Hydrothermal growth of large-scale micropatterned arrays of ultralong ZnO nanowires and nanobelts on zinc substrate†

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Large-scale, ultralong ZnO nanowire and nanobelt arrays with honeycomb-like micropatterns have been fabricated by hydrothermal oxidation of zinc foil in aqueous alkaline $(NH_4)_2S_2O_8$ solutions.

One-dimensional (1D) ZnO nanostructures, such as nanorods, nanowires, nanobelts, and nanotubes, have attracted a great deal of interest because of their intriguing optical, electronic, and mechanical properties and potential applications in optoelectronics, photonics, field emission, energy conversion, catalysis, and sensing.[1–6] In particular, well-aligned or micropatterned arrays of 1D ZnO nanostructures (nanoarrays) on substrates are highly desirable for promising device applications. For example, it has been demonstrated that ZnO nanorod/nanowire arrays on proper substrates can emit ultraviolet laser at room temperature,[1] act as piezoelectric nanogenerators,[2c] be used to construct nanowire dye-sensitized solar cells,[3] and show reversible super-hydrophobicity to super-hydrophilicity transition.[4] Moreover, large-area, hexagonal-patterned ZnO nanorod arrays are expected to find potential applications as nano-optoelectronic devices and nanosensor arrays.[5] For the controlled growth of aligned ZnO nanoarrays on substrates, high-temperature vapor-phase approaches including physical vapor deposition[7] and chemical vapor deposition[8] have been widely employed; however, these processes are generally expensive and energy-consuming. Alternatively, various low-temperature solution-phase approaches have recently been developed to fabricate ordered ZnO nanoarrays on suitable substrates because of their good potential for scale-up production and commercial feasibility. In this regard, oriented ZnO nanorod/nanowire arrays[9–11] and nanotube arrays[11,12] were fabricated through a two-step wet chemical process involving the coating of a substrate with nanosized ZnO seeds and the subsequent decomposition of Zn–amide complexes under mild hydrothermal conditions (90–95 °C). Furthermore, aligned or patterned ZnO nanorod arrays were successfully grown from solution on substrates pre-coated by various metals.[13–15] Notably, the direct growth of oriented ZnO nanorod/nanoneedle arrays on a zinc substrate was recently realized by the natural surface-oxidation of zinc foil in solution at room temperature or under hydrothermal conditions;[16–19] moreover, large-scale ZnO nanotube arrays were directly grown on Zn foil.[20] Generally, the length of the aligned ZnO nanorods grown from solution is less than 10 μm while the diameter is relatively tunable. On the other hand, since the first report on ZnO nanobelts,[2a] they have attracted intensive interest due to their unique properties and widespread potential applications.[21] While numerous vapor-phase-deposition routes to ZnO nanobelts have been reported, there are only a few reports on the wet chemical synthesis of ZnO nanobelts.[22] Recently, novel ZnO nanobelt arrays were grown directly on zinc substrates by controlled thermal oxidation at high temperatures (~600 °C).[23] However, it remains a great challenge to fabricate ZnO nanobelt arrays grown on substrates in solution at low temperatures. Herein, we report a solution-phase growth of large-scale, ultralong ZnO nanowire/nanobelt arrays with honeycomb-like micropatterns on zinc substrates under hydrothermal conditions.

In a typical synthesis, a piece of zinc foil (1 cm × 1 cm, ~1 mm in thickness, 99.99%, Alfa Aesar, pretreated by sonication in acetone and water successively and dried in air) was added to an autoclave containing 10 mL aqueous solution of NaOH (0.48 M or 2 M) and $(NH_4)_2S_2O_8$ (0.095 M or 0.4 M), which was then put into an oven at 150 °C for 2 days (or 18 h). After the hydrothermal reaction, the foil was collected from solution, rinsed with deionized water and dried in air. The obtained ZnO nanowires/nanobelt arrays were characterized by scanning electron microscopy (SEM, AMARY 1910, 10 kV), transmission electron microscopy (TEM, JEOL JEM 200CX, 160 kV), high-resolution TEM (HRTEM, FEI Technai F30, 300 kV), powder X-ray diffraction (XRD, Rigaku Dmax-2000, Cu Kα) and photoluminescence (PL) spectroscopy (F-4500, He–Cd laser of 325 nm).

When the zinc foil was immersed in the alkaline oxidant solution containing 0.48 M NaOH and 0.095 M $(NH_4)_2S_2O_8$ at room temperature (~22 °C), a gray solid film gradually grew on the Zn foil, which was accompanied by the evolution of gas bubbles with an ammoniac pungent odor, indicating the formation of NH_3. After 2 days of reaction under ambient conditions, large-area arrayed ZnO nanorods ~30 nm in diameter were grown on the Zn foil (Fig. 1). An overview SEM image is presented in Fig. 1a, which shows that highly uniform and dense ZnO nanorods were formed on the Zn substrate. A side view shown in Fig. 1b suggests that these well-aligned ZnO nanorods are oriented almost perpendicularly to the surface of the substrate and are typically ~30 nm in diameter and ~200 nm in length. The XRD pattern of the ZnO nanorod arrays grown on the Zn substrate together with that of the original Zn foil is presented in Fig. S1, which suggests that the blank Zn substrate consists of pure metallic Zn (JCPDS card no. 04-0831) whereas the nanorod arrays grown on the substrate show reflections clearly indexed to the wurtzite ZnO (JCPDS card no. 36-1451) in addition to the reflections attributed

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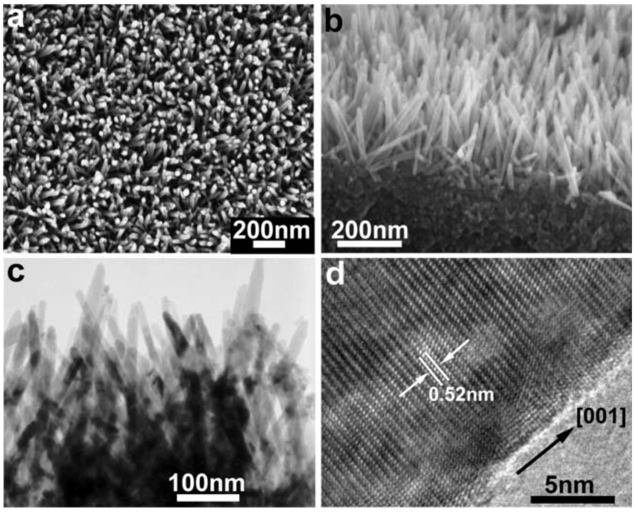

Fig. 1 SEM (a,b), TEM (c), and HRTEM (d) images of ZnO nanorod arrays grown on Zn foil at room temperature for 2 days. [$(NH_4)_2S_2O_8$] = 0.095 M; [NaOH] = 0.48 M.

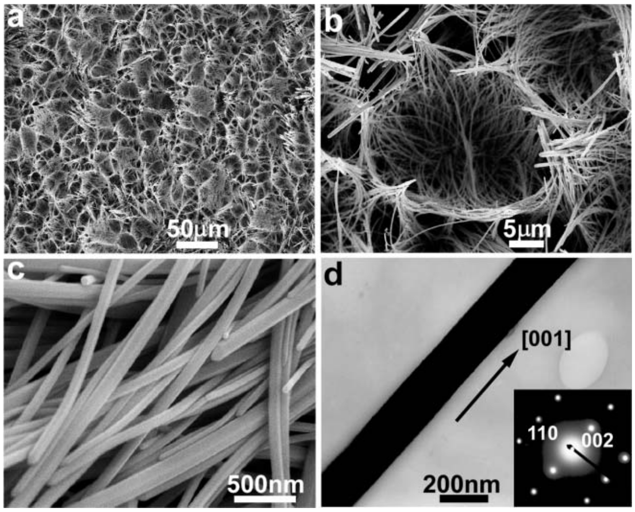

Fig. 2 SEM (a–c) and TEM (d) images of ZnO nanowire arrays hydrothermally grown on Zn foil at 150 °C for 2 days. Inset shows the related ED pattern. [$(NH_4)_2S_2O_8$] = 0.095 M; [NaOH] = 0.48 M.

to the Zn substrate. Fig. 1c illustrates a typical TEM image of the ZnO nanorods peeled off from the Zn substrate, which confirms that the nanorods are uniform in diameter ($\sim$30 nm). The HRTEM image shown in Fig. 1d reveals clear lattice spacing of 0.52 nm corresponding to the *d* spacing of the (001) crystal plane, indicating the preferential growth of the ZnO nanorods along the [001] direction. The reaction that accounts for the ZnO nanorod growth is essentially a surface oxidation process:

$$\begin{gathered} \mathrm{Zn} + 4\ \mathrm{NaOH} + (\mathrm{NH_4})_2\mathrm{S_2O_8} \rightarrow \\ \mathrm{ZnO} + 2\ \mathrm{Na_2SO_4} + 2\ \mathrm{NH_3}\uparrow + 3\ \mathrm{H_2O} \end{gathered}$$

This oxidation process is reminiscent of the reaction between copper and $(NH_4)_2S_2O_8$ in NaOH solution, which was previously used to grow $Cu(OH)_2$ nanotube arrays on the Cu substrate.[24]

Interestingly, ultralong ZnO nanowire (longer than 20 μm) arrays with honeycomb-like micropatterns can be grown on the Zn substrate if the synthesis is carried out at elevated temperatures under otherwise similar conditions. As shown in Fig. 2a, a large-scale thin film of long ZnO nanowire (20–50 μm) arrays formed unique micropatterns of honeycomb-like structures typically ranging from 10 to 30 μm in size on the Zn substrate after the Zn foil was immersed in the reaction solution containing 0.48 M NaOH and 0.095 M $(NH_4)_2S_2O_8$ and hydrothermally treated at 150 °C for 2 days. The corresponding XRD pattern suggests that pure wurtzite ZnO formed on the Zn substrate (Fig. S1). An enlarged image of the honeycomb-like structure is shown in Fig. 2b, which indicates that these structures were formed when the collapsing ZnO nanowires from opposite directions met to bundle together between two neighboring areas. The diameter of the ZnO nanowires is measured to range from 60 to 200 nm (Fig. 2c) and the electron diffraction (ED) pattern of a single nanowire suggests that each ZnO nanowire is a single crystal oriented along the *c*-axis (Fig. 2d), similar to the growth direction of the ZnO nanorods obtained at room temperature. It has been reported that aligned carbon nanotubes were forced to bend and bundle together under the surface tension effects of the evaporating water between the nanotubes[25] and aligned carbon nanotubes self-assembled into honeycomb-like micropatterns due to capillary forces when a water droplet was spreading between the nanotubes.[26] Such a capillary-driven self-assembly of flexible 1D structures represents a new type of coalescence process[27] and may be also used to explain the current formation of the honeycomb-like micropatterns consisting of ultralong ZnO nanowire arrays. Namely, the aligned ZnO nanowires grew vertically on the Zn substrate in solution and then the capillary action forced these long nanowires to bend and bundle together during drying. To the best of our knowledge, this is the first observation of capillary-driven self-assembly of ZnO nanowire arrays into complex hierarchical patterns.

If the NaOH and $(NH_4)_2S_2O_8$ concentrations were increased to 2 M and 0.4 M, respectively, the hydrothermal growth of ZnO on the Zn foil at 150 °C resulted in the formation of ultralong ZnO nanobelt arrays with honeycomb-like micropatterns on the Zn substrate. The overview image shown in Fig. 3a suggests that long wire-like ZnO nanostructures (mostly more than 50 μm in length) were densely aligned into large-area honeycomb-like micropatterns on the substrate, which were demonstrated to be pure wurtzite ZnO crystals by the related XRD pattern (Fig. S1). An enlarged SEM image (Fig. 3b) and a representative TEM image (Fig. 3c) show that most of the 1D ZnO nanostructures are actually ZnO nanobelts $\sim$60 nm in thickness and $\sim$100–400 nm in width. Fig. 3d presents a typical HRTEM image of the nanobelt together with the related ED pattern, which reveals that the ZnO nanobelt is a single crystal grown along the [001] direction and enclosed by the $\pm(2\bar{1}0)$ and $\pm(010)$ planes as the top/bottom and side surfaces, respectively.

In order to trace the morphological evolution, the ZnO nanoarrays obtained at the earlier stages of the hydrothermal growth of ZnO on the Zn foil were examined by SEM observation (Fig. S2). After 0.5 h of reaction at 150 °C, nearly vertically oriented arrays of ZnO nanorods with diameters mostly less than 60 nm and lengths around 200 nm were obtained. When the reaction time was increased to 2 h, honeycomb-like micropatterns consisting of ZnO nanowires/nanobelts up to $\sim$5 μm in length with the nanobelts being the minority product were obtained.

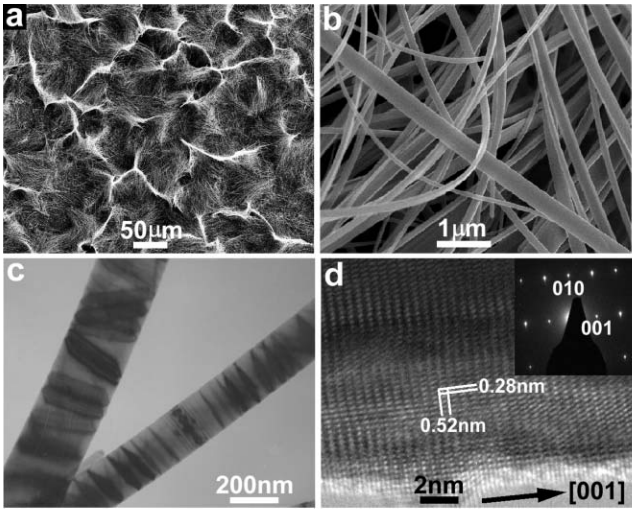

Fig. 3 SEM (a,b), TEM (c), and HRTEM (d) images of ZnO nanobelt arrays hydrothermally grown on Zn foil at 150 °C for 18 hours. Inset shows the related ED pattern. $[(NH_4)_2S_2O_8] = 0.4$ M; $[NaOH] = 2$ M.

After 10 h of reaction, a large number of longer nanobelts ($\sim$20 μm in length) were evident. If the reaction time was further prolonged to 18 h, the micropatterned arrays of ZnO nanobelts $\sim$50 μm in length would be produced as shown in Fig. 3. This result indicates that relatively short and thin [001]-oriented ZnO nanorods were grown on the Zn substrate at the beginning. With increasing reaction time, the nanorods gradually grew longer along the [001] direction and became wider along the [010] direction with the area of the $(2\bar{1}0)$ plane gradually widened, leading to the formation of the final ultralong ZnO nanobelt arrays. It has been documented that the growth kinetics plays a key role in determining the morphology of the ZnO nanostructures produced by thermal evaporation.[2b] The formation mechanism of the ZnO nanobelts grown on the Zn substrate in alkaline oxidant solution is still under investigation. Generally, the hydrothermal growth at higher NaOH and $(NH_4)_2S_2O_8$ concentrations would significantly accelerate both the dissolution process of Zn from the substrate and the deposition process of ZnO onto the growing ZnO nanostructures, which might exert subtle control over the growth kinetics. Under suitable kinetic growth conditions, ZnO nanobelts would evolve from the original ZnO nanorods accompanying the growth along the length direction.

The room temperature PL spectra of the as-prepared ZnO nanoarrays grown on the Zn substrate were measured (Fig. S3). It can be seen that the ZnO nanorods grown at room temperature show three broad peaks around 395 nm, 468 nm, and 526 nm. It was reported that the ZnO nanorods obtained by the CVD method showed three emitting bands including a strong UV emission $\sim$386 nm attributed to the near band edge emission of the wide band-gap ZnO, a weak blue band (440–480 nm) with its mechanism not yet clear, and a very weak green band (510–580 nm) attributed to the deep level emission due to oxygen vacancies.[8a] Accordingly, the three PL peaks observed for the current ZnO nanorod arrays may be interpreted in a similar way. In contrast, the micropatterned arrays of ZnO nanowire grown at 150 °C exhibit a strong excitonic emission at 389 nm together with the blue emission but do not show the green emission, indicating that the ZnO nanowires have negligible oxygen vacancies. The micropatterned arrays of ZnO nanobelts grown at the same temperature do not show the green emission either, but the excitonic emission slightly red-shifts to 396 nm and becomes somewhat broader.

In conclusion, the hydrothermal synthesis of large-scale, ultralong ZnO nanowire and nanobelt arrays with honeycomb-like micropatterns has been realized by simple surface oxidation of zinc foil in aqueous solutions of NaOH and $(NH_4)_2S_2O_8$ at 150 °C. This solution approach to fabricate 1D ZnO nanostructures with controlled morphologies and micropatterns can be easily scaled up and potentially extended to the fabrication and assembly of 1D nanostructures of other oxide systems.

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