A novel ZnO nanostructure: rhombus-shaped ZnO nanorod array†

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A facile scalable two-step approach based on a low-temperature aqueous electrodeposition and a solid-state crystal phase transformation process was developed to grow rhombus-shaped ZnO nanorod arrays which showed markedly improved hydrogen storage capacity.

Zinc oxide (ZnO), an important semiconductor with a direct wide-band-gap of ~3.37 eV and a high exciton binding energy of 60 meV at room temperature,1 has been extensively investigated because of its great potential use for piezoelectric transducers,2 optical waveguides,3 surface acoustic wave filters,4 chemical and gas sensors,5 light-emitting diodes,6 dye-sensitized solar cells (DSSCs),7 and so forth. Various synthesis methods have been developed to produce 1D ZnO nanostructure arrays, such as chemical vapor deposition,8 physical vapor deposition,9 metal–organic vapor phase epitaxy,10 and anodic aluminium oxide (AAO) templates induced fabrication.11 However, because of the intrinsic growth habit of the hexagonal wurtzite ZnO, most of the 1D nanostructures were obtained. Here, the electrochemical deposition achieved the goal. Subsequent heat treatment of the original hexagonal Zn(OH)F NRs resulted in easily rhombus-shaped ZnO NRs, which were then used as the precursor to prepare 1D ZnO nanostructures with the same rhombic cross-section by thermal treatment.

In a typical electrodeposition procedure, the rhombus-shaped Zn(OH)F nanorod arrays were directly electro-deposited onto a tin doped indium oxide (ITO) glass substrate with a pre-prepared seedlayer of ZnO from an aqueous electrodeposition route toward large-scale arrays of rhombus-shaped Zn(OH)F NR arrays. From this SEM image, it can be seen that the Zn(OH)F NRs are 80–120 nm in diameter, and their end planes hold a clear-cut rhombic contour. The cross-section SEM (Fig. S3 ESI†) of Zn(OH)F NR arrays shows that the as-synthesized NRs are vertically aligned on the substrate. XRD results prove the feasibility of formation of Zn(OH)F by electrodeposition, and all of the diffraction peaks can be indexed to a pure orthorhombic phase (SG: \textit{Pna2}_1) with lattice constants \(a = 10.13\ \text{Å}, \ b = 4.760\ \text{Å}, \) and \(c = 3.120\ \text{Å}, \) which is in good agreement with the literature values for the orthorhombic system Zn(OH)F (JCPDS 74-1816). In the previous reports on Zn(OH)F samples synthesized by chemical precipitation, no ordered 1D nanostructures were obtained. Here, the electrochemical deposition achieved the goal. Subsequent heat treatment of Zn(OH)F NRs resulted in easily rhombus-shaped ZnO NRs, as shown in Fig. 1(c). Fig. 1(d) shows the XRD pattern of rhombus-shaped ZnO NRs with hexagonal wurtzite crystal structure (SG: \textit{P6}_3mc, JCPDS 36-1451), corroborating a crystal phase transformation from orthorhombic Zn(OH)F to hexagonal ZnO upon thermal treatment, without altering the original rhombic shape of Zn(OH)F NRs.

![Fig. 1](a) SEM image and (b) XRD pattern of as-electrodeposited Zn(OH)F NR arrays; (c) SEM image and (d) XRD pattern of rhombus-shaped ZnO NR arrays derived from Zn(OH)F NR arrays.

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ZnO NRs with rhombic cross-section are radically different in shape from those hexagon-shaped ZnO NRs obtained by electrodeposition in the absence of NaF, as displayed in Fig. 2(a). The experimental investigation revealed that NaF played a decisive role in the formation of rhombus-shaped NRs.

Under the same conditions, by replacing NaF with NaCl in the electrolyte, 2D arrays of hexagonal nanosheets about 50 nm in thickness were obtained (Fig. 2(b)), suggesting that the presence of F⁻ ions was crucial for the growth of rhombus-shaped NRs, instead of hexagon-shaped ZnO NRs. Besides, we also demonstrate that applied electrochemical parameters make no contribution to the emergence of rhombic end planes.

A low electrodeposition potential of −0.5 V resulted in the formation of flower-like 3D nanostructures composed of rhombus-shaped NRs, as shown in Fig. 2(c), which suggested that the applied potential merely affected the alignment pattern of rhombic NRs, not their shapes. Fig. 2(d) indicates that at the initial electrodeposition stage (5 min), NRs exhibited the shape of a rhombic prism, not a gradual shape evolution process. Rhombic ZnO crystals were also synthesized even on naked ITO substrates without ZnO seeds, the only difference being the size (Fig. S4 ESI†).

Fig. 3(a) and (b) show the typical high-resolution TEM (HRTEM) images of an acute angle and an obtuse angle of the same rhombic end plane. It is obvious that the rhombus-shaped ZnO NRs are polycrystalline and composed of many tiny single crystals with different growth orientations. The ring-like selected area electron diffraction (SAED) patterns on the rhombic end plane (insert in Fig. 3(b)) further confirm this structure characteristic. Identically, the as-electrodeposited Zn(OH)F NRs have been proved to be polycrystalline as well by HRTEM observations (see Fig. S6 ESI†). These HRTEM and XRD characterizations demonstrate that the polycrystalline nature of rhombus-shaped ZnO NRs results from the polycrystalline precursor Zn(OH)F NRs.

Based on the above facts, the fabrication process of the unique rhombus-shaped ZnO nanorod arrays is illustrated schematically in Fig. 4. The formation of the well-defined Zn(OH)F NR arrays and ZnO NR arrays is supposed to be based on three ionic reactions (1–3). Different from the previous chemical synthesis approach,15 in our case, a pH value increase was observed during the electrodeposition process, suggesting that extra OH⁻ ions were produced in the solution and only part of them were in reaction with Zn²⁺ and F⁻ ions to form small Zn(OH)F crystals. These crystals might agglomerate into rhombic crystalline particles, which then form polycrystalline rhombic shaped NR arrays via vertical extensive growth. Subsequent high temperature pyrolysis of the Zn(OH)F arrays afforded polycrystalline rhombus-shaped ZnO NR arrays.

![Fig. 2](image2.png)

**Fig. 2** SEM images of (a) hexagon-shaped NR arrays as-electrodeposited in the absence of NaF and (b) hexagonal nanosheets as-electrodeposited by replacing NaF by NaCl in the electrolyte; SEM images of (c) flower-like 3D nanostructures composed of rhombus-shaped NRs obtained at a low potential of −0.5 V and (d) rhombus-shaped crystals at the initial electrodeposition stage of 5 min.

![Fig. 3](image3.png)

**Fig. 3** Typical high-resolution TEM images of (a) an acute angle and (b) an obtuse angle of the rhombic end plane of the same ZnO NR. The inset in (b) represents the SAED pattern on the rhombic end plane.

To evaluate the crystalline quality of the sample prepared by this novel two-step approach, room-temperature photoluminescence (PL) behavior of the polycrystalline rhombus-shaped ZnO NR arrays was investigated, as shown in Fig. 5. Similar to the widely reported single-crystalline ZnO NR arrays, our polycrystalline ZnO NR arrays also exhibit a similar high-intensity ultraviolet (UV) emission centered at 392 nm which is believed to originate from free excitonic emission of ZnO.16 However, the well-known stronger and broader emission situated in the yellow–green part of the visible spectrum is extremely weak, which indicates that our
rhombus-shaped ZnO NR arrays have low intrinsic defects. In view of the above analysis, generally speaking, comparing the ratio of the relative PL intensity of the excitonic emission to the visible emission \( (I_{\text{exc}}/I_{\text{vis}}) \) is a way to evaluate the quality of the ZnO films.\(^1\) Therefore, in our PL results, the high intensity ratio of \( I_{\text{exc}}/I_{\text{vis}} \) is evidence of the highly crystalline quality of the obtained polycrystalline rhombus-shaped ZnO NR arrays since their visible emission is weak.

Hydrogen adsorption and desorption experiments were performed at room temperature and under the pressure of 5.05 MPa (the high-point pressure of the apparatus). As shown in Fig. 6, the hydrogen storage capacity of the rhombus-shaped polycrystalline ZnO NRs is 2.53 wt% at 5.05 MPa, and about 72% of the stored hydrogen can be released under ambient pressure, which is superior to the reported results for Mg doped ZnO NRs\(^1\) and single-crystalline ZnO NRs\(^1\) under identical conditions, indicating that our polycrystalline ZnO NRs can take up much more hydrogen. In addition, our results also show that high pressure is beneficial for hydrogen incorporation in ZnO NRs, although the mechanism is not clear at present, especially for polycrystalline ZnO NRs. Based on a recent first-principle density functional theory presented by Van de Walle,\(^2\) Pan et al.\(^3\) and Wan et al.\(^4\) tentatively divided the absorbed hydrogen located in various ZnO lattice sites (see Fig. S7 ESI\(^\dagger\)) into different existing states, including H\(^+\), H\(^-\), neutral atomic hydrogen H\(^0\), and H\(_2\). The H\(^+\) is absorbed at oxygen sites, forming an O–H bond. This leads to irreversible hydrogen uptake, so only about 72% of the stored hydrogen can be released under ambient pressure. The formation of an O–H bond leads to oxygen deficiency which can be verified by PL analysis of hydrogen desorbed ZnO NRs. After a hydrogen absorption and desorption cycle, the intensity of the UV emission peak of the NRs became comparatively weak, and the intensity of the green emission peak related to oxygen vacancies\(^5\) obviously increased (see Fig. S8 ESI\(^\dagger\)). H\(_2\), H\(^+\), and H\(^-\) located in the interstitial channel, near Zn\(^{2+}\), and oxygen vacancies, respectively, are energetically metastable, resulting in a reversible hydrogen adsorption and desorption.

In conclusion, polycrystalline rhombus-shaped ZnO NR arrays with markedly improved hydrogen storage capacity were synthesized. This configuration is a new member of the family of 1D ZnO nanostructures. The synthesis of the rhombus-shaped ZnO NR arrays could enrich our knowledge of wurtzite crystal growth, and furthermore provide a new avenue for the preparation of unique nanostructures of other functional materials.

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Notes and references