Chemical solution route to synthesize claw-like ZnO nanorod array and its optical properties*

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By using a low-cost and facile hydrothermal method, a peculiar claw-like ZnO nanorod array is successfully synthesized. The hydrothermal growth is done in an aqueous solution with equimolar zinc acetate (ZAc, $Zn(CH_3COO)_2{\cdot}2H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$). The obtained ZnO nanorod array is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results indicate that the nanorods are high-quality monocrystals. The photoluminescence (PL) spectrum is performed to investigate the optical properties of this product.

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Recent years, one-dimensional nanoscale materials have attracted much attention owing to their unique and fascinating properties as well as their potential applications in nanodevices[1,2]. Zinc oxide (ZnO) with the wide direct band gap of 3.37 eV and the high exciton binding energy of 60 meV at room temperature is an important II-VI compound semiconductor material. It has been demonstrated that ZnO has various applications in many fields, including ultraviolet (UV) lasers[3], light-emitting diodes[4], solar cells[5,6] and gas sensors[7,8]. For example, Pasrichar et al[7] synthesized a composite consisting of ZnO and graphene oxide sheets. In the composite, ZnO nano-crystallites serve as a primary sensing transducer for gas sensing applications, which demonstrated the parts-per-million level detection of common industrial toxins, like CO, NH_3 and NO, with high sensitivity at room temperature. Park et al[8] fabricated a new type of flexible gas sensor using hybrid structure of ZnO and graphene sheet. This new type gas sensor enabled the parts-per-million level detection for ethanol vapor with very high sensitivity.

To date, various methods have been developed to synthesize ZnO nanostructures, including sol-gel process[9,10], hydrothermal method[11-13], electrochemical reaction[14-16], thermal evaporation[17-19] and laser ablation[20,21]. Among all these methods, the hydrothermal method developed by Lionel Vaysseires et al[11,22] has advantages of low temperature, large scale productivity and economical synthesis. Boyle et al[23] developed a two-step approach, which involves a pre-coating step of ZnO template layer and a subsequent solution deposition process, to produce perpendicularly oriented ZnO submicrorods.

In this paper, we report a hydrothermal growth of large-area, high-quality, perpendicularly oriented and uniformly distributed claw-like monocrystal ZnO nanorods, which aggregate together and have uniform size and morphology. Our procedure contains two steps, the first is the hydrothermal growth, which is a modification of the method developed by Vayssieres et al[22], and the second is a rapid drying process in a drying oven. The hydrothermal growth is performed in a mixed aqueous solution of equimolar zinc acetate (ZAc, $Zn(CH_3COO)_2{\cdot}2H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$). The formation mechanism and optical properties of this product are also investigated.

The ZnO nanorod array was prepared from a mixed aqueous solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (Sigma-Aldrich, ≥99.0% purity) and $C_6H_{12}N_4$ (Sigma-Aldrich, ≥99.0% purity) under hydrothermal conditions. The procedure consists of two steps. Firstly, a 10 nm-thick ZnO seed layer was deposited on the Si (100) substrate by radio frequency (RF)-magnetron sputtering. The Si substrate was cut into small pieces with the size of 1 cm×2 cm, and ultrasonically cleaned with acetone, ethanol and deionized water, respectively. After this, the substrate was blow-dried with N_2 gas and put into an RF-magnetron sputtering system. RF-magnetron sputtering was performed by a 99.99 % pure ZnO target at 2.0 Pa working pressure of oxygen and argon mixture with the flow rate ratio of 1:10. The sputtering power was 100 W, and the sputtering time was 3 min. The second step is the hydrothermal growth of ZnO nanorods in aqueous solution. In detail, equimolar aqueous solutions (0.05

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mol) of both reagents were prepared using deionized water. The hydrothermal growth was carried out at 95 °C in a sealed kettle by immersing the pre-modified substrate face-downward in the aqueous solution. After 2 h growth, the substrate was taken out of the solution, rinsed with deionized water, and then fast dried in a drying oven at 80 °C.

The morphology and structure of as-synthesized ZnO nanorod array were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffractometer (XRD). The photoluminescence (PL) spectroscopy measurements were performed at room temperature under a 325 nm UV fluorescent light excitation.

Fig.1 shows the typical SEM images of as-synthesized ZnO nanorod array grown on Si substrate with different magnifications. From Fig.1 we can clearly see that our products consist of a large number of uniformly distributed claw-like nanostructures. Every claw-like nanostructure is aggregated by several tens of nanorods. These nanorods have an average diameter of about 30 nm. Through a series of experiments, we find that the height of the ZnO nanorod array and the diameter of the nanorods can change with the reaction time and the thickness of the seed layer pre-modified on Si sbustrate. In our experiment, the concentrations of the two reagents were both 0.05 mol, and the potential of hydrogen (PH) was around 6.5. A tension junction model[24] can be used to explain the formation mechanism of this peculiar ZnO nanorod array. When the product was taken out of the solution, rinsed with deionized water and fast dried at a temperature as high as 80 °C, the water film on the top of the ZnO nanorod array evaporated and contracted rapidly to form tiny drops. Therefore, the water has a centripetal surface tension, making the nanorods bent and aggregated to form this peculiar claw-like structure.

Fig.2 shows a typical TEM image of a ZnO nanorod cut off from the substrate. The high resolution TEM (HRTEM) image exhibits the clear lattice fringes of the ZnO nanorod, and the interplanar distance is 0.26 nm, which is in good agreement with the d-spacing of the (0001) lattice plane of ZnO wurzite hexagonal structure. Selected area electron diffraction (SAED) pattern of the nanorod shown in the inset of Fig.2 can also be indexed to the [001] zone axis diffraction pattern of wurtzite structured ZnO. Additionally, the diffraction patterns taken from different parts of the same nanorod shown in Fig.2 are identical, which indicates that the whole nanorod has the single crystallinity.

The crystal structure of the product was also analyzed by XRD. A typical XRD pattern is shown in Fig.3(a). The stronger diffraction peaks appear at 31.8°, 34.3° and 36.5°, which correspond to (100), (002) and (101) planes of wurtzite ZnO, respectively. This is well indexed to the standard diffraction pattern of wurtzite ZnO (JCPDS card No.36-1451) with lattice constants of a=0.3248 nm and c=0.5206 nm. The largely enhanced (002) diffraction peak strongly indicates that the nanorods grow along the [001] direction, which is in good agreement with the HRTEM and the SAED results shown in Fig.2. Clearly, the ZnO nanorod array is highly crystallized. It is necessary to note that the pre-modified ZnO nanoparticles as seed layer help to form well aligned ZnO nanorods in the hydrothermal process.

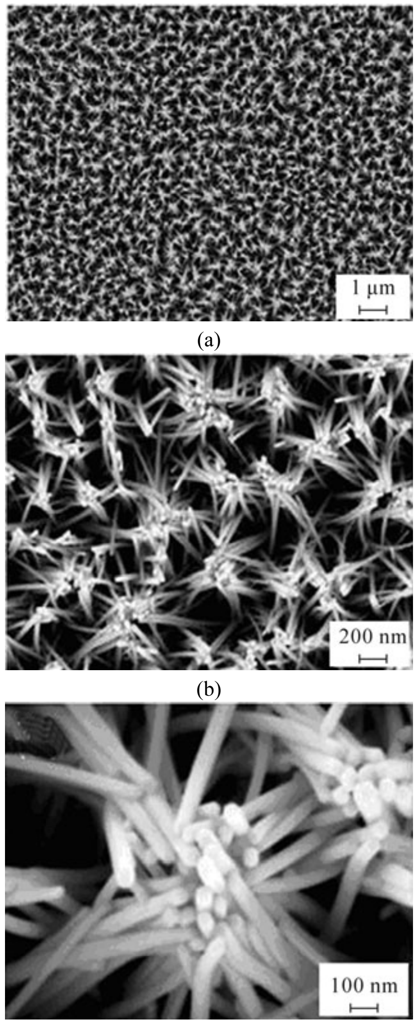

Fig.1 SEM images of synthesized claw-like ZnO nanorod array in (a) low, (b) median, and (c) high magnifications

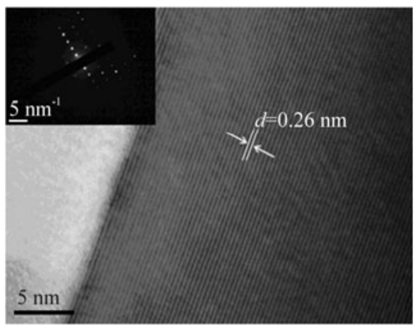

Fig.2 HRTEM image of single ZnO nanorod (The inset shows the corresponding SAED pattern.)

To investigate optical properties of this claw-like ZnO nanorod array, PL spectrum at room temperature was measured under 325 nm UV fluorescent light excitation. Fig.3(b) shows the PL spectrum of the ZnO nanorod array. Clearly, a strong UV emission at 384 nm is observed in the spectrum. The UV emission corresponds to the near band edge (NBE) emission of ZnO, and can be attributed to the recombination of free excitons. No defect-related emission is observed in the PL spcectrum, indicating that the ZnO nanorod array is of high optical quality, and this is consistent with TEM and XRD results shown above.

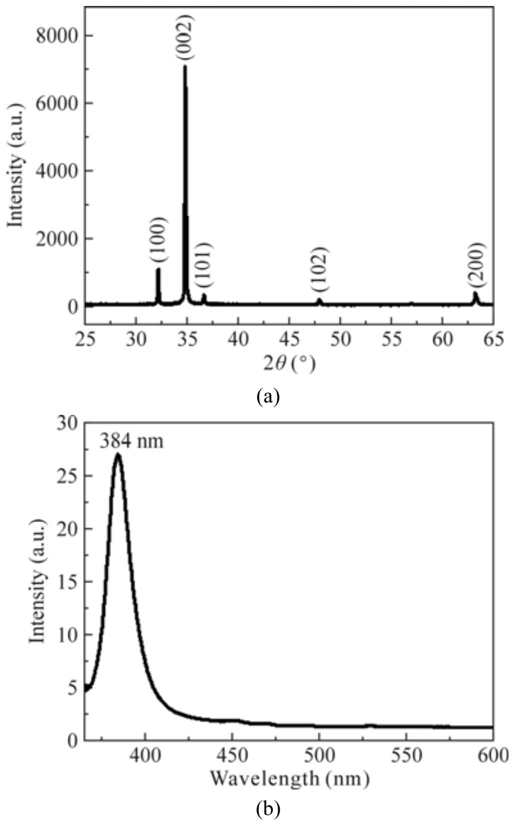

Fig.3 (a) XRD pattern and (b) PL spectrum of the synthesized claw-like ZnO nanorod array

In summary, a peculiar claw-like ZnO nanorod array is successfully synthesized on Si substrate through a low-cost and facile hydrothermal method. The obtained ZnO nanorod array is characterized by XRD, SEM, TEM and fluorescence spectrophotometer. The XRD analysis shows that the nanorods are high-quality monocrystals, which are confirmed by the SEM and TEM analyses. Formation mechanism of the nanostructure and its optical properties are also discussed.

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