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Electronic Supplementary Material

Heteroepitaxial Growth of ZnO Branches Selectively on TiO_2 Nanorod Tips with Improved Light Harvesting Performance

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Experimental Section

Synthesis method:

TiO_2 nanorod film: TiO_2 nanorod films were prepared by a facile hydrothermal method[1]. 15mL of deionized water was mixed with 15mL of concentrated hydrochloric acid (36.5%~38% by weight). After 5min stirring, 0.5mL of tetrabutyl titanate (97%, Aldrich) was added. After another 5min stirring, the mixture was transferred into a 50mL Teflon-lined autoclave, and a piece of clean FTO substrate was placed at an angle against the wall of the autoclave with the conducting side facing down. The hydrothermal synthesis was maintained at 150~180^{o}C for 3h~5h. After the reaction, the autoclave was cooled to room temperature naturally. Then, the product was rinsed with deionized water and dried at 80^{o}C for 60min.

Synthesis of ZnO/TiO_2 HNs: Firstly, a thin layer of ZnO seeds was coated on the surface of TiO_2 nanorod film. Without any surface modification, the film was wet with two droplets of 5 mM zinc acetate dihydrate (98%, Aldrich) in ethanol, rinsed with ethanol and blown dry. After repeating three times, the film was covered with a layer of zinc acetate crystallites and heated at 300^{o}C for 20min. Then, the seeded film was suspended upside down in aqueous solutions containing 0.01~0.025M zinc nitrate hydrate, 0.005~0.0125M hexamethylenetetramine (HMT), and 0.004~0.005M polyethylenimine (PEI) at 95^{o}C for 15~120min. The ZnO/TiO_2 HNs were then rinsed with deionized water and blown dry. Finally the HNs were annealed at 450^{o}C for 30min to improve the crystallinity.

(1) B. Liu, E. S. Aydil, *J. Am. Chem. Soc.*, 2009, **131**, 3985.

Characterization

Scanning electron micrograph (SEM) images were taken with HITACHI S-4800 field-emission scanning electron microscopy, equipped with energy dispersive spectrometer (EDS Oxford). Transmission electron microscope (JEM-2100) and high-resolution transmission electron microscope (JEM-2010F) were used to characterize the samples. The X-ray diffraction (XRD) patterns of the samples were measured by using Japan Rigaku D/Max 2550, Cu Ka radiation. ater CAs were measured with a contact angle measuring device (Powereach JC2000D3, China) at ambient temperature. Diffuse reflectance spectra (DRS) were obtained for the dry-pressed disk samples using a Scan UV-Vis-NIR spectrophotometer (Varian, Cary 500) equipped with an integrating sphere assembly. The excitation and photoluminescence (PL) spectra of the sample were measured with a Jobin Fluorolog-3-p spectrophotometer with a Xe lamp at room temperature.

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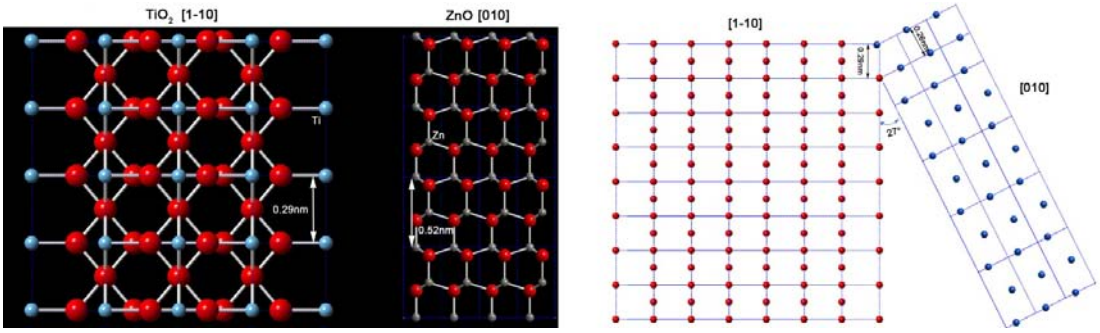

Fig. S1 (a) Strucuture models of the atomic arrangement with zone axis of [1-10] and [010] for TiO_2 and ZnO, respectively.

(b) A 2D atomic arrangement with a twisted angle of 27^o demonstrating the epitaxial relationship between TiO_2 and ZnO.

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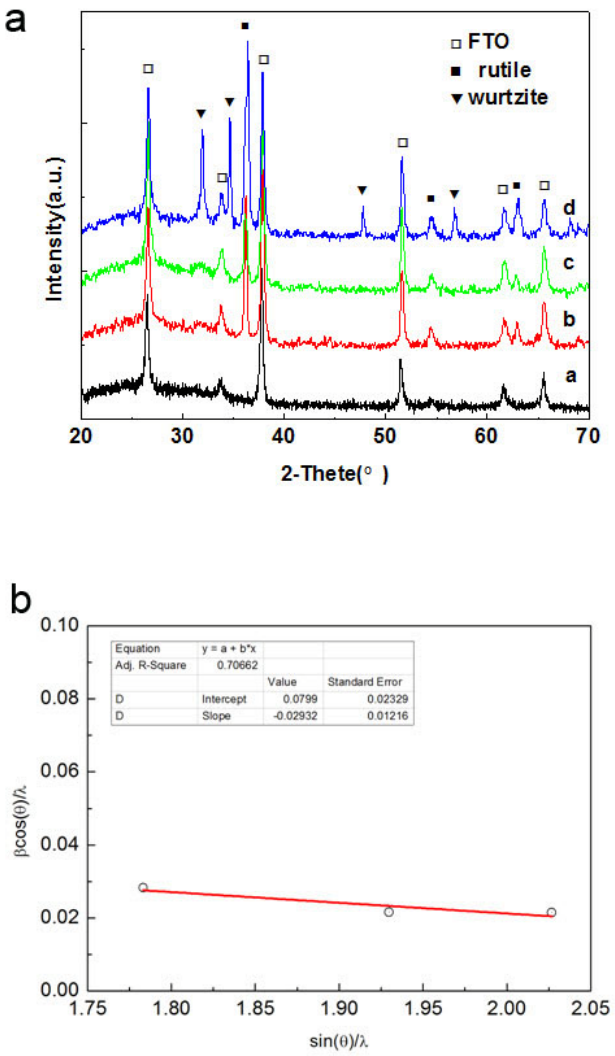

Fig. S2 (a) XRD patterns of FTO substrate a), TiO_2 nanorod film b), seeded TiO_2 nanorod film c) and ZnO/TiO_2 HNs d). (b) $\beta\cos\theta/\lambda$ vs $\sin\theta/\lambda$ for the obtained HNs.

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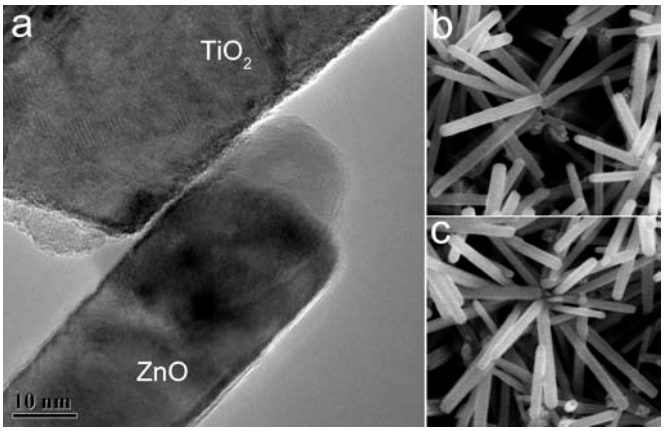

Fig. S3 TEM and SEM images of the ZnO/TiO_2 HNs showing ZnO branch anchoring to TiO_2 nanorod with point contacts..

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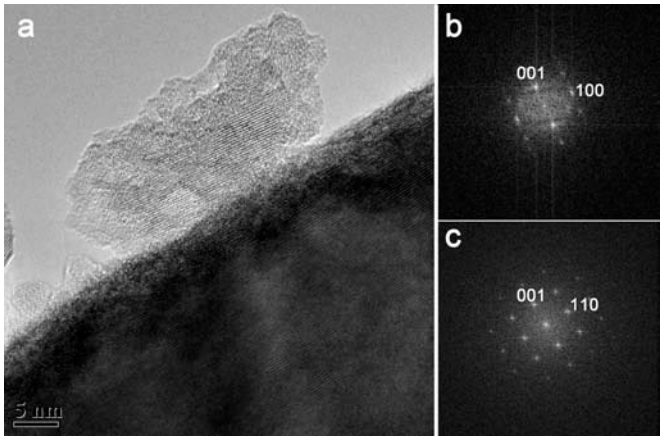

Fig. S4 HRTEM image and corresponding fast Fourier transform (FFT) patterns showing one ZnO seed anchoring to the outsurface of TiO_2 nanorod also with the epitaxial correlation.

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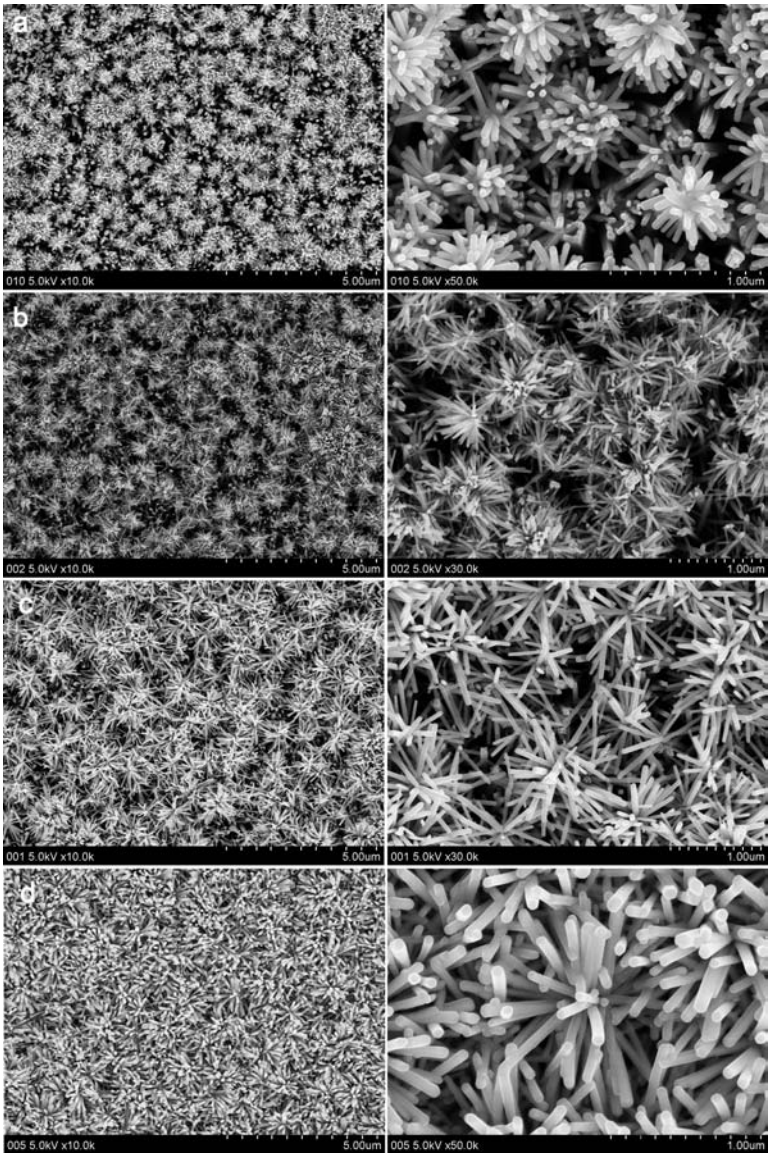

Fig. S5 SEM images of the ZnO/TiO_2 HNs with different branch lengths: a) 200nm, b) 300nm, c) 600nm, d) 1000nm.

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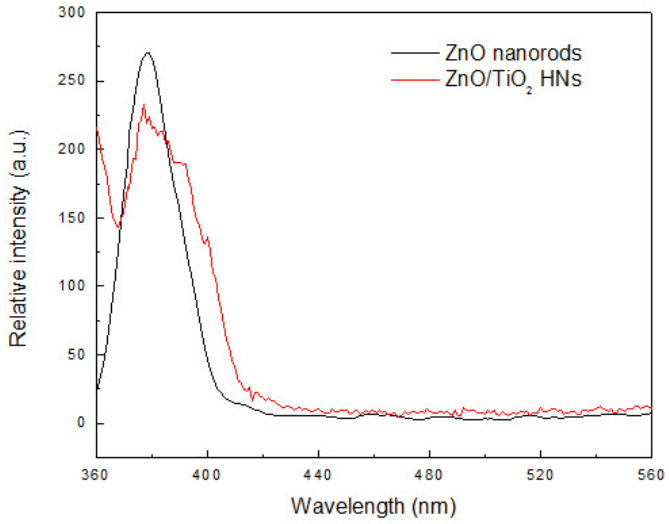

Fig. S6 Photoluminescent spectra of ZnO nanorod film and ZnO/TiO_2 HNs with similar ZnO nanorod length.

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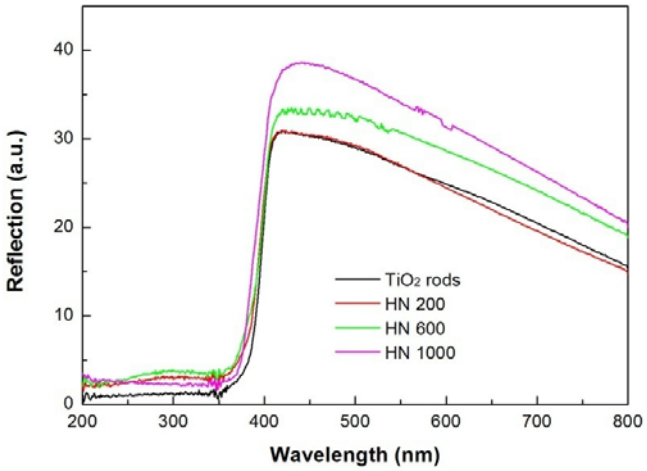

Fig. S7 UV-Vis diffused reflection spectra of the ZnO/TiO_2 HNs film and TiO_2 nanorod film.