Investigations on surface wettability of ZnO nanowires using UV LEDs for biosensing applications

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Investigations on surface wettability of ZnO nanowires using UV LEDs for biosensing applications

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Abstract. ZnO is a biocompatible material suitable for biosensors and microfluidic devices. Nanowires of ZnO tend to show hydrophobic nature which decelerates the adhesion/adsorption of biomolecules on the surface. This paper discusses the investigations on tuning the wettability of ZnO nanowires using UV LEDs. The spectral effect of LED emission on ZnO nanowires wettability has been studied. Results indicate that UV LEDs offer an advanced control on tuning the wettability of ZnO nanowires. The spectral investigations have provided significant insight into the role of irradiating wavelength of light on the wettability.

1. Introduction

Nanowires have become one of the hot research topics due to their special properties and huge application potential. Semiconductor based nanowires, especially based on ZnO have been explored for photonics, electronics, biomedical and energy related applications [1]. ZnO is a wide bandgap (3.37 eV) semiconducting biocompatible and biodegradable material [2]. The properties of nanowires depend highly on their surface and structural properties and are also linked to the synthesizing method [3]. Various nanostructures of ZnO can be synthesized using a low cost and scalable hydrothermal method [4]. The surface properties (hydrophilic or hydrophobic nature) of ZnO play a crucial role in biosensing, biomedical and microfluidic applications [5]. Adsorption/adhesion of the cells, biomolecules (such as protein, RNA, DNA) on the surface and their reaction depends on the surface energy and it closely relates to the wetting nature of the surface, and strongly correlates with the biological interactions [6].

ZnO nanowires tend to show hydrophobic nature [7] and therefore, presumably decelerate the biological surface interactions in the aqueous environments. Also, it has been reported that a biomaterial surface with moderate hydrophilic nature improves the biological interactions [5]. Modification in the wetting nature (hydrophobicity) shown by the ZnO nanowires can lead to improved surface interactions. However, the major problem arises in the control over surface wettability which is significant for improving the biological interaction between the surface and surrounding medium. Therefore, it is important to have a well-defined control over the surface energy of ZnO nanowires. UV light irradiation can be used to control the surface wettability of ZnO nanowires [8] and the intensity and wavelength irradiation can be used to control the wettability. Several papers have reported on the tunable wettability shown by ZnO nanowires exposed to UV lamps [8-10]. However, these lamps are relatively slow to switch on, stabilize and also, generate a considerable amount of heat. Further, they are not eco-friendly, they are a potential health hazard due to the UV exposure and limit the miniaturization of the devices. A

UV lamp imposes the problem of destroying the biomolecules/cells on the surface because of deep UV light (UV-C) irradiation [11]. Also, the major problem arises in the control over surface wettability which is significant for improving the biological interaction between surface and surrounding medium. Therefore, it is important to have well defined control over the light intensity and wavelength which modulates the surface energy of the ZnO nanowires. UV LEDs are inexpensive, energy efficient, have a narrow emission spectrum and offer better tunability of various control parameters leading to controlled surface wettability shown by ZnO nanowires.

Investigations on the surface morphology of ZnO nanostructures, ZnO nanocomposites and the effect of UV light irradiation time on their surface wettability have been reported [9,10,12]. However, the role of UV wavelength in controlling the surface wettability of ZnO nanowires is unclear. So far, to our knowledge, this is the first study on the spectral effect of UV light on the wettability of ZnO nanowires. Initial investigations on the spectral effects of narrow band UV light irradiation, using UV LEDs (λ_p = 365 nm, 385 nm), on the hydrophobicity of ZnO nanowire films have been carried out and discussed in this paper. Also, the effects of UV light irradiation time and transition rate (rate of change in contact angle) have been studied. Results show that spectral overlap between LED emission spectra and ZnO nanowire absorption spectra defines the rate of change in hydrophobicity of ZnO nanowires. LED with λ_p = 365 nm have shown very high transition rate compared to the λ_p = 385 nm.

2. Materials and methods

2.1 Materials
All the materials used in the experiment were analytical grade. Zinc acetate ($Zn(CH_3COO)_2$), zinc nitrate hexahydrate ($Zn(NO_3)_2$•$6H_2O$) and ammonium hydroxide (NH_4OH) were purchased from the Sigma Aldrich, UK. All glassware was cleaned in deionized water prior to the experiment.

2.2 Synthesis of ZnO nanowire films
ZnO nanowires were grown on glass substrates using hydrothermal synthesis method [13]. 10 mM Zinc acetate was drop casted on the glass substrates and annealed on a hotplate for one min at 100°C for better adhesion. The process was repeated 5 times to get a uniform thick seed layer. ZnO nanowires were grown by immersing the seeded substrates into the mixture of 125 ml 20 mM zinc nitrate and 7 ml 28-30% ammonium hydroxide and annealed on a hotplate at 95° C for 5 hours. Thereafter, substrates were removed from the growth solution and rinsed with de-ionized water several times. The substrates were allowed to dry at room temperature and atmospheric pressure before characterization.

2.3 Characterizations
Surface analysis of the synthesized ZnO nanowire films has been carried out using a Scanning Electron Microscope from ZEISS (EVO LS10). Surface wettability has been characterized using contact angle measurement system from the First Ten Angstrom (FTA 200) at room temperature (RH - 8%).

3. Experiments
A pictorial view of experimental setup for irradiating the sample with UV LED is shown in Figure 1. UV light from LED was coupled through a bi-convex lens and irradiated over the sample placed on a sample stage. A dichroic mirror was used in the path to tap a fraction of the UV light for monitoring the power level with a Coherent (FieldMaster GS) power meter and/or LED spectra with Stellernet (EPP2000C) spectrometer. Surface wettability of the developed ZnO nanowires has been studied using the contact angle measurement system, by measuring the water contact angle before and after the UV light irradiation for different irradiation times. All experiments were performed using 2 μl water drop under ambient conditions.

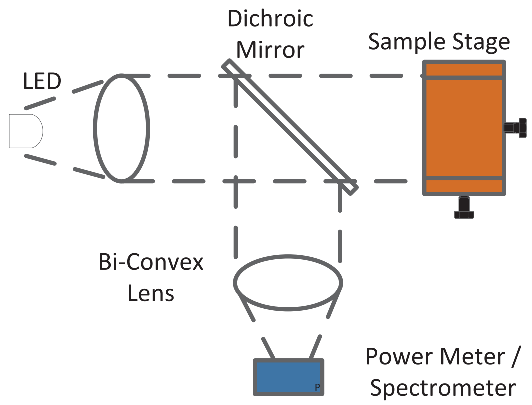

Figure 1. A pictorial view of experimental set-up.

4. Results and discussions

Figure 2 shows the SEM image of ZnO nanowires at different magnifications. From the SEM image, it can be seen that the synthesized ZnO nanowires are preferentially oriented towards the c-axis perpendicular to the glass substrate. Hexagonal structure of the ZnO nanowires can be seen in the magnified SEM image. Also, the magnified view of the nanowire tip reveals the growth of layered hexagonal nanostructures on the tip. This nanoscale roughness on the tip reduces the contact area between solid and the droplet which allows the entrapping of a large amount of air below the droplet, and therefore, enhances the hydrophobicity of the surface [7]. Length and diameter of the synthesized ZnO nanowires were about 11-12 μm and 400-500 nm respectively.

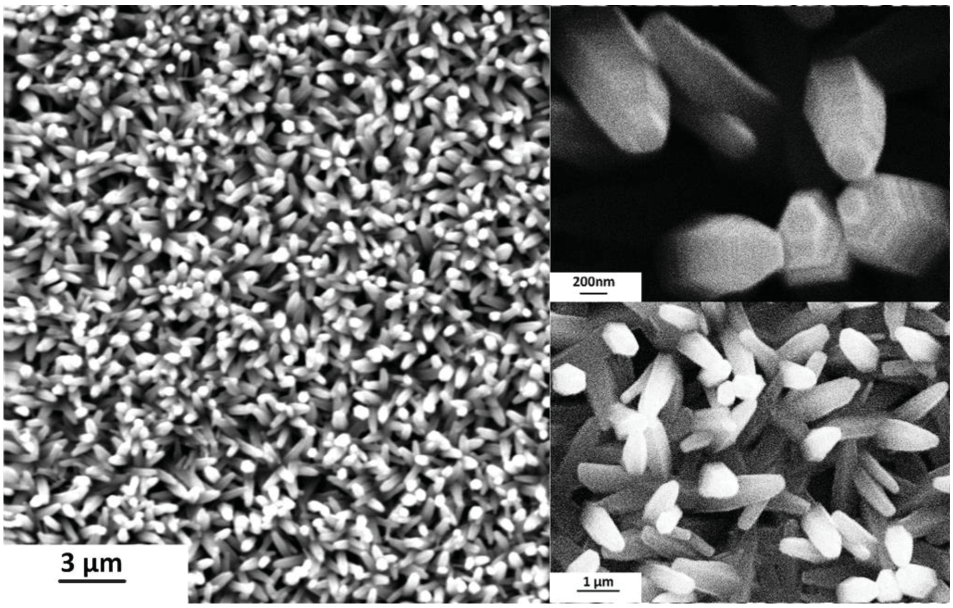

Figure 2. SEM image of ZnO nanowires with different magnifications.

The water contact angle was measured immediately after the synthesis of ZnO nanowires and found to be about 0°. This super hydrophilic nature shown by the synthesized ZnO nanowires using hydrothermal method can be attributed to the hydroxyl groups on the surface. Thereafter, substrates were left to dry under ambient conditions for 72 hours. ZnO nanowires have shown the contact angle of 125°.

Surface wettability of the synthesized ZnO nanowires have been analysed by measuring the static contact angle. ZnO nanowires surface wettability can be considered conferring to the Cassie-Baxter [14] or Wenzel [15] models.

A Young contact angle, θ_y, on the smooth surface can be defined in terms of surface energy as [16]:

$$\cos\theta_y = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv}$$

where, γ_{sv}, γ_{sl} and γ_{lv} are surface tension of solid-vapour, solid-liquid and liquid-vapour, respectively. Considering the surface roughness, the Wenzel model defines the apparent contact angle θ, defined as:

$$\cos\theta = r \cos\theta_y$$

where, r is a surface roughness factor. This suggests the effect of change in surface roughness on the hydrophobicity (contact angle). But the Wenzel model assumes that the liquid penetrates inside the rough surface which is the case after irradiation of UV light.

Under unexposed condition, ZnO nanowires tend to show a hydrophobic surface where liquid does not penetrate inside the rough surface (nanowire groves). Therefore, this condition refers to the Cassie-Baxter state [14].

$$\cos\theta = f(\cos\theta_y + 1) - 1$$

where, f is the area fraction of actual solid surface area to the projected solid surface area. Therefore, upon UV exposure, ZnO nanowires follow the wettability transition from Cassie-Baxter state to the Wenzel state.

UV light irradiation has been carried out on the ZnO nanowires using UV LEDs with a peak emission wavelength λ_p = 365 nm and 385 nm. Static water contact angles (WCA) have been measured on each sample before and after UV light irradiation, WCA_0 and WCA respectively. Figure 3 (a) and (b) shows the relative change in measured water contact angle and gradient with irradiation time, respectively. Rapid change in wetting angle has been observed for the LED with λ_p = 365 nm. Also, the gradient over the irradiation time indicates that the change in wetting angle is very high for the first 30 mins, thereafter, it slows down gradually. The reason behind this observed change in wettability by irradiating UV light on the ZnO nanowires can be explained as follows:

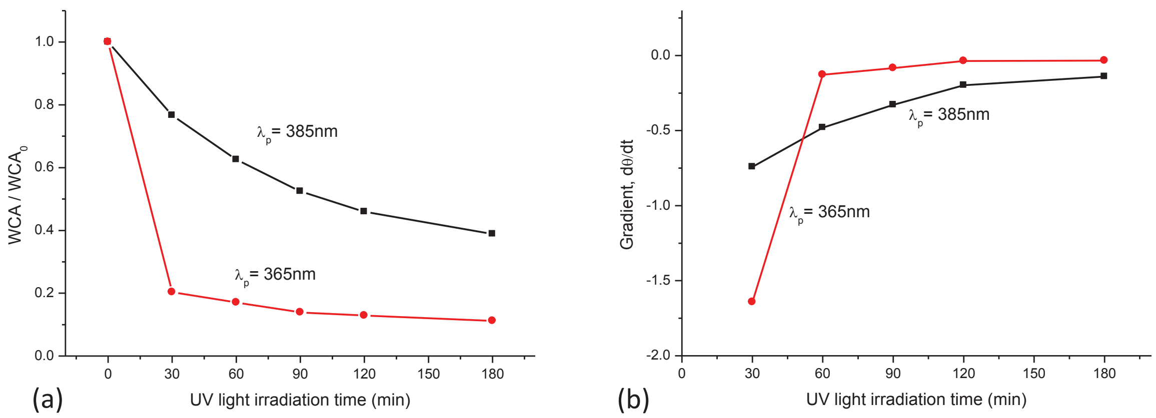

Figure 3. (a) Measured relative contact angle and (b) the gradient with irradiation time for the LED emission at λp = 365nm and 385nm.

UV light irradiation generates electron-hole pairs in the ZnO surface. These electron-hole pairs will create the surface defects/composition change leading to different wettability of the surface. The process which leads to the surface composition change can be expressed as [9]:

$ZnO + 2h\nu \rightarrow 2e^{-} + 2h^{+}$

$Zn^{2+} + e^{-} \rightarrow Zn_s^{+}$ (surface trapped electron)

$O^{2-} + h^{+} \rightarrow O^{-}$ (surface trapped hole)

$O^{-} + h^{+} \rightarrow 1/2O_2 + V_o$ (oxygen vacancy)

The surface trapped electrons (Zn_s^{+}) tend to react with oxygen molecules adsorbed on the surface:

$Zn_s^{+} + O_2 \rightarrow Zn_s^{2+} + O_2^{-}$

At the same time water molecules may adsorb at the oxygen vacancy (Vo) site. These defect sites are kinetically more favourable for hydroxyl groups (OH^{-}) adsorption than oxygen adsorption, hence promotes increased water adsorption at the UV light irradiated areas.

Further, to understand the observed spectral effect on the wettability, the absorption spectrum of the synthesized ZnO nanowires has been collected and plotted along with the UV LEDs emission spectra as shown in figure 4. Better spectral overlap indicates that ZnO nanowires absorb more light at 365 nm than 385 nm. Therefore, the observed change on the surface wettability of ZnO nanowires is high when irradiated with λ_p = 365 nm. This indicates that the wettability of the ZnO nanowires can be controlled by tuning the wavelength of irradiating light.

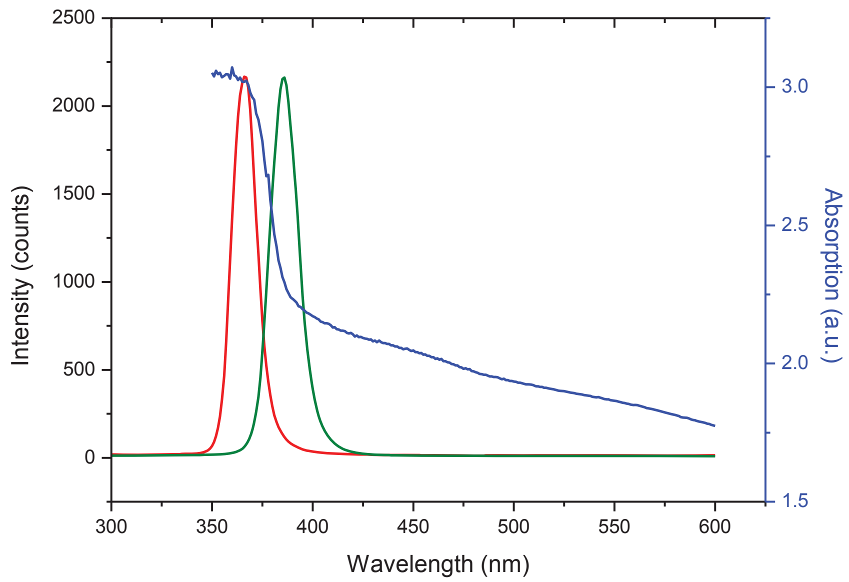

Figure 4. UV LEDs emission spectra (λp = 365 nm in red and 385 nm in green) along with ZnO nanowire absorption spectrum in blue.

5. Conclusion

The effect of irradiating UV light wavelength and irradiation time on tuning the wettability of ZnO nanwires has been studied. Results show that the wavelength of irradiating light has significant impact on tuning the surface wetting nature of ZnO nanowires. Developed ZnO nanowires have exhibited more advanced controllable wettability including a faster hydrophobic-hydrophilic switching upon UV light irradiation using LEDs. The UV LEDs offer better control over the wettability of the ZnO nanowires as well as the miniaturization of microfluidic devices and biosensors based on ZnO nanowires.

6. References

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