference in growth mechanism, TEM studies were conducted on long wires (produced from the experiment in Fig 6 (c)) and the vertically aligned short wires (produced from the experiment in Fig 6 (e)).

The length of the long wires was found to be 3.5 µm and short wires 1.5 µm and the diameter of both wires was 100 nm.

HR-TEM images of long NWs shows a growth direction of "a-axis" (Fig 7 (a) and 7 (b)), whereas the short wires were found to grow in "c-axis" (Fig 7 (c) and 7 (d).[13, 30, 31] ZnO NWs growth along the c-axis is most expected and widely reported. The diffraction patterns for long wires support the observation that the growth direction was along the a-axis. Fig 8 (a) and (b) shows the combined image of diffraction and image and corresponding assignments for diffraction patterns.

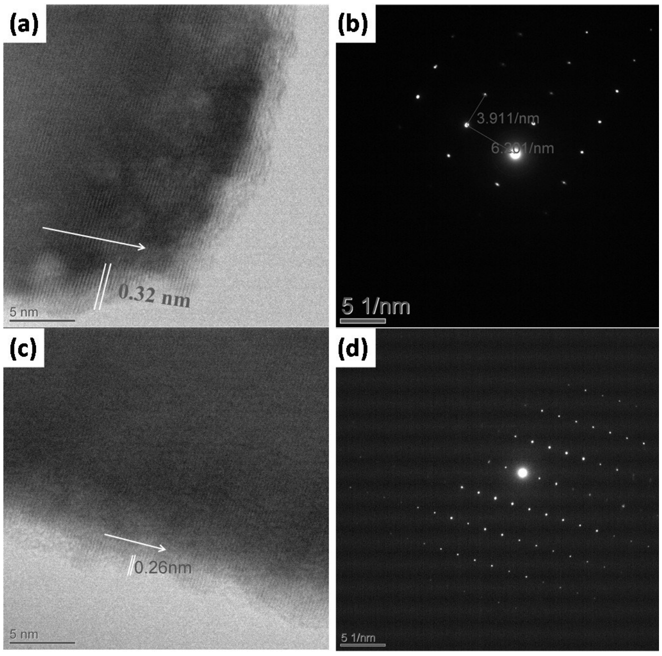

Fig 7 (a) High resolution TEM image of long ZnO NW (b) Corresponding selected area diffraction (SAED) image to (a) (c) High resolution TEM image of short NW (d) corresponding selected area diffraction image to (c)

Determination of polarity of nanostructures

Solution grown ZnO NWs are usually n-type semiconducting materials and the growth process is imagined as stacking of alternating planes of Zn and O ions along the growth direction.[1] The terminating layer, can be either O or Zn and accordingly the top surface (0001 plane), will be charged due to the disruption of the dipole.[32] These kind of native defects (or dangling bonds) are found to be high in solution grown NWs which act as binding sites for various inorganic and organic molecules such as CO_2, H_2O, O_2.[32] The adsorbed molecules can act to trap electrons or holes from the surface of the NWs, thus affecting the junction properties.[33] The higher reactivity of the basal plane of ZnO nanostructures were used for selective etching. Nanostructures synthesised by seed mediated ACG method, was treated with 3.4 M KCl at 80 ^{0}C for 20 minutes.[34] Due to the high energy of the basal plane, the central region was expected to be etched rather than the periphery of the NWs thus producing ZnO nanotubes. For ZnO short wires grown along the c-axis, corresponding nanotubes (Fig 9 (a)) after etching of the core was obtained whereas long wires grown along the a-axis and nanowalls were found either completely detached from the substrate or etched away (Fig 9 (b)). This observation confirms that the short NWs were formed along (0001) plane along c-axis.[34] In the case of long NWs, it is speculated that the etching direction was opposite to short NWs (after detaching from the substrate) which support our observation from TEM analysis.

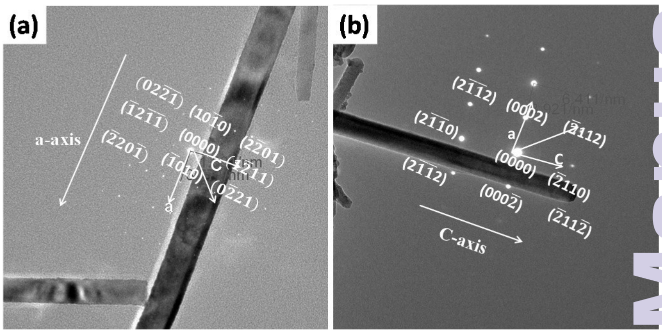

Fig 8 (a) Long ZnO NW grown along a-axis (b) Short NW grown along c-axis. For long NWs, the zone axis used was $[\bar{1}2\bar{1}6]$ and for short NWs $[01\bar{1}0]$ and in the case of short NWs, $(\bar{2}110)$ diffraction spot was found missing.[30, 31]

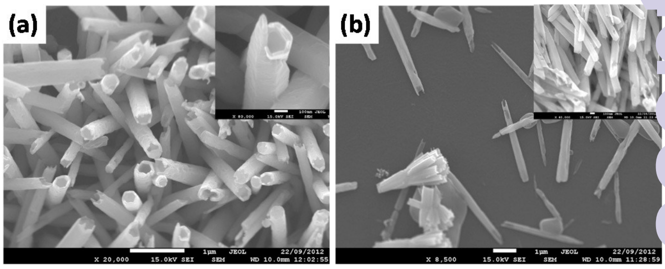

Fig 9 (a) ZnO nanotubes synthesised by etching along (000 plane in the case of short wires, inset shows a high magnification image (b) Long ZnO NWs were detached from the substrate. Inset is a high magnification image of a bunch of long NWs which were fallen off after the KCl treatment. The scale bar for both insets is 100 nm.

Water oxidation experiment

The oxidation of water on ZnO nanostructures has been reported previously[35] and was here used to probe the influence of the different nanostructures (grown on FTO) on the electrochemical behaviour. Surprisingly it was found that NWs grown in the a-axis showed a significant lower onset potential (0.77V vs SCE) for the water oxidation than the NWs grown in the c-axis (1.03V vs SCE) (Fig 10 (a)). Further it was found that light had no effect on the catalytic behaviour of the a-axis grown NWs (Fig 11 (a)) whereas the NWs grown in the c-axis direction showed light enhanced catalysis as reported elsewhere (Fig 12 (a)).[35] These results confirms that the simple change of growth conditions can alter the performance of the NWs radically and indeed that there are two very different ZnO NW configurations possible. The lower onset potential for the a-axis grown NWs is suggesting that binding and charge transfer to OH^- is energetically more favourable than in case of c-axis grown and is in line with the observation from the etching experiment described earlier where the c-axis grown NWs only showed significant affinity to etching at the end/core of the NW. On the other hand the observation that the exited a-axis grown ZnO is not able to effectively transfer the hole to the OH^- (as otherwise seen for the c-axis growth ZnO) is indeed more puzzling and requires further research.

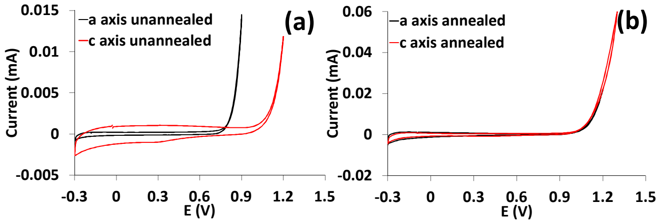

Fig 10 Water oxidation study in 0.01 M KOH of (a) Unnealed ZnO NWs and (b) annealed ZnO NWs on FTO glass electrodes.

The a-axis and c-axis NWs grown on FTO was then annealed (at 500 °C for an hour) and the electrochemical water oxidation experiments were repeated (Fig 10 (b)). The effect of the annealing on the c-axis grown NWs without and with light was essentially only an (expected) increase in current density due to more well-ordered structure, no change in onset potentials were observed (Fig 12 (a) and 12 (b)). For the a-axis grown NWs a dramatic change in the electrochemical properties occurred after annealing (Fig 11 (a) and 11 (b)), essentially converting the electrochemical behaviour to be identical to the c-axis grown NWs both without and with light and thus strongly indicating that the annealing was able to change the polarity of the a-axis growth NWs.

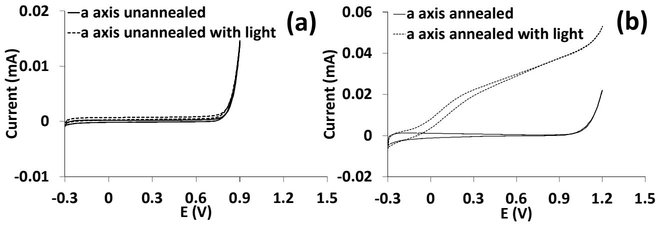

Fig 11 Water oxidation study in 0.01 M KOH of a-axis ZnO NWs (a) unannealed with and without light (b) annealed with and without light.

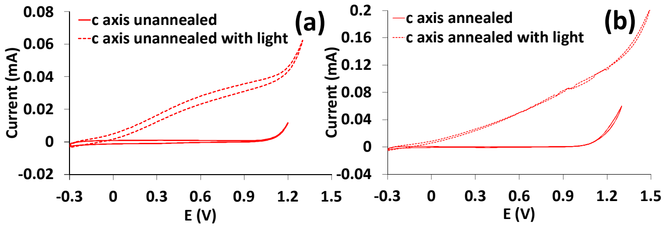

Fig 12 Water oxidation study in 0.01 M KOH of c-axis ZnO NWs (a) unannealed with and without light (b) annealed with and without light.

The nanowalls produced using APS treatment route (Fig 5 (a)) were also investigated for their water oxidation behaviour. The electrochemical experiments were performed in similar manner to the a-axis and c-axis ZnO NWs and the results shown in Fig S2. The results indicated that the ZnO nanowalls behaved similarly to the c-axis ZnO NWs.

Conclusions

Aqueous chemical method is one of the most facile and green methods to fabricate low temperature ZnO nanostructures. It was believed that the surface chemistry of the substrate does not affect the morphology of the nanostructures in the seed mediated growth. During this study, we observed that seed mediated aqueous chemical growth method depends on surface functional groups of the substrate. Carboxylic acid functional groups on the substrate cause agglomeration of seeds which inhibits the NW growth. While hydroxyl groups caused the nanowall formation, untreated PES resulted in NWs. The position of the seed deposited substrate in the growth solution affects the morphology and growth direction of the crystal and thus allowed for selecting between a-axis or c-axis growth. Vertically aligned ZnO NWs (c-axis) can be grown on 2-D and 3-D substrates by seed deposited aqueous chemical growth by placing the substrate facing down the growth solution and a-axis NWs is obtained when the substrate is placed at 45° facing up. KCl etching experiment produced hollow ZnO nanotubes from c-axis NWs by etching from the top. The a-axis NWs were etched from the bottom and then detached from the substrate. This confirms the different polarity of the a-axis and c-axis NWs. Different morphologies showed different water oxidation behaviour especially for the onset oxidation potential, where a-axis NWs had a 300mV lower onset than the c-axis NWs.

Acknowledgements

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