Fabrication and characterisation of flower-like ZnO nanostructures grown chemically on flexible PEN substrate

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Flower-like ZnO nanostructures were successfully produced on a polyethylene naphthalate (PEN) substrate through a chemical bath deposition method. Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), photoluminescence (PL), and ultraviolet-visible were utilised to investigate the structural and optical properties of grown flower-like ZnO nanostructures. FESEM image indicates that fabricated ZnO nanostructures formed from the ZnO nanoflowers with different shape and the petals of the ZnO nanoflower grow symmetrically and radially from the centre. XRD pattern of the ZnO nanoflowers indicate that the ZnO nanorods of the nanoflowers were preferentially grown along the *c*-axis. The PL results of the ZnO nanoflowers exhibited a strong violet and indigo emission peaks are centred approximately at 413 and 425 nm, respectively.

1. Introduction: Among the semiconductor nanostructures, ZnO nanostructures with a direct band gap (3.37 eV) and large exciton binding energy (60 meV) are widely used because of their potential applications for development of novel optoelectronic devices, chemical sensors, and ultraviolet (UV) light emitters, because of their faster response, specific crystalline orientation, higher optical gain, and slow electron/hole recombination rate [1, 2]. The precision control on the morphology of ZnO crystals is a matter of considerable importance for exploring the potential oxide material, because the performance of ZnO-derived devices strongly depends on the size and the shape of ZnO nanomaterials. In the past years, ZnO nanostructures with various morphologies such as nanotubes [3], nanowires [4], nanodisks [5], nanorods [6], and 3D hierarchical architectures [7] have been synthesised on diverse substrates via different methods. Specially, 3D hierarchical ZnO nanostructure that consists of lower dimension nanocrystals as the building blocks attract much attention due to their lower gas diffusion length, higher mobility, and relatively larger specific surface area than the agglomerated nanoparticles [8]. Among these 3D complex structures of ZnO, such as stars, dendrites, and flowers, the ZnO nanoflowers with a large surface area and enhance light scattering capacity [9] is highly desirable for gas sensor, photocatalysis and solar cell applications. So far, various techniques are used to fabricate ZnO nanostructures including of the chemical vapour deposition [10], pulsed laser deposition [11], hydrothermal synthesis [12, 13], sol–gel method [14], electrochemical deposition [15], and chemical bath deposition (CBD) [16]. Among these, the CBD technique is one of the appropriate chemical synthesis to produce ZnO nanostructures because of its low temperature, non-requirement of sophisticated instruments, simplicity, capability for large-scale production, affordability, and environmentally friendly processing.

To date, various substrate types are used to synthesise ZnO nanostructures with various shapes and sizes by different methods, such as gallium nitride [17], fluorine-doped tin oxide [18], indium tin oxide [19], and porous silicon [20]. Because of the increasing request for convenient and portable application devices, the development of optically transparent electronic devices fabricated on flexible polymer substrates has been the subject of much recent research. Flexible electronic devices are increasingly being applied in the next generation electronics technology such as liquid crystal display, thin film transistor, light emitting diodes, cell phones, personal digital assistants, solar cells, and digital cameras because of its great potential and functionality to enhance many industries from a commercial perspective [21]. Transparent conductive oxide materials play an important role in achieving the performance required for flexible electronic devices, and ZnO nanostructures is a good candidate transparent conductive oxide material because of their high conductivity, good optical transmittance and low-cost fabrication [22]. Polyethylene naphthalate (PEN) substrate has been selected to form ZnO nanoflowers by CBD synthesis at a low temperature because of their transparency, transportability, high resistance to impact damage, and low weight. In the recent past, various shapes of ZnO nanoflowers including self-assembled nanosheets [23], self-assembled nanorods [24], and other shaped nanoflowers [25] have been fabricated by using different physical and chemical methods. To the best of my knowledge, this study is the first to grow the ZnO nanoflowers on flexible PEN substrate by the CBD supplemented with oven heating. The present study investigates the structural and optical properties of ZnO nanoflowers fabricated on a PEN substrate via the CBD method.

2. Experimental: Nanoflower-like ZnO nanostructures on flexible PEN substrate were prepared by a three-step consisting of the cleaning PEN wafer, ZnO seed layer formation, followed by the growth of the nanoflower-like ZnO nanostructures. In the first step, the PEN substrate was cleaned ultrasonically in a beaker including an isopropyl alcohol solution at 50°C for 20 min. The second step is to create a ZnO seed layer on the prepared PEN substrates, which a radio-frequency magnetron sputtering system was used to obtain a ZnO target with 99.999% purity. The sputtering power and argon pressure were fixed at 150 W and 5.5 mTorr, respectively. The optical reflectometer system (Filmetrics F20) was used to measure the ZnO seed layer thickness. The thickness of ZnO seed layer on the PEN substrate was 95 nm. In the third stage, the ZnO nanoflowers were produced on seed-layer ZnO/PEN substrates by using the low-temperature CBD method. An aqueous solution of hexamethylenetetramine ($C_6H_{12}N_4$) and zinc nitrate hexahydrate [$Zn(NO_3)_2 \bullet 6H_2O$] was prepared for growing the ZnO nanoflowers by CBD. About 0.2 M/L of $C_6H_{12}N_4$ and an equal molar concentration of $Zn(NO_3)_2 \bullet 6H_2O$ were separately dissolved in deionised (DI) water at 80°C. The two solutions were combined in a beaker, and the prepared substrate was vertically immersed in the aqueous solution. The beaker was then placed inside an oven at 95°C for 2.5 h. Finally, the samples were rinsed by using DI water.

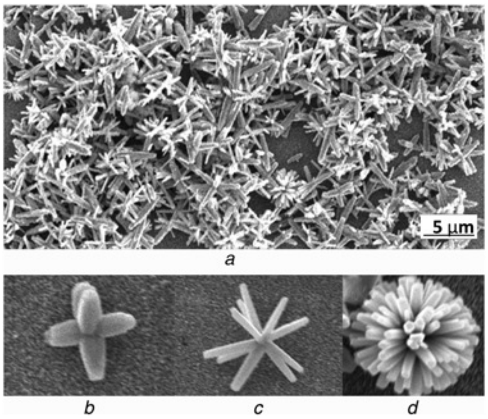

Fig. 1 *Typical FESEM images of ZnO nanoflowers prepared on PEN substrate*

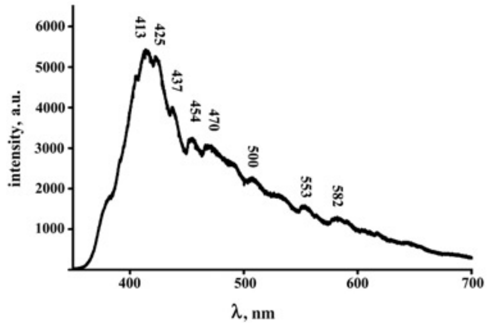

Fig. 3 *PL spectra of ZnO nanoflowers grown on PEN substrate*

The crystal structure of the ZnO nanoflowers was obtained using X-ray diffraction (XRD) (PANalytical X'Pert PRO MRD PW3040). The morphology of fabricated ZnO nanoflowers was obtained via field emission scanning electron microscopy (FESEM) (model FEI/Nova NanoSEM 450). Photoluminescence (PL) spectroscopy (Jobin Yvon HR 800 UV, Edison, NJ, USA) was utilised to determine the optical properties of the fabricated ZnO nanoflowers. The excitation wavelength and an illumination intensity of He–Cd laser were 325 nm and 20 mW, respectively. UV-visible study was done by using the spectrophotometer (Cary Series UV-Vis-NIR).

3. Results and discussion: FESEM was used to evaluate the morphology of the ZnO nanostructures. Fig. 1 shows the surface morphology of the fabricated ZnO nanostructures grown on the PEN substrate.

A close observation in Fig. 1 designates that ZnO nanostructures formed from the ZnO nanoflower with different shape. Viewing more closely in Figs. 1*b* and *c*, ZnO nanoflowers are made of 5 and 10-nanorod petals with typical diameter (length) of about 500 and 300 nm (1.1 and 2 µm), respectively. Fig. 1*d* displays high magnification FESEM image of the ZnO nanoflower, which is composed of dozens of ZnO nanorod petals with hexagonal shape. All the petals of the ZnO nanoflower grow radially and symmetrically from the centre that typical diameter (length) of the single petal ranging from 250 to 400 nm (2.1 µm), as shown in Fig. 1*d*.

An XRD experiment of the ZnO nanostructures was carried out to confirm the formation of wurtzite hexagonal of ZnO nanoflowers. The XRD spectrum of ZnO nanoflowers grown on PEN substrate is shown in Fig. 2. Typical XRD pattern of ZnO nanostructures was analysed to determine the crystalline orientation and structure of the ZnO nanoflowers synthesised on PEN substrate. The spectrum of the ZnO nanoflower structures from 27° to 70° shows the (1 0 0), (0 0 2), and (1 0 1) directions of the hexagonal ZnO wurtzite, which matched the wurtzite hexagonal phase of the standard data for ZnO (ICSD 01-080-0074). As shown in Fig. 1, the sharp diffraction peaks demonstrate the good crystallinity of the prepared crystals of the ZnO nanoflowers. The high intensity (002) peak in the XRD pattern compared with (100) and (101) peaks of the ZnO nanoflowers indicate that the ZnO nanorods of the nanoflowers were preferentially fabricated along the *c*-axis of the hexagonal wurtzite structure.

The PL spectrum of ZnO nanoflowers grown on PEN substrate is shown in Fig. 3. The high violet emission is centred approximately at 413 nm that can be attributed to the transition energy from zinc interstitial level to the valance band in ZnO. The high indigo emission is centred approximately at 425 nm that can be attributed to the transition energy from conduction band to zinc vacancy level [26, 27]. The blue emissions are centred approximately at 437 and 454 nm are attributed to the recombination between zinc interstitial energy level to zinc vacancy energy level. The green emissions at 470 and 500 nm are attributed to the recombination between the conduction bands to oxygen vacancy energy level. The small yellow and orange emissions are centred approximately at 553, and 582 nm are attributed to the transition energy between the conduction bands to oxygen interstitial and zinc interstitial to oxygen interstitial, respectively [28]. The generated green and yellow emissions shown in Fig. 3 indicate that oxygen vacancy and interstitial oxygen are the dominant defects.

The optical property of flower-like ZnO nanostructures was studied by UV-visible spectroscopy. The absorption spectrum of the ZnO nanoflowers is shown in Fig. 4. From the spectrum, it can be seen that the absorption values of the ZnO nanoflowers are high at short wavelengths (≤4000 nm) and low at long wavelengths. Therefore, the ZnO nanoflowers behaved as an opaque

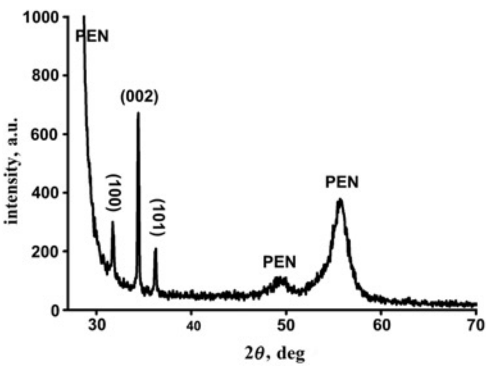

Fig. 2 *Typical XRD pattern of ZnO nanoflowers grown on PEN substrate*

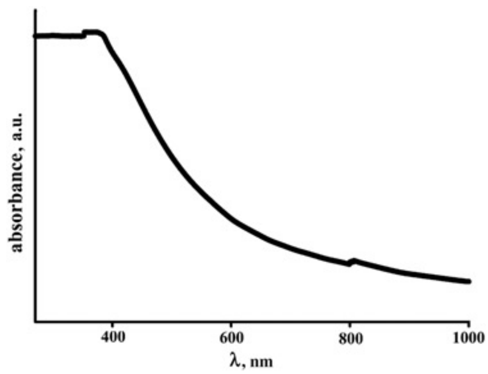

Fig. 4 *UV-visible absorption spectrum of the ZnO nanoflowers on PEN substrate*

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material because of its high absorbing properties at short wavelengths and as a transparent material at long wavelengths.

4. Conclusions: ZnO nanoflowers were synthesised on flexible ZnO/PEN substrates by wet CBD at a low temperature. FESEM image revealed that the ZnO nanoflower is composed of dozens of ZnO nanorod petals with hexagonal shape. All the petals of the ZnO nanoflower grow radially and symmetrically from the centre. The high intensity (002) peak in the XRD pattern compared with (100) and (101) peaks of the ZnO nanoflowers indicate that the ZnO nanorods of the nanoflowers were preferentially fabricated along the *c*-axis of the hexagonal wurtzite structure. The synthesis of ZnO nanoflowers with high optical quality can be very suitable for flexible and portable application devices. The optical measurements of ZnO nanoflowers revealed that the PL spectrum consist of violet, indigo, blue, green, yellow, and orange emissions.

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6 References

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