## Supporting Information

## Al<sub>2</sub>O<sub>3</sub> Buffer-Facilitated Epitaxial Growth of High-Quality ZnO/ZnS Core/Shell Nanorod Arrays

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**Fig. S1.** (a,b) Top-view and (c,d) tilt view of low- and high-magnification SEM images of the ZnO/ZnS core/shell nanorod arrays without Al<sub>2</sub>O<sub>3</sub> buffer layer.



**Fig. S2** (a) TEM image of the ZnO/ZnS core/shell nanorods with 2 nm  $Al_2O_3$  as buffer layer. (b) Corresponding SAED pattern and (c) HRTEM image of (a). (d) ADF-STEM image and corresponding elemental mappings of the core/shell nanorod. (e) EDS line scan data from the core/shell heterostructure. (f) EDS line scan data corresponding to line A. The thickness of the  $Al_2O_3$  is 1 nm.



**Fig. S3** (a) TEM image of the cross-section sample. (b) Corresponding SAED pattern and (c) HRTEM image of (a), respectively. (d) and (e) Enlarged HRTEM images recorded from regions i and ii in (c), respectively. (f) ADF image with spectrum image of the core/shell heterostructure and EELS spectra obtained from the spectrum image.



**Fig. S4** (a) TEM image of the cross-section sample. (b) Corresponding HRTEM and ADF-STEM images of (a), inset is the corresponding SAED pattern. (d) ADF image and corresponding elemental mappings of the core/shell heterostructure.



Fig. S5 XRD patterns of ZnO/ZnS core/shell nanorod arrays with different thicknesses of  $Al_2O_3$  as buffer layer.



Fig. S6. HRTEM images of the obtained (a) 2 nm and (b) 4 nm  $Al_2O_3$ -coated ZnO after heating, insets are corresponding SAED patterns.



Fig. S7. (a-d) HRTEM images of the obtained core-shell heterostructures (4 nm  $Al_2O_3$  as buffer layer) at different growth stages. Note: the heterostructures shown in (a-d) were not recorded from the same one.



Fig. S8. I–V curves of diode consisting of core/shell heterostructure without  $Al_2O_3$  in the dark (red) and in the presence of 365 nm illumination (blue), respectively.