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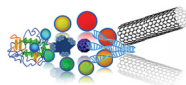
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LED-controlled tuning of ZnO nanowires' wettability for biosensing applications

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Abstract

Background: Wettability is an important property of solid materials which can be controlled by surface energy. Dynamic control over the surface wettability is of great importance for biosensing applications. Zinc oxide (ZnO) is a biocompatible material suitable for biosensors and microfluidic devices. Nanowires of ZnO tend to show a hydrophobic nature which decelerates the adhesion or adsorption of biomolecules on the surface and, therefore, limits their application.

Methods: Surface wettability of the ZnO nanowires can be tuned using light irradiation. However, the control over wettability using light-emitting diodes (LEDs) and the role of wavelength in controlling the wettability of ZnO nanowires are unclear. This is the first report on LED-based wettability control of nanowires, and it includes investigations on tuning the desired wettability of ZnO nanowires using LEDs as a controlling tool.

Results: The investigations on spectral properties of the LED emission on ZnO nanowires' wettability have shown strong dependency on the spectral overlap of LED emission on ZnO absorption spectra. Results indicate that LEDs offer an advanced control on dynamically tuning the wettability of ZnO nanowires.

Conclusion: The spectral investigations have provided significant insight into the role of irradiating wavelength of light and irradiation time on the surface wettability of ZnO nanowires. This process is suitable to realize on chip based integrated sensors and has huge potential for eco-friendly biosensing and environmental sensing applications.

Keywords: *surface energy; contact angle; surface wetting angle; hydrophobic surface; hydrophilic surface*

Nanowires have become an emerging research topic due to their special properties and huge application potential. Semiconductor nanowires, especially those based on zinc oxide (ZnO), have been explored for photonics, electronics, biomedical and energy-related applications (1). ZnO is a wide-bandgap (~ 3.37 eV)



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on developing novel hybrid sensor system for environmental monitoring applications. His research involves development of fiber optic sensors, surface plasmon resonance sensors, electrochemical sensors, and metal/metal oxide nanomaterial synthesis and their surface modifications for various biosensing and environmental-monitoring applications.



Duncan Ross completed his BSc (Hons) degree in forensic anthropology; currently, he is pursuing Master of Pharmacy degree at the Robert Gordon University. Duncan's main research interests include improving pharmaceutical manufacturing process and improving pharmaceutical technologies. His final-year project was based on the use of melt pelletization as a method for formulating modified release oral solid dosage forms, by analyzing the release profiles of pellets formulated with different meltable binders. Duncan has also undertaken research, funded by the Carnegie Trust, analyzing zinc oxide nanowires and their use within biosensors.



Radhakrishna Prabhu completed his PhD from Indian Institute of Science, Bangalore (2001), before joining for post-doctoral studies at University of Twente, the Netherlands. In 2003, he joined Robert Gordon University where he is currently a lecturer in School

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, 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 or adhesion of the cells and biomolecules (e.g. protein, RNA and DNA) on the surface and their interaction depends on the surface energy, it closely relates to the wetting nature of the surface, and it is strongly desired for the biological interactions (6). Therefore, control over the wettability is highly essential in all such applications. Broadly, there are two distinct approaches, the contact and non-contact types, for changing the wettability of the surface. In contact-type approaches, the surface is chemically modified using low- or high-energy materials, which is not desirable in most cases in the above-mentioned application areas (7). Non-contact-type approaches include high-temperature annealing (8), plasma treatment (9), ion sputtering (8) and light illumination (10). Recently, light-induced wettability tuning has grown in popularity (11–13).

ZnO nanowires tend to show a hydrophobic nature (14) and therefore, presumably, decelerate the biological surface interactions in the aqueous environments. Also, it has been reported that a biomaterial surface with a moderate hydrophilic nature improves the biological interactions (5). Recently, an adsorption study of hydrophobic protein bovine serum albumin and hydrophilic protein lysozyme on the ZnO nanorods and hydroxyapatite/ZnO-nanorod composite coatings has been carried out by Cheng and co-workers. Results have shown that after ultraviolet (UV) radiation treatment, coatings turn hydrophilic and show enhanced adsorption of both proteins (15). Modification in the wetting nature (hydrophobicity) shown by the ZnO nanowires can lead to improved surface interactions and, hence, improved sensitivity for sensors. However, the major problem arises in the control over surface wettability, which is crucial for improving the biological interaction between the surface and the surrounding medium. Therefore, it is important to have well-defined control over the surface wettability of ZnO nanowires. Several papers have reported on the tunable wettability shown by ZnO nanowires exposed to UV lamps (12, 13, 16). However, these lamps are relatively slow to switch on and stabilize, and also they generate a considerable amount of heat. Furthermore, they are not eco-friendly; they are a potential health hazard due to the UV exposure and limit the miniaturization of the devices. Again, a UV lamp can destroy the biomolecules and cells on the surface because of deep UV light (UV-C) irradiation (17). Therefore, use of UV lamps to tune the surface wettability of ZnO nanowires is not a convenient approach for biosensing and microfluidic

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Pat Pollard is professor emeritus at the Faculty of Health & Social Care. She has over 30 years' experience of applied research mostly in collaboration with industry (oil and gas, security, medical, and environmental) developing a range of sensors, including real-time and in-situ sensors, environmental sensing and monitoring, and the development of tracers/taggants which has also led to iTi, POC & KTP-funded projects. Her research includes leading pioneering work on the development of novel security taggants/tracers and optoelectronic readers for a range of applications in the security field.

applications. Also, UV lamps cannot provide well-defined control over the surface wettability. To our knowledge, this is the first study on light-emitting diode (LED)-based control of ZnO nanowires wettability and its wavelength dependency. LEDs are smaller in size, inexpensive, and energy efficient; have a narrow emission spectrum; and offer better tunability of various control parameters. Therefore, LEDs can offer advanced and dynamic control over the tuning of surface wettability. Also, LEDs can be integrated on the sensor chip.

Investigations on the surface morphology of ZnO nanostructures and ZnO nanocomposites, and the effect of UV light intensity and irradiation time on their surface wettability, have been reported (11–13). However, the role of light wavelength in controlling the surface wettability of ZnO nanowires is unclear. Herein, we report LED-controlled tuning of ZnO nanowires' wettability and, also, the role of LED emission wavelength in controlling the wettability of ZnO nanowires. Initial investigations on the spectral effects of light irradiation, using LEDs ($\lambda_p = 365$ nm, 385 nm, 454 nm and 519 nm), on the hydrophobicity of ZnO nanowire films have been carried out and discussed in this paper. Also, the effects of light wavelength and irradiation time over the hydrophobic-hydrophilic transition rate and relative 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 the wetting angle of ZnO nanowires. LEDs with $\lambda_p = 365$ nm have shown a very high transition rate compared to other wavelengths. Also, LEDs with emission wavelengths of 454 nm and 519 nm do not show change to the hydrophobic state of the ZnO nanowires even after 30 min of irradiation.

Materials and methods

Materials

All the materials used in the experiment were analytical grade. Zinc acetate, zinc nitrate hexahydrate and ammonium hydroxide were purchased from Sigma Aldrich, UK. All glassware was cleaned in deionized water prior to the experiment.

Synthesis of ZnO nanowire films

ZnO nanowires were grown on glass substrates using the hydrothermal synthesis method (18). 10 mM Zinc acetate was drop casted on the glass substrates and annealed on a hotplate for 1 min at 100°C for better adhesion. The process was repeated five times to get a uniformly thick seed layer. ZnO nanowires were grown by immersing the seeded substrates in 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 h. 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.

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 the contact angle measurement system from the first ten Angstrom (FTA 200) at room temperature (RH=8%). Absorption spectrum of the ZnO nanowires has been collected using the Lambda 950 UV/Vis Spectrometer from Perkin Elmer.

Experiments

A schematic view of the experimental setup for irradiating the samples with LEDs is shown in Fig. 1. LEDs were purchased from Nichia Corporation ($\lambda_p = 365$ nm and 385 nm) and Avago Technologies ($\lambda_p = 454$ nm and 519 nm). Full spectral widths at the half maximum

of the LEDs ($\lambda_p = 365$ nm, 385 nm, 454 nm and 519 nm) were 15 nm, 15 nm, 25 nm and 30 nm, respectively. LED emission was coupled through a bi-convex lens and irradiated over the sample placed on a sample stage. A neutral-density filter and aperture were used to control the optical power density. A dichroic mirror was used in the path to reflect a fraction of the light for monitoring the power level with a Coherent (FieldMaster GS) power meter and/or LED spectra with a StellerNet (EPP2000C) spectrometer. The surface wettability of the developed ZnO nanowires has been studied using the contact angle measurement system, by measuring the water contact angle (WCA) before and after the light irradiation for different time durations. All light irradiation experiments were performed at constant optical power. All contact angle measurements were carried out using 2- μ l water drop under ambient conditions.

Results and discussion

Figure 2 shows a scanning electron microscopy (SEM) image of ZnO nanowires at different magnifications. From the SEM image, it can be seen that the synthesized ZnO nanowires are preferentially oriented toward the c-axis perpendicular to the glass substrate. The 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 the 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 (13, 14). The length and diameter of the synthesized ZnO nanowires were about 11–12 μ m and 400–500 nm, respectively.

The WCA was measured immediately after the synthesis of ZnO nanowires and found to be about 0°. This super-hydrophilic nature, shown by the as-synthesized ZnO nanowires using the hydrothermal method, can be attributed to the hydroxyl groups on the surface. Thereafter, substrates were left to dry under ambient conditions for 72 h. During this process, adsorbed hydroxyl groups on the surface were replaced by atmospheric oxygen, leading to the formation of a hydrophobic surface. Therefore, we measured the WCA of ZnO nanowires after drying the substrate, and it was around 125°.

ZnO is a large-bandgap semiconducting material; therefore, light with energy higher than the bandgap energy is absorbed by the ZnO. This absorption of light (photons) generates electron–hole pairs on the ZnO surface. These electron–hole pairs will further create the surface defects and composition change that lead to different surface energy and, hence, surface wettability.

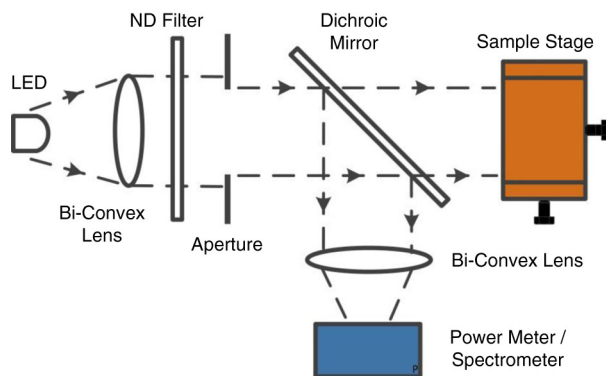


Fig. 1. A schematic view of the experimental set-up.

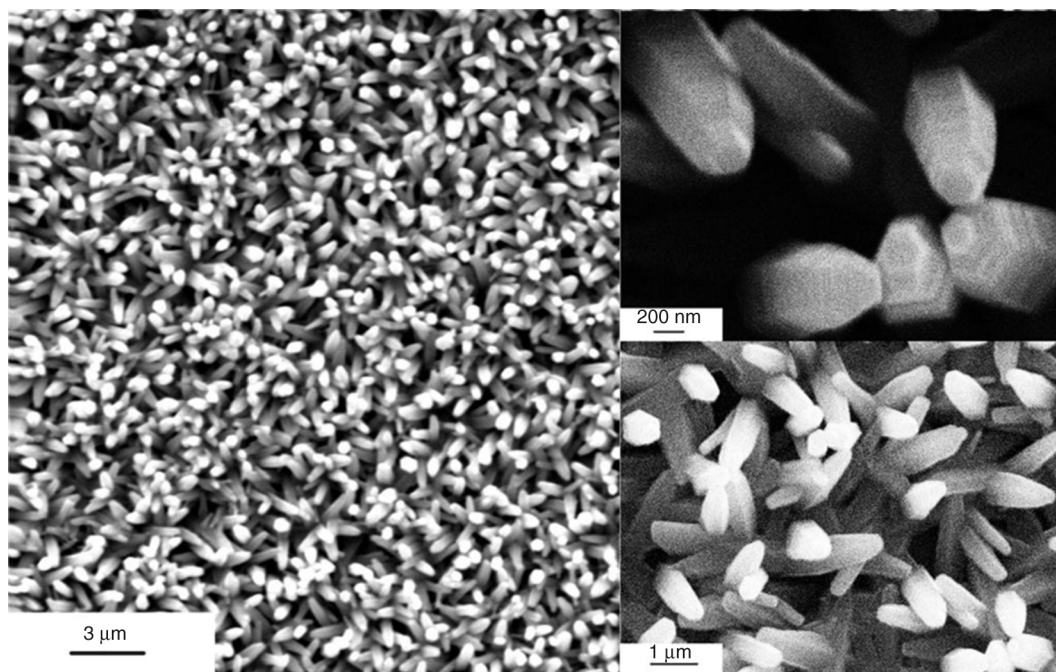
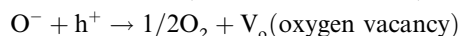
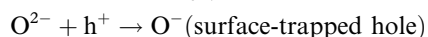
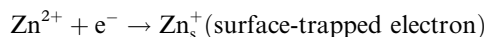
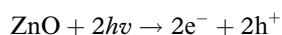
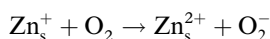


Fig. 2. SEM image of the synthesized ZnO nanowires on glass, with different magnifications.

The process which leads to the surface composition change can be expressed as (13):



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



At the same time, water molecules may adsorb at the oxygen vacancy (V_o) site. These defect sites are kinetically more favorable for hydroxyl group (OH^-) adsorption than oxygen adsorption, and hence promote increased water adsorption at the UV light-irradiated areas. However, the adsorption of OH^- on the defective sites creates distortion in the electronic structure of the surface and makes it energetically unfavorable. Therefore, after the UV illumination stops, the surface tries to recover to its original hydrophobic state by replacing the adsorbed OH^- with the atmospheric oxygen. During this process, OH^- and atmospheric oxygen compete to dissociatively adsorb on the defect sites. Therefore, an oxygen-rich environment can promote the recovery rate (19).

As discussed, the whole process of change in wettability depends on the absorption of light by ZnO nanowires. Therefore, to understand the spectral effect on the wettability, the absorption spectrum of the

synthesized ZnO nanowires has been collected. A normalized absorption spectrum of ZnO nanowires along with the LED's normalized emission spectra are shown in Figure 3. Better spectral overlap indicates that ZnO nanowires absorb more light at 365 nm than other wavelengths.

To see the effect of light absorption by ZnO nanowires on their surface wettability, a static WCA has been measured on the ZnO nanowire sample before and after the light irradiation using UV LED (emission wavelength, $\lambda_p = 365$ nm). Figure 4 shows the measured WCA for the 0–30 min light illumination period, and the inset pictures show the captured images of the water droplet on the sample before (hydrophobic) and after (hydrophilic) light

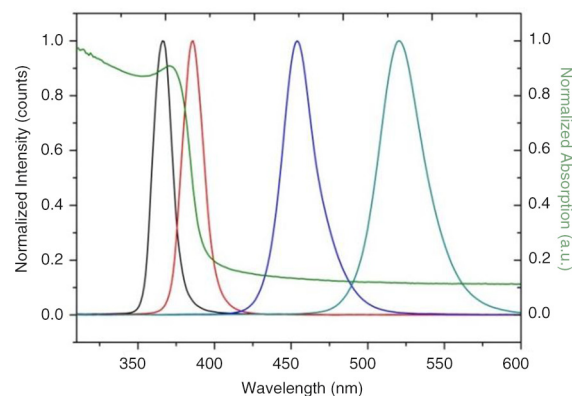


Fig. 3. LED normalized emission spectra ($\lambda_p = 365$ nm, 385 nm, 454 nm, 519 nm), along with a ZnO nanowire normalized absorption spectrum in green.

irradiation. Within 5 min, the ZnO nanowire surface undergoes a hydrophobic-to-hydrophilic transition. This rapid transition rate can be attributed to the nanoscale structures on the tip (13). Gradual change in WCA continues for a further 5 min, and thereafter it slows down. The reason behind this observed change in wettability by light irradiation on the ZnO nanowires can be explained as follows:

Surface wettability of the synthesized ZnO nanowires has been analyzed by measuring the static contact angle. ZnO nanowires' surface wettability can be considered, referring to the Cassie–Baxter (20) or Wenzel (21) models.

A Young contact angle, θ_y , on the smooth surface can be defined in terms of surface energy as (22):

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

where γ_{sv} , γ_{sl} , and γ_{lv} are the surface tension of solid–vapor, solid–liquid and liquid–vapor, respectively. Considering the surface roughness, the Wenzel model defines the apparent contact angle, θ , 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 the rough surface, which is the case after irradiation of UV light.

Under unexposed conditions, ZnO nanowires tend to show a hydrophobic surface where liquid does not penetrate inside the rough surface (nanowire groves).

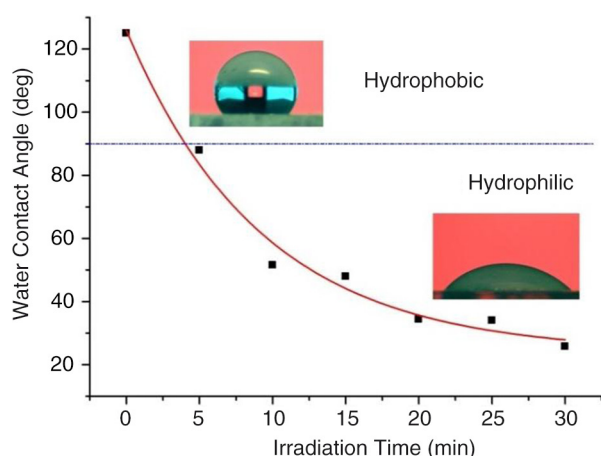


Fig. 4. Measured WCA change over time on ZnO nanowires irradiated with 365 nm LED. Inset pictures are captured images of water droplet on the ZnO nanowire sample, before (hydrophobic) and after (hydrophilic) the light illumination. Trend line is the exponential curve fit to the measured WCA data.

Therefore, this condition refers to the Cassie–Baxter state (20):

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

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

To further understand the effect of wavelength, light irradiation has been carried out on the ZnO nanowires using LEDs with a peak emission wavelength $\lambda_p = 365$ nm, 385 nm, 454 nm and 519 nm. WCA has been measured on each sample before and after the light irradiation, and referred to as WCA_0 and WCA , respectively. Figure 5 shows the relative change in WCA/WCA_0 measured with irradiation time for different illumination wavelengths. Rapid change in the wetting angle observed for the LED with $\lambda_p = 365$ nm can be attributed to the higher rate of change in surface energy. A small change observed in the wetting angle under 454 nm and 519 nm illuminations can be attributed to the small fraction of light absorbed by ZnO nanowires due to the native defects. Although the spectral width of LEDs emitting at 454 nm and 519 nm is slightly higher than that of the other LEDs used in the experiment, a negligible effect has been anticipated due to very low absorption by ZnO nanowires in that range. Trend lines in the graph indicate that the change in wetting angle slows down gradually with increasing wavelength. In addition, results for the illumination wavelengths of 454 nm and 519 nm reveal that there was no clear hydrophobic-to-hydrophilic transition observed within 30 min of irradiation. These results indicate that the wettability of the ZnO nanowires

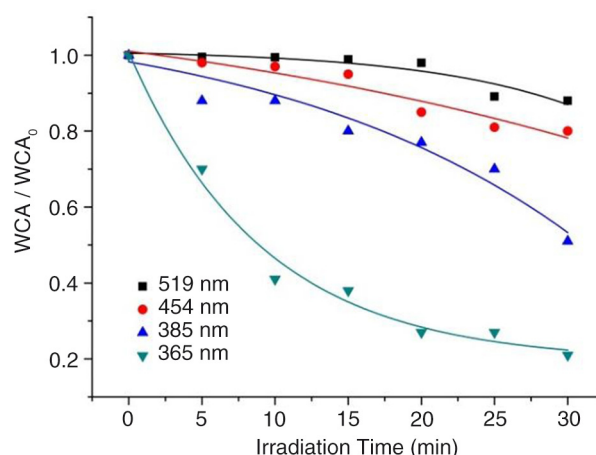


Fig. 5. Measured relative contact angle change with irradiation time for different LED emissions at $\lambda_p = 365$ nm, 385 nm, 454 nm, and 519 nm. Trend line indicates the respective exponential fit to the data.

can be controlled by tuning the wavelength of irradiating light.

Conclusion

The effect of irradiation wavelength and time on tuning the wettability of ZnO nanowires has been studied for the first time, using different LEDs. Results have provided significant insight into the role of wavelength on tuning the wettability of ZnO nanowires. Results show that the spectral overlap between ZnO absorption spectra and LED emission wavelength controls the hydrophobic-to-hydrophilic transition rate. Various controllable parameters of LEDs can provide advanced control in tuning the desired surface wettability of the ZnO nanowires. Also, LEDs can be integrated on the biosensor chip, which allows miniaturizing the sensor and microfluidic devices.

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Conflict of interest and funding

There is no conflict of interest in the present study for any of the authors.

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