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A template-free aqueous route to ZnO nanorod arrays with high optical property

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A mild template-free aqueous route was successfully established to synthesize well-aligned ZnO nanorod arrays, which were proved to exhibit high optical property by PL spectra.

Zinc oxide is a very interesting multifunctional material for its promising application in light emission, gas sensors, catalyst and solar cells. With its appropriate energy gap and a large exciton bonding energy of 60 MeV, ZnO has been recognized as a valuable photonic material in the blue-UV region. Accordingly, a low-dimensional ZnO nanostructure might be used in novel nano-devices. Although 1-D ZnO nanostructures have been synthesized by various methods, it is must be acknowledged that these need to be ordered into large three-dimensional arrays to find application as a nanodevice. The report of the room temperature lasing action of ZnO nanorod arrays further demonstrates that the functional design of ZnO nanostructure in a highly oriented and an ordered array is of crucial importance for the development of a device with high performance.[1]

Regular procedures based on evaporation and condensation processes such as catalyst- or AAO template-assisted routes have been developed to obtained ZnO nanorod arrays.[2] However, expensive raw materials for the device, complex process control and high temperatures are unfavorable for an industrialized process. A solution-based approach is a better alternative, with the advantages of mild synthetic conditions, simple manipulation and large scale-up production. An organic amine-assisted hydrothermal process was adopted to synthesize ZnO 1-D nanostructures including microrod and nanorod arrays on conducting glass substrates.[3] A similar two-step procedure was developed to achieve highly oriented nanowire films with high surface area on wafer, which opens a door for future electronic devices based on ZnO nanostructure arrays.[4] In the solution approach, amine induced oriented crystallization of ZnO and developed into 1-D nanostructure. However, these ZnO 1-D nanostructures that crystallized from solution always had a high defect concentration. Template-free growth of ZnO nanorod arrays in solution with high optical properties is still a challenge. Direct synthesis of copper oxide nanoribbon arrays on a copper surface inspired us to evaluate whether such a simple route can be applied to ZnO nanorod arrays on a zinc surface.[5] The experimental results show consistency with our expectation. Furthermore, the ZnO nanorod arrays hold high optical quality.

Well-aligned ZnO nanorod arrays were grown directly on zinc foil substrate. The experimental procedure was designed as follows: 35 ml 0.05 M NaOH solution, 5 ml 30% H_2O_2 and 1 × 1 cm^2 zinc foil were added to a 50 ml autoclave and then put into an oven at 160–200 °C for 3–6 h. The foil was then collected from solution, rinsed with deionized water and dried in air at 40 °C. The morphology of the nanorod arrays were observed by field emission scanning electron microscopy (FESEM), performed on a JEOL-JSM-6700F Scanning electron microanalyzer. The oriented growth direction and crystallinity can also be analyzed by X-ray diffraction measurement (Rigaku X-ray diffractometer with Cu Kα radiation) and electron diffraction (Hitachi Model 800 at 200 KV). Photoluminescence spectra were recorded on a JY LABRAM-HR Laser MicroRaman Spectrometer using the 325 nm excition line of the He-Cd laser at room temperature.

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The general morphology of the ZnO rod arrays is shown in Fig. 1a and Fig. 1b, well-aligned hexagonal rod arrays with well-defined crystallographic faces of {100} grow along the [0001] direction perpendicular to the substrate. The densely packed arrays of ZnO nanorods have diameters ranging between 80–150 nm and lengths of 1.5–2.0 μm. As an obvious characteristic property of the as-obtained rod arrays, all the tips are contracted with six regular faces of {103} (Fig. 1c), which might be beneficial for optical emission in an optical-electronic device. Between the substrate and the rod arrays can be found some nanoparticles with similar size and distribution to the diameter of the rods, which suggests those particle might act as seeds for the development of rod arrays. No obvious variation of the morphology can be found over the range of the temperature and time listed above. Fig. 2 shows the XRD pattern of the rod arrays. As expected, the highly enhanced (002) peaks can be seen as a result of the vertical orientation of the rods. The SAED pattern (not shown here) taken from a single nanorod can be exactly indexed to a hexagonal ZnO single-crystalline with [0001] orientation.

ZnO nanorods can grow in aqueous solution under the assistance of several kinds of organic amine which were regarded as chelating agents to induce anisotropic development.[3] Therefore, the formation of ZnO nanorod arrays in our experiment suggests a different mechanism, contrasting with the previous template-induced growth. Single crystalline ZnO nanorods can also be self-assembled from nanoparticles by orientation attachment.[6] However, the growth system and precusor is quite different in our designed experiment. As mentioned above, at the root of these rods some nanoparticle hold the size approximate to that of the diameter of the nanorods. Our reaction process might be deduced as a typical Ostwald ripening model. We describe the growth procedure as follows: at the beginning of the hydrothermal reaction, the zinc

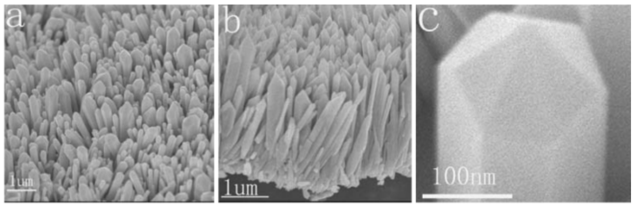

Fig. 1 (a) FESEM image of ZnO nanorod arrays grown onto zinc foil; (b) cross-sectional FESEM image of the array; (c) an enlarged image of a single nanorod.

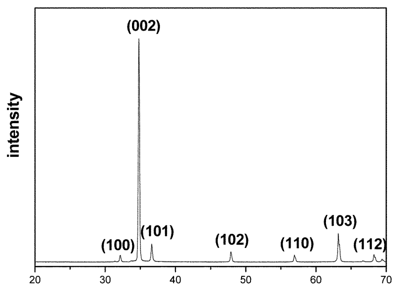

Fig. 2 XRD pattern of the ZnO well-aligned nanorod arrays on zinc foil.

surface was first oxidised into a large quantity of ZnO nanoclusters which served as the nuclei for the crystal growth. The growth of zinc oxide stemmed from these clusters and continued. In this period a typical disolution–crystallization state was established in the hydrothermal condition, the fresh ZnO can be dissolved into alkaline solution, in the peculiarly alkaline solution high concentration H_2O_2 will greatly influence subsequent ZnO crystallization on the nuclei, although there is natural tendency for ZnO anisotropic growth, we still think the growth was supported by a certain driving force, which seemed to originate from the added H_2O_2, because controlled experiments carried out without H_2O_2 showed the final products to consist just of some nanoparticles on the surface of zinc foil (not shown here). In accounting for the evolution of the morphology of CdSe, Peng suggested that when two precursors were adopted to synthesize semiconductor nanocrystals, excess of the less reactive precursor often generated elongated nanoparticles with a higher aspect ratio.[7] That is, precursor concentration in the reaction solution plays a key role for the determination and evolution of the shapes of the resulting nanocrystals, simply mixing Zn^{2+} with OH^- in hydrothermal condition just gives the dot shape which is thermodynamically more stable than others. Only under an unequilibrium state by controlling the local concentration might non-dot shape structure be produced. It was based on this idea that we introduced H_2O_2 into the alkaline hydrothermal system. Similar to other semiconductor nanocrystals, the formation of 1-D structure was founded to be a highly kinetics-driving reaction. Supersaturation in growing regions is favorable to anisotropic growth. The decomposition of the H_2O_2 greatly increased the oxygen concentration, and made the oxygen largely excessive on the surface of the growth layer. As a result, the kinetics in the course when ZnO crystallized and grew on the nuclei can be simply controlled by the kinetic factor (H_2O_2 concentration). High oxygen concentration produced by decomposition H_2O_2 gave the kinetic force for the anisotropic development along *c*-axis direction with its most stable crystal habit.[3] As the reaction continued, the concentration of H_2O_2 decreased, and the driving force, accordingly, became weaker. When the H_2O_2 was exhausted entirely the growth terminated, however, we still can find some particles left because development of the rod arrays preferentially occur at the upper particle.

Study of photoluminesence spectra is an effective method to both evaluate ZnO defects and its optical properties available as a photonic materials. Fig. 3a shows a typical PL spectrum of high quality ZnO rod arrays measured at room temperature. Two sharp peaks in the vicinity of band edges were observed at 378 nm (3.29 eV) and 389 nm (3.20 eV), which can be attributed to the exciton transitions. On the other hand, the deep level emission, known to be related to the structure defects, centered at 520 nm (2.39 eV), was quite weak. The sharp excitonic emission and weak deep level emission peaks indicate that the ZnO nanorods have a lower defects concentration and high optical property. To our knowledge, the ZnO nanorods have the highest intensity ratio of the band-edge emission to the deep level emission among those obtained in solution methods. Previous studies were mostly concentrated on the relationship between the annealing conditions with the defects concerning about the oxygen by monitoring the PL spectrum in the visible range because those visible emissions were considered to originate from the structure defects associated with oxygen (*e.g.*, the green results from the recombination of electrons with holes trapped in singly ionized oxygen vacancies). However, little attention was paid to the atmosphere of the solution also having a predominant effect on the defect of the crystallized ZnO nanostructure. The reason we call the effect "predominant" is that control experiments carried out without H_2O_2 suggested that the obtained ZnO particles have a high defects concentration. The PL spectra of the samples showed a weak band-edge emission and broad green emission at a similar position but a different intensity ratio (Fig. 3b). Additionally, the previous study also showed the ZnO nanostructures obtained from the solution often have a stronger visible emission and a high defects concentration. As a result, it can be safely deduced that the added H_2O_2 effectively decreased the defects concentration of the ZnO nanorods. As previous discussed, decomposition of H_2O_2 will inevitably enhance the oxygen concentration and give an oxidation-hydrothermal atmosphere. In such an "oxidising–annealing" condition the crystallized ZnO might have a lower vacancy concentration associated with oxygen which seems contrary to the traditional observation that UV light emission can be greatly enhanced by annealing ZnO in reducing ambient. Accordingly, emission related with the singly ionized oxygen vacancies was suppressed and emission from exciton recombination became stronger. Further investigation is needed to better understand the detailed mechanism about the novel strengthening reaction, especially the role of H_2O_2. The ability to growth high purity ZnO nanorods is expected to greatly increase the versatility and power of these building block for "bottom-up" designed nanoscale photonic and electronic device application.

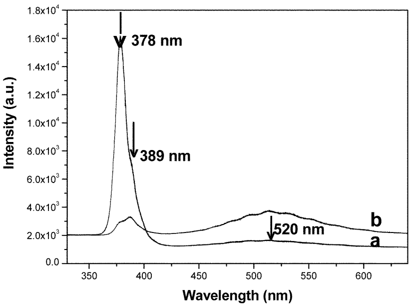

Fig. 3 PL spectrum of ZnO nanorod arrays obtained by a H_2O_2-assisted hydrothermal route (curve a) and nanoparticle in the absence of H_2O_2 (curve b). A dominant free exciton peak two sharp peaks lied at 378 nm and 389 nm and almost undetectable weak deep level emission were showed in curve a; While curve b suggested a higher defect concentration.

In summary, a H_2O_2-assisted hydrothermal method was designed to synthesize ZnO nanorod arrays with high optical property on a large scale. H_2O_2, at least, takes a double role of promoting the high quality 1-D arrays structure and enhancing its exciton emission effectively. All these enhanced effects can be ascribed to the high oxygen concentration by introducing H_2O_2 in the hydrothermal condition although the binding state of oxygen in course of the reaction is still unknown. The high quality ZnO rod arrays were expected as an ideal functional components for photonic and electronic device. Furthermore, well-oriented Cu_2O film with a novel optical property have been directly obtained on Cu foil in the metal–alkali–H_2O_2 hydrothermal system, and In_2O_3 nanocubes with strong PL emission in the blue-green region have also been synthesized by a similar route. This novel oxidising model might be also applied to obtain other metal oxide/metal nanostructures and holds promise for the design of nanoelectronic and optoelectronics devices. Further work is under way.

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