Supporting Information

Solid-State Cation Exchange Reaction to Form Multiple Metal Oxide Heterostructure Nanowires

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Table S1. Plane distance comparison of critical planes of κ-Al_2O_3 and ZnO.

	κ-Al_2O_3		**ZnO**	
d-space	200	03-1	0001	1-100
reference (nm)	0.242	0.265	0.520	0.280
present work (nm)	0.257	0.269	0.521	0.276

Table S2. Structural comparison between κ-Al_2O_3 and α- Al_2O_3

		κ-Al_2O_3	**α-Al_2O_3**
structure		**Orthorhombic**	**Rhombohedral**
Cell Parameter	**a**	**4.843 Å**	**4.764 Å**
	b	**8.330 Å**	**4.764 Å**
	c	**8.954 Å**	**13.009 Å**
Static Dielectric Constant		**10.99**[1]	**9.72**[1]
thermal conductivity With(fraction porosity 0.3 μ m)		**0.1(W.cm-^{1}K-1)** [2]	**0.075(W.cm-^{1}K-1)** [2]

The ZnO NWs were grown on Si wafer through vapor-liquid-solid mechanism; we cut the wafer into pieces, then soaked one of it into ethanol, and vibrating it to let the NWs detached from the substrate by sonication. The ethanol with ZnO NWs, was dropped onto the TEM observation samples. In order to make sure the right amount of NWS on the membrane (too much, the NWs tend to overlap or entangle; too little, no enough observed sample), we tried to cut Si substrate into similar size, and control the amount of ethanol; to make the liquid look a little turbid and appear slightly blue. Finally, we checked there's proper amount of NWs on the membrane through OM.

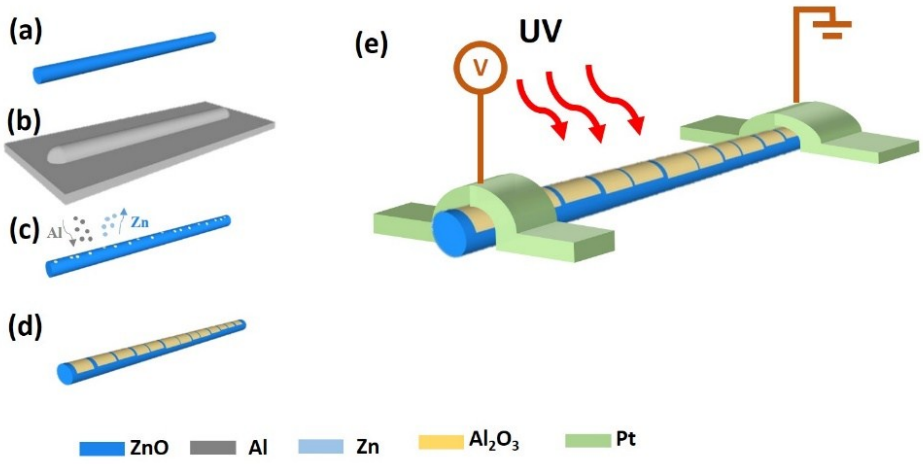


Figure S1. A schematic of the device fabrication process.

In this experiment, the maximum cation reaction radius of the Al_2O_3 at different diameters template zinc oxide not more than 50 nm, even the film thickness of the Al metal at the same thickness. Figure S2 (a) shows the average crystals radial diameter about 40 nm with 110 nm thickness of Zn template.

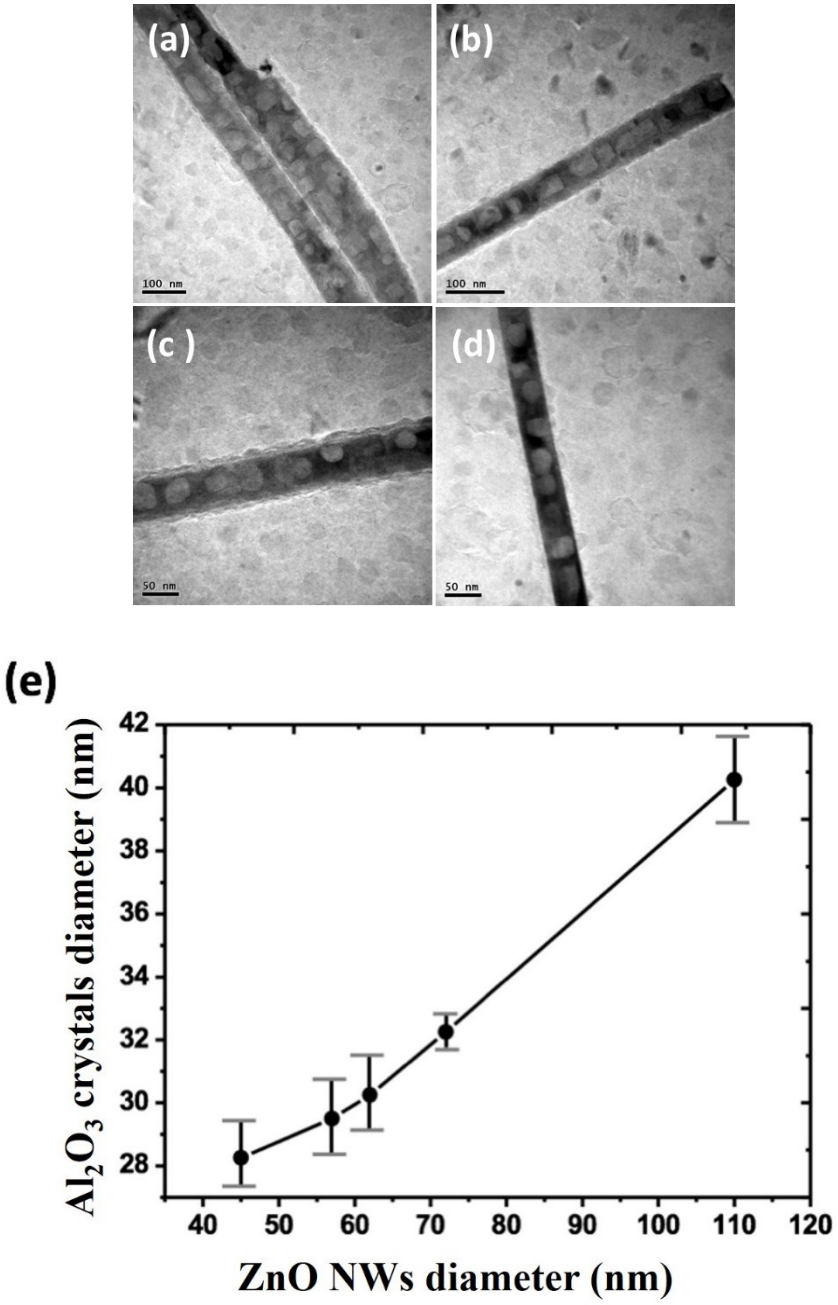


Figure S2. (a-d) Other ZnO/Al_2O_3 multiple heterostructure nanowires (NWs). (e) Plot of average Al_2O_3 crystals diameter as a function of ZnO NW diameter.

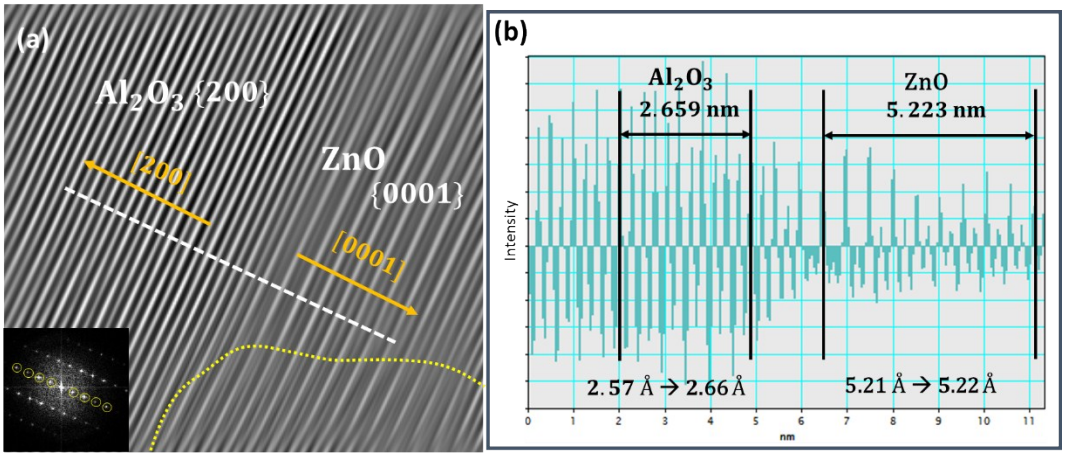


Figure S3. (a) To observe heterostructure epitaxy clearly, we selected specific electron diffraction points, as indicated in the inset, and used reverse FFT to obtain the filter FFT image, which revealed only Al_2O_3 $\{^{200}\}$ and ZnO $\{^{0001}\}$. The dotted line indicates the position of the plane-distance measurement shown in (b). (b) The plane distance of Al_2O_3 $\{^{200}\}$ and ZnO $\{^{0001}\}$ near the interface. The average plane distance of Al_2O_3 $\{^{200}\}$ is 2.66 Å. Compared with lattice relatively far from the interface shown in Figure 2c, lattice near the interface is 3.5% larger. This result illustrates that the Al_2O_3 lattice tended to match up with the ZnO lattice, whereas the ZnO lattice essentially remained the same.

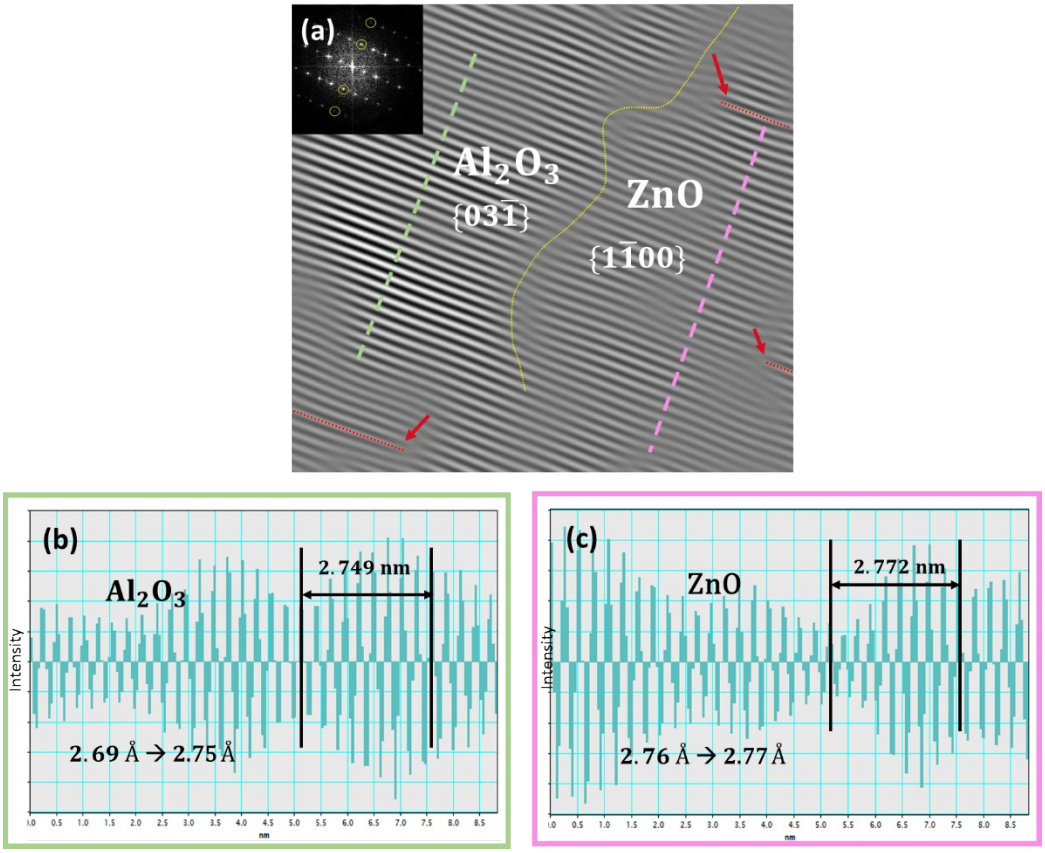


Figure S4. (a)We selected specific electron diffraction points, as indicated in the inset, and used reverse FFT to obtain the filter FFT image, which revealed only Al_2O_3 $\{03\bar{1}\}$ and ZnO $\{1\bar{1}00\}$. The yellow dotted line indicates the position of the interface, which shows slight lattice distortion. The red arrows indicate the misidentifies dislocations, which were generated to release the strain of lattice mismatch. The dotted lines indicate the position of the plane-distance measurements shown in (b, c), and correspond by color. (b) The plane-distance measurement of Al_2O_3 $\{03\bar{1}\}$ near the interface. The average plane-distance of Al_2O_3 $\{03\bar{1}\}$ is 2.75 Å. We discovered results similar to those shown in Figure S3; Al_2O_3 lattice near the interface is 2.2% larger than lattice far from the interface. (c) The plane-distance measurement of ZnO $\{1\bar{1}00\}$ near the interface. The average plane-distance is 2.77 Å, and no obvious lattice differences were observed with respect to distance from the interface.

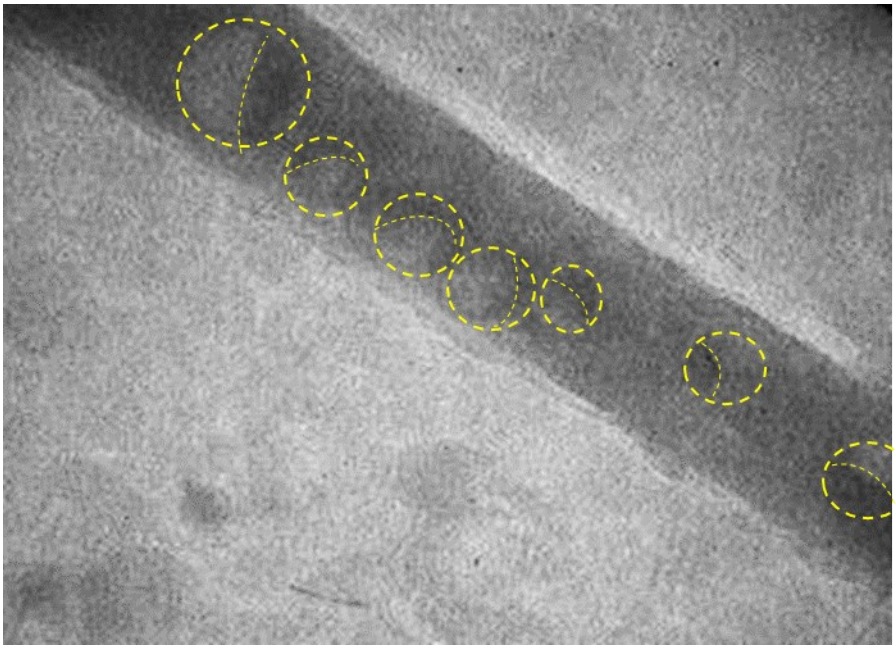


Figure S5. An in situ TEM image taken from a video with higher magnification at reaction time 03:30. The dotted lines indicate the formation of Al_2O_3 and the adjacent dark-color regions.

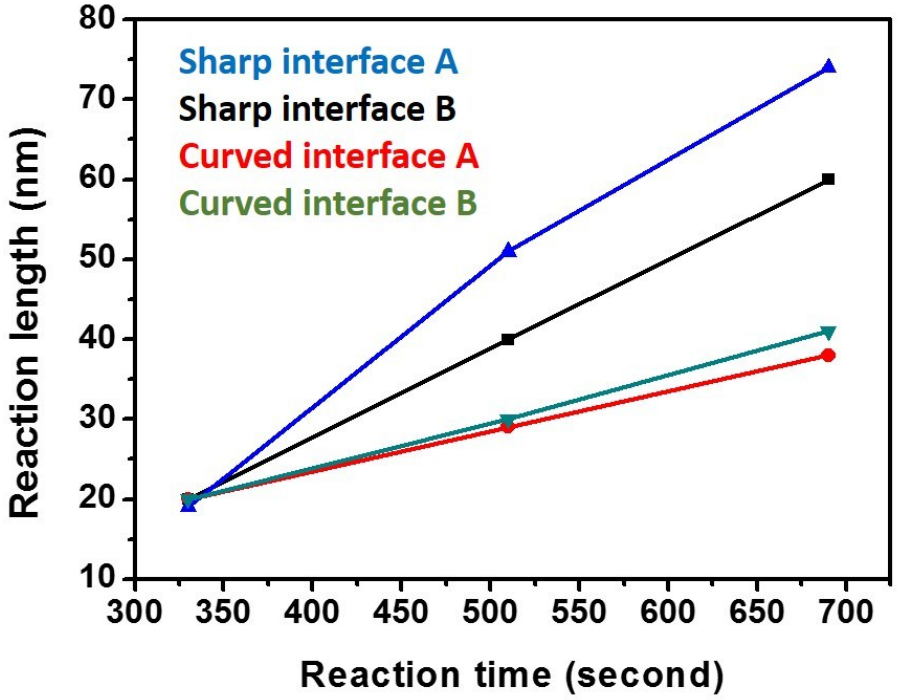
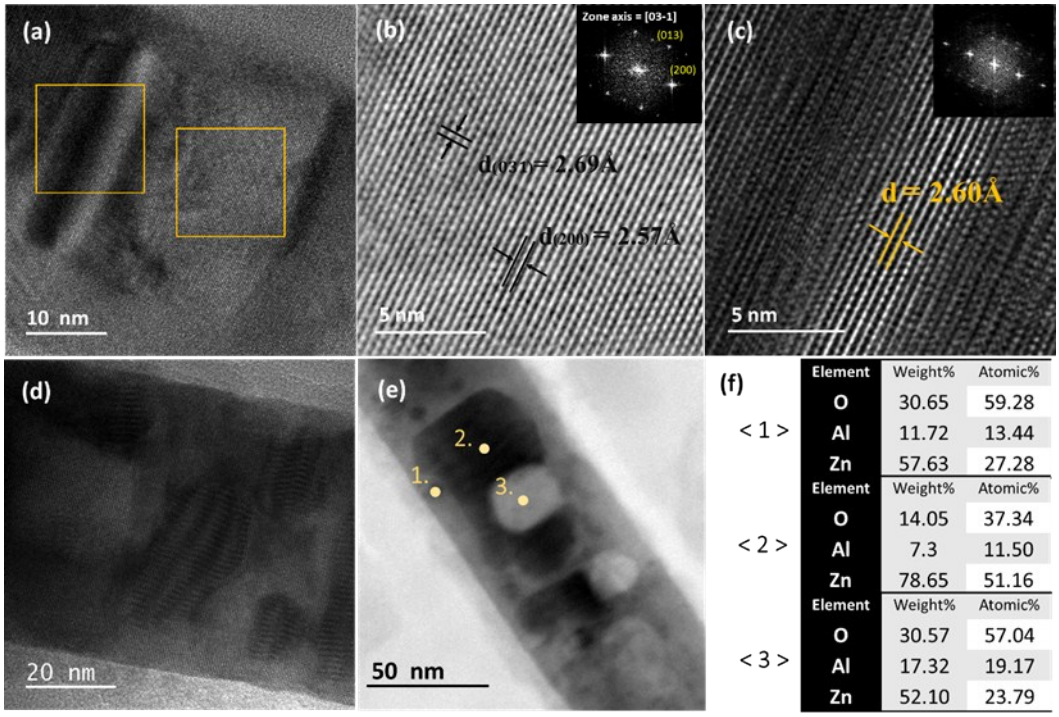
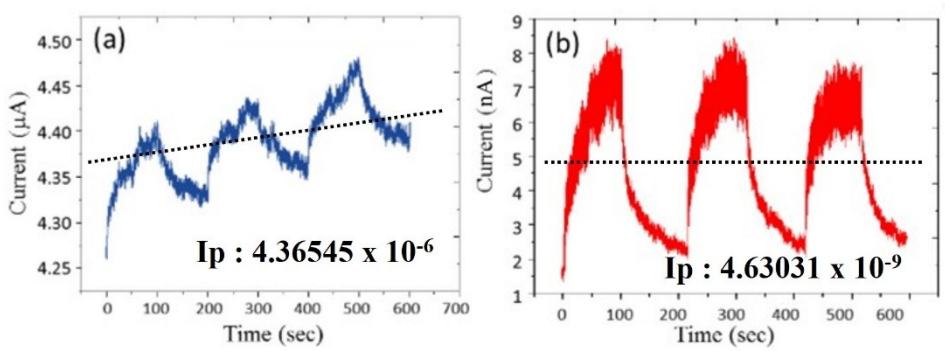


Figure S6. Plot of length of reaction Al_2O_3 as a function of time. The sharp interfaces grow more rapidly than curved interfaces.



	Element	Weight%	Atomic%
< 1 >	O	30.65	59.28
	Al	11.72	13.44
	Zn	57.63	27.28
	Element	Weight%	Atomic%
< 2 >	O	14.05	37.34
	Al	7.3	11.50
	Zn	78.65	51.16
	Element	Weight%	Atomic%
< 3 >	O	30.57	57.04
	Al	17.32	19.17
	Zn	52.10	23.79

Figure S7. HRTEM and HAADF STEM images of defects appearing during the formation of a ZnO/Al_2O_3 multiple heterostructure NW. (a) Low-magnification HRTEM image of a heterostructure NW. The light-color crystal (the right square) was enlarged in (b) and was identified as κ-Al_2O_3 with zone axis [$03\bar{1}$]. The dark stripe beside the Al_2O_3 crystal (the left square) is shown enlarged in (c). (b) The enlarged HRTEM image of the right square in (a) was identified as Al_2O_3 with zone axis [$03\bar{1}$]. (c) The enlarged HRTEM image of the left square in (a). The plane distance of the light-color stripe is 2.6 Å, which suggests κ-Al_2O_3. In the dark stripe region, some additional planes were being inserted into the main lattice. According to the information above and the dynamic dark stripes observed from in situ video, we suggest that the excess zinc ions induced the mixed Al_2O_3 lattice that showed dark TEM imaging contrast. (d) The TEM image of the heterostructure NW with Moiré fringes. (e, f) The HAADF image of the heterostructure NW with Moiré fringes and corresponding point analysis. According to the point analysis, point 3 is likely a small crystalline Al_2O_3 region, and it illustrates that the reaction was stopped in its early stage due to nonuniform TEM sample heating. The Moiré fringe regions show significant high percentages of zinc and lower oxygen percentages than the other regions; therefore, we suggest that high concentration of zinc ions crystallized into Zn crystals after cooling, and then induce the Moiré fringes in TEM imaging.



$$R = \frac{Ip}{Poutput}\,(\mu A/w)$$

Figure S8 The responsivity for heterostructure ZnO/Al_2O_3 and ZnO was R_{Heter} : 1.475μA/w and R_{ZnO} : 1390μA/w, respectively. The heterostructure had good sensitivity but normal responsivity due to its structure with lower current value.

Reference

1. C. K. Lee, E. Cho, H. S. Lee, K. S. Seol, and S. Han, Physical Review B, 2007, **76**, 245110.
2. E. J. Gonzaleza, G. Whitea and L. Weia, Journal of Materials Research, 2000, **15**, 744-750.