Controlled one-step fabrication of highly oriented ZnO nanoneedle/nanorods arrays at near room temperature†

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Highly oriented ZnO nanoneedle/nanorods arrays have been fabricated by direct oxidation of zinc foil in alkaline zincate ion solution at near room temperature (20 °C for nanoneedles, 30 °C for nanorods).

One-dimensional (1D) semiconductor nanostructures have received a great deal of attention in recent years because their unique optoelectronic, mechanical, magnetic and chemical properties provide various potential applications.[1] The properties of 1D nanomaterials depend strongly on their dimensions and morphologies.[2] Thus, the controlled synthesis of 1D nanomaterials on a large scale and under mild conditions is very important from the viewpoint of both basic science and technology.[3,4] On the other hand, zinc oxide (ZnO) is one of the important semiconductors, mainly due to its wide band gap (3.37 eV) and large excitation binding energy (60 meV). Therefore, 1D ZnO nanostructures have potential applications in room-temperature ultraviolet lasing,[5] blue-ultraviolet (UV) region optoelectronic devices,[6] photocatalysts,[7] field emission devices,[8] piezoelectric transducers and actuators,[9] solar cells and so on.[10] For the growth of aligned ZnO nanostructures (*e.g.* nanowires, nanorods, nanoneedles), gas-phase deposition is one of the principal technologies. Although this method can produce high quality ZnO nanostructures, it is a high-energy consumption route. For example, thermal evaporation approach, vapor-transport and metal-organic chemical vapor depositions (MOCVD) have to be carried out at 900 °C,[11] 600–900 °C,[12,13] and 400–600 °C,[14–16] respectively. Various solution-phase reactions[17] also have been applied for fabricating homogeneous ZnO nanoarrays at low temperature (90–95 °C) through a two-step wet chemical process including the coating of a substrate with nanosized ZnO seeds and successively the thermal decomposition of Zn-organic complexes.[18–21] Several electrochemical deposition methods have been reported for fabricating ZnO nanorods arrays; the products were always limited to the electrode area.[22] However, it is still a challenge to fabricate highly oriented ZnO nanorods arrays to a sub-100 nm regime at a low temperature and on a large scale.[23] Here, we report a simple one-step wet method for growing highly oriented uniform 1D ZnO nanostructures arrays on a large scale by direct oxidation of a zinc foil in an aqueous alkali solution of zincate ions ($(Zn(OH)_4{}^{2-})$) at near room temperature. Furthermore, the shape of the ZnO nanostructures can be modulated from needles to rods by the control of reaction temperature.

Typically, the alkali zincate solution was prepared by dropping 10 mL 0.5 M aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ into 10 mL 4.0 M aqueous solution of KOH under stirring. The growth of well-aligned ZnO nanostructures was achieved by suspending a clean zinc foil (1 cm × 2 cm, 99.98%, Strem Company pretreated by sonication in ethanol for 5 min and dried with a dry nitrogen stream) upside down in 20 mL zincate solution and sealing the system in a beaker. After reaction at 20 °C or 30 °C for 12 h, the zinc foil was taken out and rinsed with de-ionized water and dried with a dry nitrogen stream under ambient conditions before characterization. Scanning electron micrographs (SEM) were taken by the use of an FEI Sirion 200 scanning electron microscope. X-ray diffraction (XRD) was carried out by using an X-ray diffractometer model D8 Advance (Bruker) with $Cu_{K\alpha}$ radiation (λ = 1.5418 Å). Transmission electron micrographs (TEM) and high resolution TEM were taken on a JEM 2010 (200 kV) (JEOL) or Tecnai G2 F20 (200 kV) (FEI) transmission electron microscope.

The morphology of the ZnO nanoneedles film prepared at 20 °C was characterized by SEM (Fig. 1A&B). As shown in Fig. 1A, highly uniform and dense ZnO nanoneedles were grown on the zinc foil and oriented perpendicularly to the surface of the substrate. Fig. 1B is a tilt view of the needles array. It is clear from this figure that the needles are typically 800–900 nm in length. The diameters of the needle tips and roots are 6–10 nm and 90–100 nm,

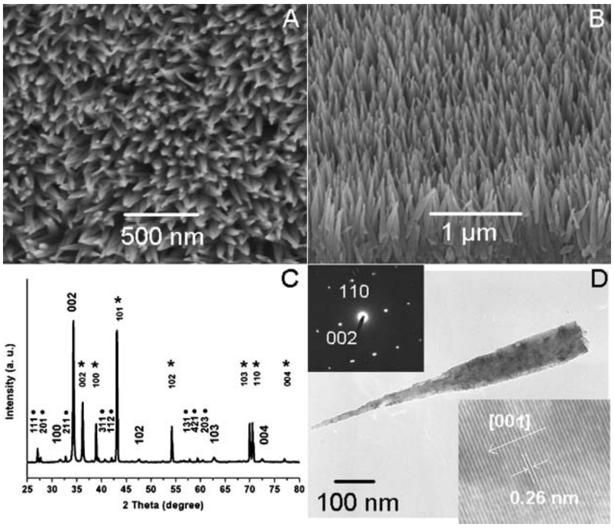

Fig. 1 SEM (A, B), XRD (C) and TEM (D) of as-formed ZnO nanoneedles prepared by reaction at 20 °C for 12 h.

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respectively (Fig. 1D). The XRD pattern of the nanoneedles shows a strong diffraction peak at $2\theta = 34.4^\circ$ (002) with full width at half-maximum of only 0.2–0.3°, indicating the highly preferential growth of ZnO nanoneedles along their *c*-axis (perpendicular to the substrate surface, JCPDS 36-1451).[22] The diffraction peaks related to the other crystal phases are either very weak or nonexistent. Those peaks marked with stars are attributed to the zinc foil and there are small amounts of orthorhombic $Zn(OH)_2$ resulting from the side reaction $Zn(OH)_4{}^{2-} = Zn(OH)_2\downarrow + 2OH^-$ (marked with dots, JCPDS 38-0385, Fig. S1). $Zn(OH)_2$ nanocrystal can be completely removed by sonication of the sample in potassium hydroxide aqueous solution for 5 s (Fig. S2); the SEM image shows no obvious change in the morphology of the array, and no crystalline $Zn(OH)_2$ diffraction line was detected in the XRD pattern. Furthermore, the selected area electron diffraction (SAED) pattern and the high-resolution TEM image of tens of ZnO nanoneedles reveal that they are a single crystal. According to the features of the diffraction pattern, the preferential growth direction of the needle-like ZnO nanocrystals is their [001] direction. The displayed lattice spacing of 0.26 nm corresponds to the lattice spacing of the wurtzite ZnO (002) plane, which also indicates that the [001] direction is the preferential growth direction of ZnO nanoneedles.[24]

The morphology of the ZnO nanostructures was sensitive to reaction temperature. Fig. 2 illustrates the morphology and structural characterization results of the ZnO nanostructures prepared by reaction at 30 °C for 12 h. It is interesting to find that hexagonal ZnO nanorods were produced at this temperature. The nanorods are vertical to the substrate and covered the substrate compactly and uniformly on a large scale (Fig. S3). They are typically 550–850 nm in length, 30–40 nm in diameter at their top parts (Fig. 2A&B) and 50–60 nm in diameter at their bottom parts (Fig. 2D). The XRD diffraction pattern, SAED and high-resolution TEM results shown in Fig. 2C and 2D, respectively, also confirm that the nanorods are single crystals and that they were grown preferentially in their [001] direction.

The room temperature photoluminescence (PL) spectrum of the as-prepared ZnO nanoneedle/nanorods array has been measured. The PL spectrum of the nanoneedles array is similar to that of the nanorods array. Figure S4 is the PL spectrum of the as-prepared ZnO nanoneedles array. Broad-band UV-Visible luminescence over the 370–600 nm region is observed. This phenomenon may indicate there is a large fraction of oxygen vacancies in the as-prepared ZnO nanostructures.[25]

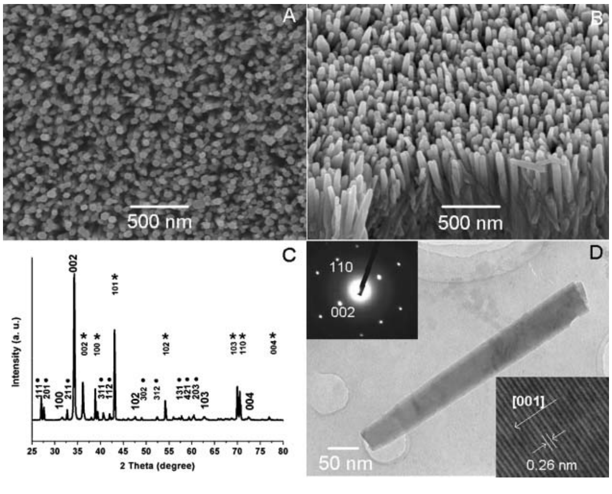

Fig. 2 SEM (A, B), XRD (C) and TEM (D) of as-formed ZnO nanorods prepared by reaction at 30 °C for 12 h.

In order to fully understand the effects of reaction temperature, we investigated the nanostructures grown for different times. The morphology of the nanostructures grown at 30 °C for 15 min is similar to that of the nanostructures grown at 20 °C for the same time; needle-like ZnO nanocrystals covered the zinc foil compactly (Fig. S5A&C). When the growth time was increased to 300 min, reaction at 20 °C resulted in the formation of a nanoneedles array with sharp tips (several nanometers in diameter, Fig. S5B). In contrast, reaction at 30 °C produced needles with thicker tips (about 20 nm in diameter, Fig. S5D). On further increasing the reaction time to 12 h, as can be seen from Fig. 1A and Fig. 2A, the shapes of the nanostructures prepared at different temperatures are obviously different.

The growth of ZnO nanostructures in alkaline zincate solution with Zn foil as a reactant can be simply represented by the following reactions: $Zn + 2H_2O + 2OH^- \rightarrow Zn(OH)_4{}^{2-} + H_2\uparrow$, $Zn(OH)_4{}^{2-} = ZnO\downarrow + H_2O + 2OH^-$. During the process of ZnO nanocrystal growth, the dissolution of Zn atoms into the solution caused a concentration gradient of zincate ion in the region closest to the zinc foil. As a result, the growing rates along the ZnO (001) planes decreased from the nanocrystal roots to the tips and finally nanoneedles were formed. However, the effect of the concentration gradient was weakened by slightly increasing the reaction temperature. Therefore, ZnO nanorods were produced at a temperature of 30 °C, while nanoneedles were generated at 20 °C.

The heterogeneous nucleation at the initial deposition stage is crucial for the growth of a highly oriented perpendicular nanoneedle/rods array. Did the naturally formed oxide coating on the zinc surface cause the heterogeneous nucleations? We treated the surface of an as-received Zn foil by reaction with 1 M HCl for 5 min or polishing with an abrasive paper (1200 mesh) to remove its oxide coating. After reaction in the alkaline zincate solution for 5 h, ZnO nanoneedles or nanoplates covered the foil surface in a disorderly and unsystematic fashion (Fig. S6&7). These phenomena indicate that ZnO seeds can nucleate on the freshly formed Zn surface. The inhomogeneous morphology of the nanostructures resulted from the inhomogeneity of the treated substrate surface. It was reported that an oriented ZnO 1D nanostructure can be grown epitaxially on bare substrates such as Al_2O_3 (17% lattice mismatch).[15a] Furthermore, Zn and ZnO crystals have the same hexagonal structures, a relatively small lattice mismatch of 4.9 and 18.0% along the *c* and *a* axes.[23] Thus, ZnO 1D nanostructures may be formed when a continuous Zn resource can be provided.[23] We also investigated the source of the zinc in the ZnO nanostructures by replacing zincate solution with potassium hydroxide or neutral zinc nitrate solution. In these two cases, no ZnO 1D nanostructure was formed on the zinc surface. These may indicate that the zinc in the ZnO rods comes from both the zinc foil and the solution. In the literature, formation of ZnO nanorods always needs a relatively high temperature; this is mainly due to it being necessary for decomposition of Zn-organic complexes to provide a Zn resource continuously.[15,18,19,23] In our conditions, a Zn resource can be continuously provided by zincate solution and the reaction of Zn foil with hydroxide at room temperature. Thus, a highly oriented ZnO nanoneedle/rods array is formed on the Zn surface.

In conclusion, highly oriented uniform ZnO nanoneedle/hexagonal nanorods arrays can be fabricated by simple oxidation of zinc foil in an alkaline aqueous zincate ion ($Zn(OH)_4^{2-}$) solution at different temperatures (20 °C for the needles array and 30 °C for the rods array). To the best of our knowledge, this is the first one-step wet approach for fabricating ZnO 1D nanostructure arrays in such mild conditions. The method developed here can be easily scaled up to fabricate ZnO nanostructures for many important applications in the nanomaterials community.

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