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# Morphology controlled growth of ZnAl-layered double hydroxide and ZnO nanorod hybrid nanostructures by solution method<sup>+</sup>

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We report the morphological evolution of ZnAl-based hybrid nanostructures from ZnAl layered double hydroxide (LDH) to ZnO nanorods (NRs) grown by a hydrothermal method depending on the thickness of the  $Al_2O_3/ZnO$  double seed layer. The thickness of the  $Al_2O_3/ZnO$  double seed layer was controlled by an atomic layer deposition system. We found that the ZnAl-LDH growth can mainly be attributed to the hydroxide reactions between the base solution and  $Al_2O_3$  as a sacrificial layer. As the ZnO seed layer covered the  $Al_2O_3$  film, the concentration of Al hydroxide was significantly reduced, but that of the Zn hydroxide increased enough to make ZnO NRs. Our results show that hybridizing these ZnAl-LDH and ZnO NRs by controlling the amount of Al cations is possible, and thus we can design a new material system by taking advantage of the unique properties of ZnAl-LDH and ZnO NRs for future applications.

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# 1. Introduction

Over the past few decades, ZnO has achieved considerable attention for its superior properties including a large exciton binding energy, a superior piezoelectric constant, and excellent thermal and chemical stability. Due to these attractive properties, ZnO is used in various applications such as ultraviolet detectors,<sup>1,2</sup> nanogenerators,<sup>3–5</sup> light-emitting diodes,<sup>6,7</sup> and chemical sensors.<sup>8</sup> Moreover, the easy fabrication of ZnO-based nanostructures has made them available as basic building blocks with various morphologies, flakes, needles, ribbons, particles, flowers, and rods.<sup>9–12</sup> ZnO nanorods (NRs) have gained much attention because their crystal structure possesses the intrinsic potential to grow along with the *c*-axis under controlled growth factors such as the selection of a hydroxide anion generating agent, the pH of the solution, the zinc ion precursor, and the type of seed layer.<sup>9,13,14</sup>

In addition, when  $\text{Zn}^{2+}$  cations are isomorphously substituted by trivalent cations, layered double hydroxide (LDH) structures are obtained.<sup>15-20</sup> The general formula of LDH compounds is  $[\text{Zn}_{(1-x)}M^{\text{III}}_{(x)}(\text{OH})_2][A^{n-}_{x/n} \cdot m\text{H}_2\text{O}]$  ( $M^{\text{III}} = \text{Al}$ , Cr, Ga;  $A^{n-} = \text{CO}_3^{2-}$ , Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>).<sup>21,22</sup> The excess charges of the trivalent cation produce an overall positive charge in brucite-type structures, which is balanced by the intercalation of anions between LDHs.18 ZnAl-LDH has been mainly introduced as part of the LDH family because of the wide tunability of the metal cations, the Zn<sup>2+</sup>/Al<sup>3+</sup> molar ratios, and the anion exchange capacity that results in a variety of host-guest assemblies. Twodimensional (2-D) layered nanostructures with versatile physical and chemical properties are driven by a wide range of molecules that can be introduced into the interlayer.23 For these reasons, ZnAl-LDH has been studied as an efficient luminescence source,<sup>24</sup> nanocomposite hydrogel,<sup>25</sup> catalyst,<sup>26</sup> energy storage,<sup>27</sup> absorbent and anion-exchanger,28 chemical nanocontainer,29 and biological nanocarrier,<sup>30</sup> as well as a precursor for metal oxide and mixed metal oxide.<sup>31,32</sup> Therefore, hybridizing these ZnO NRs and ZnAl-LDH structures is expected to be promising due to their complementary effects. Especially, controllable luminescence centers provided by ZnO NR and ZnAl-LDH hybrid nanostructures would be beneficial for their applications to the optoelectronic device and photocatalyst which are corresponding to their spectral wavelength ranges. In this work, we propose an novel approach for the controlled fabrication of ZnAl-LDHs, ZnO NRs, and their hybrid structures on Si substrate by combining the atomic layer deposition (ALD) method and a hydrothermal process. In addition, we report on the formation mechanism of ZnAl-LDH and ZnO NR layers and the evolution mechanism between them by controlling the Al<sub>2</sub>O<sub>3</sub>/ZnO seed layer. And a controllable luminescence mechanism has been reported from these ZnAl-LDH and ZnO NR hybrid nanostructures.

## 2. Experimental

#### 2.1 Fabrication of ZnAl-LDH and ZnO NR hybrid structures

A p-type Si (100) wafer with a resistivity of 1–10  $\Omega$  cm was used as a substrate. To remove organic contaminants, the wafer pieces



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were immersed in a boiling solution of NH<sub>4</sub>OH (30%)/H<sub>2</sub>O<sub>2</sub> (30%)/H<sub>2</sub>O (1 : 1 : 5, v/v) at 60  $^{\circ}$ C for 30 min. The wafer pieces were then rinsed thoroughly with deionized water. Thicknesscontrolled Al<sub>2</sub>O<sub>3</sub>/ZnO double seed layers were prepared by the ALD method using trimethylaluminum (TMAl), diethylzinc (DEZn), and water (H<sub>2</sub>O) as precursors for Al, Zn, and O, respectively. Under optimal conditions, the growth rates of the  $Al_2O_3$  film and the ZnO film were 0.9 Å per cycle and about 1.5 Å per cycle for a substrate temperature of 200 °C, respectively. After growing a 10 nm-thick Al<sub>2</sub>O<sub>3</sub> layer on the Si substrates, ZnO layers with different thicknesses (3, 6, 9, and 15 nm) were grown on the Al<sub>2</sub>O<sub>3</sub> layer to form the double seed layer. ZnAl-LDH and ZnO NR layers were grown on the seed layergrown Si substrate by using a low temperature hydrothermal method. Zinc nitrate hexahydrate  $(Zn(NO_3)_2 \cdot 6H_2O, 99.99\%)$ purity, Aldrich Company) and hexamethylenetetramine ((HMT;  $C_6H_{12}N_4$ ), Aldrich Company) were used as a precursor. ZnO NR and ZnAl-LDH layers were grown by dipping the seed layerdeposited substrates into a mixed solution of 60 mM zinc nitrate hexahydrate and 60 mM HMT in deionized (DI) water at 90 °C for 2 h. After the reaction, the samples were cleaned in flowing DI water for 10 min to completely remove the residues from the samples.

# 2.2 Characterization of ZnAl-LDH and ZnO NR hybrid structures

The morphological properties of all the samples were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Hitachi HF-3300) for the cleaved ZnAl-LDH and ZnO NR structures, which were prepared by using a focused ion beam (FIB, Hitachi NB 5000). X-ray diffraction (XRD, RIGAKU D/MAX 2200H) was used to obtain crystallographic structures. Surface chemical states were investigated by X-ray photoelectron spectroscopy (XPS). The optical properties of the ZnAl-LDH and ZnO NRs were investigated by photoluminescence (PL) with a He–Cd 325 nm laser and Raman spectrometer.

### 3. Results and discussion

Fig. 1 shows cross-sectional and top-view SEM images of the synthesized ZnAl-LDH and ZnO NRs with a variation of the thickness of the ZnO layer in the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer. Fig. 1(a) and (b) clearly show the existence of a plate-like structure when single Al<sub>2</sub>O<sub>3</sub> without the ZnO layer was used as a seed layer. This plate-like structure is regarded as a ZnAl-LDH structure,15-18 and was further investigated in the present study by using its structural and optical properties. As the thickness of the ZnO layer in the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer increases to 3 nm, a hexagonal-shaped ZnO NR structure starts to appear between the ZnAl-LDH plates as shown in Fig. 1(c) and (d). As the thickness of the ZnO layer increases further to 6 and 9 nm, the ZnO NR structure is dominantly formed on the surface, as shown in Fig. 1(e)-(h). The increased proportion of the ZnO NRs over the ZnAl-LDH plate structure with an increasing the ZnO layer thickness can be attributed to the presence of a latticematched ZnO buffer layer. However, when the thickness of the ZnO layer reaches 15 nm, no ZnAl-LDH structures were observed; only ZnO NRs were densely packed on the substrate, as shown in Fig. 1(i) and (j). This indicates that the ZnO thickness in the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer plays a crucial role in the formation of the ZnAl-LDHs and ZnO NRs. We will discuss this point later in this study.

To investigate the crystalline structural evolution of the ZnAl-LDH and ZnO NR composites, XRD was performed as shown in Fig. 2. The XRD patterns of the sample grown on an  $Al_2O_3$  layer without a ZnO layer show two strong diffraction peaks corresponding to (003) and (006) reflections of a crystal-line ZnAl-LDH phase with  $R\bar{3}m$  rhombohedral symmetry.<sup>33</sup> The presence of (003) and (006) reflections confirms the layered structure of the ZnAl-LDH materials. With increasing the ZnO layer thickness, ZnAl-LDH diffraction peaks are significantly reduced, and another phase was detected in the XRD spectra.



Fig. 1 FE-SEM images of ZnO NR and ZnAl-LDH hybrid structures grown on Si (100) substrates with variation of the ZnO thickness in the ZnO/Al\_2O\_3 double seed layer.

New observed peaks at  $2\theta = 31.87^{\circ}$ ,  $34.45^{\circ}$ , and  $36.31^{\circ}$  correspond to the (100), (002), and (101) planes of the wurtzite phase ZnO crystal, respectively. Therefore, with increasing the ZnO seed layer thickness up to 6 nm, the ZnAl-LDH and ZnO NRs are mixed on the surface. As increasing the ZnO seed layer to a thickness greater than 9 nm, only the diffraction peaks from ZnO NRs were observed. These results are in good agreement with morphological evolutions observed through SEM. Evidently, the as-prepared ZnAl-LDH on an Al<sub>2</sub>O<sub>3</sub> seed layer and the ZnO NRs on an Al<sub>2</sub>O<sub>3</sub>/ZnO seed layer were of good quality in terms of phase purity and crystallinity.

The detailed crystalline nanostructures were further investigated by using TEM, which provides high spatial resolution and analytical sensitivity. Fig. 3(a)-(c) show low magnification cross-sectional TEM images of the nanostructures on the Al<sub>2</sub>O<sub>3</sub>/ZnO double seed layer with ZnO layer thicknesses of 0, 6, and 15 nm, respectively. Morphology changes from the ZnAl-LDHs to the ZnO NRs, depending on ZnO layer thickness, were clearly observed in the TEM results. Also, from the TEM images, the ALD-deposited Al<sub>2</sub>O<sub>3</sub> and ZnO seed layer of each sample can be seen. The corresponding high resolution-TEM (HR-TEM) images of the selected areas marked by a red box in Fig. 3(a)-(c) are shown in Fig. 3(d)-(f), respectively. As can be seen in Fig. 3(d), most of the amorphous Al<sub>2</sub>O<sub>3</sub> film was turned into a crystal structure with a constant spacing corresponding to the plane of LDHs (Fig. 3(g)). On the other hand, as the ZnO layer thickness increased, the underlying Al<sub>2</sub>O<sub>3</sub> films tended to retain their pristine structure during ZnO NR growth (Fig. 3(e) and (f)). The corresponding HR-TEM images, and the fast Fourier transformation (FFT) micrographs of the selected areas marked by a red box in Fig. 3(d)-(f), are shown in Fig. 3(g)-(i), respectively. As shown in Fig. 3(g), the lattice fringes with a constant spacing of 0.15 nm and 0.20 nm correspond to the (110) and (018) planes of LDH, and the FFT micrograph taken from the magnified area also shows a spot pattern (Fig. 3(g)).



Fig. 2 Normalized  $\theta$ -2 $\theta$  XRD patterns of ZnO NR and ZnAl-LDH hybrid structures grown on Si (100) substrates with variation of the ZnO thickness in the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer.

This indicates that the LDHs have a relatively ordered internal structure with the same orientation. On the other hand, the ZnO NR grown on an  $Al_2O_3/ZnO$  double seed layer with a ZnO layer thickness of 6 and 15 nm are highly crystalline, with a lattice spacing of about 0.26 nm, corresponding to the distance between the (0002) planes in the ZnO crystal lattice as shown in Fig. 3(h) and (i). The FFT patterns of the ZnO NR area confirm that the NR area has a single crystalline structure along the [0001] direction.

Fig. 4 shows Raman spectra for the ZnAl-LDH and ZnO NR hybrid structures. The Raman spectra for all samples show similar spectral shapes with two main Raman-active regions: one for ZnO NRs and the other for Si substrates. The ZnO has a wurtzite crystal structure belonging to the  $C_{6\nu}^4$  space group. The ZnO NRs on Si mainly show two peaks, at 331 and 438  $\text{cm}^{-1}$ , which are assigned as  $E_2^{\text{high}} - E_2^{\text{low}}$  and  $E_2^{\text{high}}$ , respectively.<sup>34,35</sup> Strong peaks near  $E_2^{\text{high}}$  correspond to the transverse optic (TO) component, which indicates that the number of ZnO NRs greatly increased and their crystal quality was enhanced with increasing ZnO seed layer thickness. We note that a shoulder peak at 1056 cm<sup>-1</sup> was observed for the samples on the double seed layer with a ZnO layer thicker than 9 nm. The band at 1056 cm<sup>-1</sup> is attributed to symmetric stretching modes of nitrate.36 This indicates that the ZnAl LDH in our results contains nitrate interlayer because we used zinc nitrate as a Zn source. This fact has been also verified by the Fourier transform infrared spectroscopy result which show a band near 1381 cm<sup>-1</sup>, which can be assigned to the v3 nitrate group, NO<sub>3</sub><sup>-</sup>, the counter anion in the ZnAl-LDH.<sup>37</sup> (see Fig. S1 in ESI<sup>†</sup> for more details).

Fig. 5 shows the XPS results of the hybrid nanostructures grown on the Al<sub>2</sub>O<sub>3</sub>/ZnO double seed layer with a ZnO layer thickness of 0, 6, and 15 nm to investigate the surface chemical states. As shown in Fig. 5(a), the O 1s peaks from the samples with a ZnO layer thickness of 6 and 15 nm were deconvoluted into two peaks centered at 529.9 and 531.4 eV, which are corresponding to the low and middle binding energy components, respectively.38 The low binding energy peak is attributed from the fully oxidized  $O^{2-}$  ions and indicates that the signals are from ZnO NR layers. And the middle binding energy peak is due to the non-stoichiometric  $O^{x-}$  ions (x < 2) which are attributed from the oxygen vacancies in the ZnO lattice. The XPS data from the sample grown directly on Al<sub>2</sub>O<sub>3</sub> shows two peaks centered at 530.1 and 532 eV, which are corresponding to the low and high binding energy components, respectively. The high binding energy peak is attributed from the OH<sup>-</sup> ion groups.38 And this indicates that the surface is mainly composed on hydroxide compounds which are corresponding to the Zn-Al LDH component. These peak shifts to the high binding energy are clearly observed in the XPS spectra of Zn 2p and Al 2p due to hydroxide reaction. Fig. 5(b) shows the Zn  $2p_{3/2}$ peaks, and the samples with a ZnO layer thickness of 6 and 15 nm shows peaks at 1021.2 eV while the sample grown directly on Al<sub>2</sub>O<sub>3</sub> shows peak at 1021.8 eV. The peak shift of the Zn 2p binding energy in the direction of the higher energy side means more Zn oxidation states in ZnAl-LDH compare to ZnO nanorods.38 Fig. 5(c) shows the Al 2p peaks for the samples. The main



Fig. 3 HR-TEM images and FFT patterns of the ZnO NR and ZnAl-LDH hybrid structures on the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer with ZnO thicknesses of (a), (d), and (g) 0 nm; (b), (e), and (h) 6 nm; and (c), (f) and (i) 15 nm, respectively.

peak at 74.2 eV is clearly shown on the sample grown directly on  $Al_2O_3$  and disappear with increasing the ZnO seed layer thickness. The samples with thicker ZnO seed layers show much reduced Al 2p peaks around 73.9 eV and this indicates less



Fig. 4 Normalized Raman spectra measured at room temperature for ZnO NR and ZnAl-LDH hybrid structures grown on Si (100) substrates with variation of the ZnO thickness in the  $ZnO/Al_2O_3$  double seed layer.

incorporation of Al ions into the ZnO NR layers because  $Al_2O_3$  has not dissolved into the solution due to thicker ZnO seed layers as discussed in TEM results. The peak shift of the Al 2p binding energy to the higher energy without ZnO seed layer supports our suggestion. Further information about the ratio between Zn and Al was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for the ZnAl-LDH grown on the  $Al_2O_3$ /ZnO double seed layer with ZnO layer thicknesses of 0 nm. The ICP-MS result showed that the Zn/Al ratio in the ZnAl-LDH was around 2 (see Fig. S2 in ESI† for more details).

Based on our experimental observations, the growth mechanism of ZnAl-LDH and ZnO NR structures, depending on the layer thickness of the  $Al_2O_3/ZnO$  double seed layer, can be described as follows. Firstly, hydroxide ions are provided by using HMT as a provider of the ammonia and its hydride reaction as follows:<sup>39</sup>

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \tag{1}$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
(2)

Secondly, in the basic solution, ALD-deposited  $Al_2O_3$  and ZnO film can be dissolved in the form of  $[Al(OH)_4]^-$  and  $[Zn(OH)_4]^{2-}$  by hydroxide reactions, respectively:<sup>40,41</sup>

$$Al_2O_3 + 3H_2O + 2OH^{-}(aq) \rightarrow 2[Al(OH)_4]^{-}$$
 (3)

$$ZnO + H_2O + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$$
(4)



Fig. 5 XPS spectra of (a) O 1s, (b) Zn  $2p_{3/2}$ , and (c) Al 2p from the ZnO NR and ZnAl-LDH hybrid structures on the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer with ZnO thicknesses of 0, 6, and 15 nm. The elementary XPS spectra shown by dashed lines were obtained by deconvolution.

Lastly, the hydrothermal reactions are involved in the formation of ZnO and ZnAl-LDH in the aqueous solutions, as described in other literatures:<sup>17,42</sup>

$$Zn(NO_3) \cdot 6H_2O \rightarrow Zn^{2+} + 2(NO_3)^- + 6H_2O$$
 (5)

$$Al(OH)^{4-} + Zn(OH)_4^{2-} + 2(NO_3)^- + H_2O \rightarrow ZnAl-LDH$$
 (6)

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^-$$
(7)

$$Zn(NH_3)_4^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O$$
 (8)

here, the ZnAl-LDH can be in the form of  $Zn_{1-x}Al_x(OH)_6(NO_3)_2$ -·2H<sub>2</sub>O depending on the solute concentration in the hydrothermal solutions. We suggest that as the aluminum hydroxide dissolves from the surface of Al<sub>2</sub>O<sub>3</sub> film, it encounters relatively large concentrations of zinc hydroxide in its immediate vicinity, thereby spontaneously forming nuclei of ZnAl-LDH at the interface of the Al<sub>2</sub>O<sub>3</sub> layer. However, with the surface of the Al<sub>2</sub>O<sub>3</sub> being progressively covered by a ZnO layer, the concentration of available aluminum hydroxide decreases, and zinc hydroxide in the bulk reacts with OH<sup>-</sup> to produce ZnO NRs according to reactions (7) and (8). Based on our structural investigations, a schematic diagram of the shape evolution mechanism of the ZnAl-LDH and ZnO NR structures with variation of the ZnO layer thickness in the Al<sub>2</sub>O<sub>3</sub>/ZnO double seed layer is shown in Fig. 6. Without the ZnO layer in the Al<sub>2</sub>O<sub>3</sub>/ZnO double seed layer, ZnAl-LDH can be formed by the  $[Al(OH)_4]^-$  ions supplied from the  $Al_2O_3$  surface as shown in Fig. 6(a). With a thin ZnO layer covering the Al<sub>2</sub>O<sub>3</sub>, a mixed structure of ZnAl-LDH and ZnO NRs can be formed because of easy penetration of the OH<sup>-</sup> ions, especially through week grain boundary regions in thin ZnO layers. In this case, ZnAl-LDHs can be formed by an hydroxide reaction based on reaction (6), and the ZnO NRs can be grown on the ZnO seed layer at the same time. However, a further increase of the thickness of the ZnO seed layer can block penetration of the OH<sup>-</sup> ions and hinder dissolution of the Al<sub>2</sub>O<sub>3</sub> to form the  $[Al(OH)_4]^-$  for hydroxide reactions. Therefore, ZnO NRs start to grow on the top ZnO seed surface and finally protect the Al<sub>2</sub>O<sub>3</sub> from dissolution by hydroxide reaction. Therefore, only the ZnO NRs can be formed on the thick ZnO seed layers.

Fig. 7 shows the room temperature PL spectra for the samples grown on the Al2O3/ZnO double seed layer with ZnO layer thicknesses of 0, 6, and 15 nm to investigate the optical properties of ZnAl-LDH and ZnO NR hybrid structures. The ZnAl-LDH on the Al<sub>2</sub>O<sub>3</sub> layer without a ZnO layer showed a single symmetric PL peak at 397 nm. This peak position is similar to previously reported results.43-45 However, the PL spectra of the ZnO NR and ZnAl-LDH hybrid structures on 6 and 15 nm-thick ZnO seed layers exhibit two main emission bands: a sharp asymmetric peak in the ultraviolet (UV) range (near 380 nm) and a broad peak (600 nm) in the visible range. The peak at the lower energy side corresponds to the deep level-related emission of ZnO crystals. We note that the peak in the UV region is composed of multiple peaks and could be deconvoluted into two peaks at 379 and 388 nm. The peak at 379 nm is attributed to the band-edge emission from the ZnO crystal. The other peak at 388 nm is attributed to the ZnAl-LDHs.44,45 As the ZnO seed layer thickness increased from 6 to 15 nm, the band-edge emission from the ZnO NRs was greatly enhanced, whereas the deep level emission was suppressed due to the enhancement of ZnO NR crystallinity. Therefore, the emission properties of the ZnO NR and ZnAl-LDH hybrid structures can be controlled by the double seed layers and this result can be applied to novel optoelectronic devices.



Fig. 6 Schematic diagram of ZnO NR and ZnAl-LDH hybrid structures with variation of the ZnO thickness in the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer.



Fig. 7 Normalized room temperature PL spectra of ZnO NR and ZnAl-LDH hybrid structures on the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer with ZnO thicknesses of 0, 6, and 15 nm. The elementary PL spectra shown by dashed lines were obtained by deconvoluting the PL spectra. The inset shows the PL spectra for the whole spectral range.

## 4. Conclusion

In conclusion, we described the morphological evolution mechanism between ZnAl-LDH and ZnO NR structures by controlling the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer on Si substrate. The structural and optical investigations showed that the ZnAl-LDHs were grown on the Al<sub>2</sub>O<sub>3</sub> seed layer only, whereas ZnO NRs started to appear and their proportion increased with increasing ZnO thickness in the ZnO/Al<sub>2</sub>O<sub>3</sub> double seed layer. Structural investigation by TEM revealed that the morphological evolution is mainly due to the hydroxide reactions between the basic solution and dissoluble seed layer. As the ZnO seed layer covered the Al<sub>2</sub>O<sub>3</sub> film, the concentration of Al hydroxide was significantly reduced, but that of Zn hydroxide increased

enough to form ZnO NRs. Our results suggest that hybridizing these ZnAl-LDH and ZnO NRs could pave the way to enhanced material properties, as well as create a new material system with unique properties for future applications.

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## References

- C. Soci, A. Zhang, B. Xiang, S. A. Dayeh, D. P. R. Aplin, J. Park,
   X. Y. Bao, Y. H. Lo and D. Wang, *Nano Lett.*, 2007, 7, 1003–1009.
- 2 S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu and H. Shen, *J. Cryst. Growth*, 2001, **225**, 110–113.
- 3 Z. L. Wang and J. H. Song, Science, 2006, 312, 242-246.
- 4 M. R. Hasan, S.-H. Baek, G. S. Sung, J. H. Kim and I. K. Park, *ACS Appl. Mater. Interfaces*, 2015, 7, 5768–5774.
- 5 J. I. Sohn, Y. I. Jung, S.-H. Baek, S. Cha, J. E. Jang, C.-H. Cho, J. H. Kim, J. M. Kim and I. K. Park, *Nanoscale*, 2014, 6, 2046– 2051.
- 6 A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino,
  M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa,
  H. Ohno, H. Koinuma and M. Kawasaki, *Nat. Mater.*, 2005,
  4, 42–46.
- 7 Y. S. Lee, Y. I. Jung, B. Y. Noh and I. K. Park, *Appl. Phys. Express*, 2011, 4, 112101.
- 8 Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li and C. L. Lin, *Appl. Phys. Lett.*, 2004, 84, 3654–3656.
- 9 S. Xu and Z. L. Wang, Nano Res., 2011, 4, 1013-1098.
- 10 Q. Zhang, E. Uchaker, S. Candelariaz and G. Cao, *Chem. Soc. Rev.*, 2013, **42**, 3127–3171.
- 11 Y.-S. Lee, S.-N. Lee and I.-K. Park, *Ceram. Int.*, 2013, **39**, 3043–3048.

- 12 R. Dom, H. Kim and P. Borse, *CrystEngComm*, 2014, 16, 2432–2439.
- 13 B. Weintraub, Z. Zhou, Y. Li and Y. Deng, *Nanoscale*, 2010, 2, 1573–1587.
- 14 L. Chen, Y. Yin, C. Chen and J. Chiou, *J. Phys. Chem. C*, 2011, **115**, 20913–20919.
- 15 W. Chen, L. Feng and B. Qu, *Chem. Mater.*, 2004, **16**, 368–370.
- 16 L. Wang, C. Li, M. Liu, D. G. Evans and X. Duan, *Chem. Commun.*, 2007, 123–125.
- 17 S. Cho, S.-H. Jung, J.-W. Jang, E. Oh and K.-H. Lee, *Cryst. Growth Des.*, 2008, **8**, 4553–4558.
- 18 S. Cho, S. Kim, E. Oh, S.-H. Jung and K.-H. Lee, *CrystEngComm*, 2009, **11**, 1650–1657.
- 19 S. Radha, S. V. Prasanna and P. V. Kamath, *Cryst. Growth Des.*, 2011, **11**, 2287–2293.
- 20 K. Dutta, S. Das and A. Pramanik, *J. Colloid Interface Sci.*, 2012, **366**, 28–36.
- 21 F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, 1991, **11**, 173–301.
- 22 U. G. Nielsen, Z. Gan and C. P. Grey, *Science*, 2008, **321**, 113–117.
- 23 K. Xu, G. Chen and J. Shen, RSC Adv., 2014, 4, 8686–8691.
- 24 Z. Zhang, G. Chen and K. Xu, *Ind. Eng. Chem. Res.*, 2013, **52**, 11045–11049.
- 25 Z. Hu and G. Chen, Adv. Mater., 2014, 26, 5950-5956.
- 26 N. Ahmed, Y. Shibata, T. Taniguchi and Y. Izumi, *J. Catal.*, 2011, **279**, 125–135.
- 27 M.-Q. Zhao, Q. Zhang, J.-Q. Huang, J.-Q. Nie and F. Wei, *Carbon*, 2010, **48**, 3260–3270.
- 28 A. I. Khan, A. Raghavan, B. Fong, C. Markland, M. O'Brien,
  T. G. Dunbar, G. R. Williams and D. O'Hare, *Ind. Eng. Chem. Res.*, 2009, 48, 10196–10205.

- 29 M. Wei, Q. Yuan, D. G. Evans, Z. Wang and X. Duan, *J. Mater. Chem.*, 2005, **15**, 1197–1203.
- 30 S. Vial, V. Prevot, F. Leroux and C. Forano, *Microporous Mesoporous Mater.*, 2005, 208, 1–20.
- 31 X. Zhao, F. Zhang, S. Xu, D. G. Evans and X. Duan, *Chem. Mater.*, 2010, **22**, 3933–3942.
- 32 Y. Sun, Y. Zhou, Z. Wang and X. Ye, *Appl. Surf. Sci.*, 2009, 255, 6372–6377.
- 33 N. Thomas, Cryst. Growth Des., 2012, 12, 1378-1382.
- 34 S. Sahoo, G. L. Sharma and R. S. Katiyar, J. Raman Spectrosc., 2012, 43, 72–75.
- 35 G. H. Nam, S.-H. Baek, C.-H. Cho and I. K. Park, *Nanoscale*, 2014, 6, 11653–11658.
- 36 R. L. Frost and A. W. Musumeci, J. Colloid Interface Sci., 2006, 302, 203–206.
- 37 P. Fu, K. Xu, H. Song, G. Chen, J. Yang and Y. Niu, J. Mater. Chem., 2010, 20, 3869–3876.
- 38 V. Gaddam, R. R. Kumar, M. Parmar, G. R. K. Yaddanapudi, M. M. Nayak and K. Rajanna, *RSC Adv.*, 2015, 5, 13519– 13524.
- 39 X. Yan, Z. Li, R. Chen and W. Gao, *Cryst. Growth Des.*, 2008, **8**, 2406–2410.
- 40 Z. P. Xu and G. Q. Lu, Chem. Mater., 2005, 17, 1055-1062.
- 41 J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, *Chem. Mater.*, 2002, **14**, 4172–4177.
- 42 J. Liu, X. Huang, Y. Li, K. M. Sulieman, X. He and F. Sun, *J. Phys. Chem. B*, 2006, **110**, 21865–21872.
- 43 G. H. Nam, S.-H. Baek and I. K. Park, *J. Alloys Compd.*, 2014, 613, 37–41.
- 44 Y. Chen, S. Zhou, F. Li, F. Li and Y. Chen, *J. Lumin.*, 2011, **131**, 701–704.
- 45 Z. Huang, P. Wu, B. Gong, Y. Fang and N. Zhu, *J. Mater. Chem. A*, 2014, **2**, 5534–5540.