Electronic supplementary information

Enhanced charge transfer and separation of hierarchical hydrogenated TiO_2 nanothorns/carbon nanofibers composites decorated by NiS quantum dots for remarkable photocatalytic H_2 production activity

Xin Zhang, Yajie Chen,* yuting Xiao, Wei Zhou, Guohui Tian* and Honggang Fu

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China; School of Chemistry and Materials Science, Heilongjiang University, 150080 Harbin P. R. China.

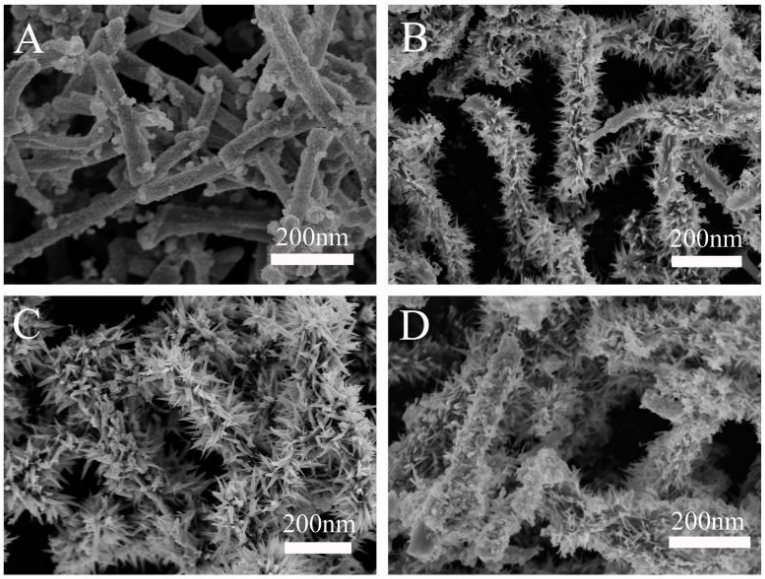

Fig. S1 SEM images of H-TiO_2/CNFs precursors prepared from different reaction time. (A) 0.5 h, (B) 6 h, (C) 12 h, and 24 h.

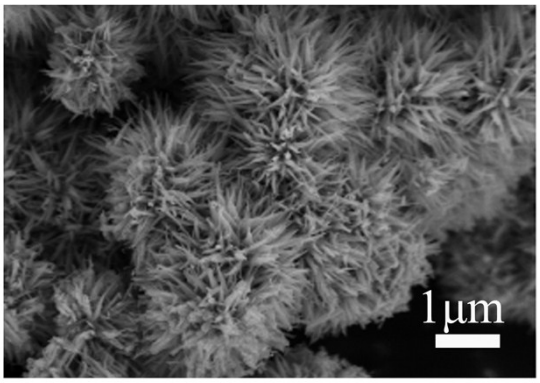

Fig. S2. SEM image of the pure TiO_2 precursor.

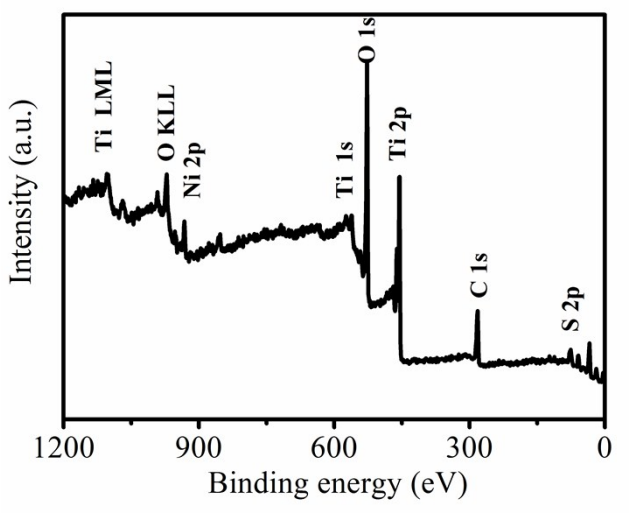

Fig. S3. The survey XPS spectrum of the NiS/H-TiO_2/CNFs.

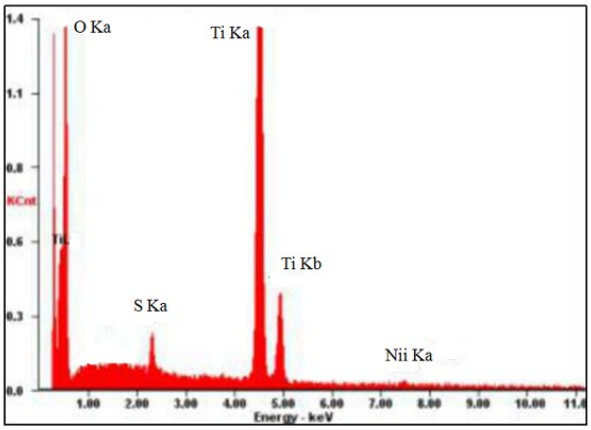

Fig. S4. The energy dispersive spectrum (EDS) of the NiS/H-TiO_2/CNFs.

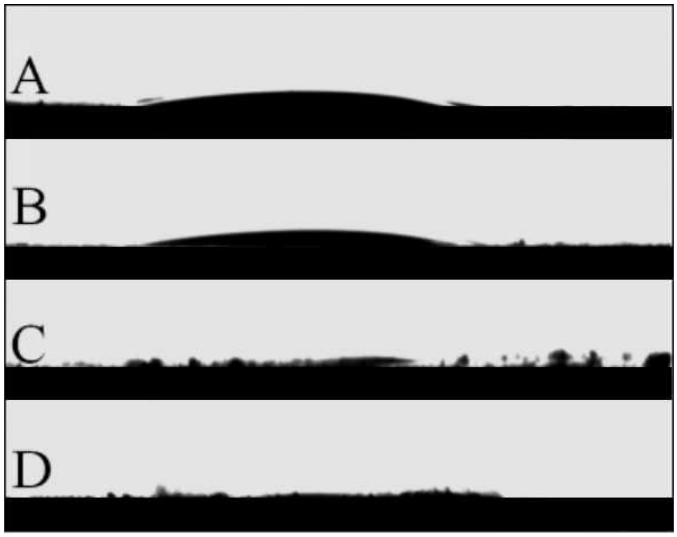

Fig. S5. (A), (B), (C) and (D) are the water contact angle photographs of TiO_2, TiO_2/CNFs, H-TiO_2/CNFs, and NiS/H-TiO_2/CNFs after AM 1.5 irradiation, respectively.

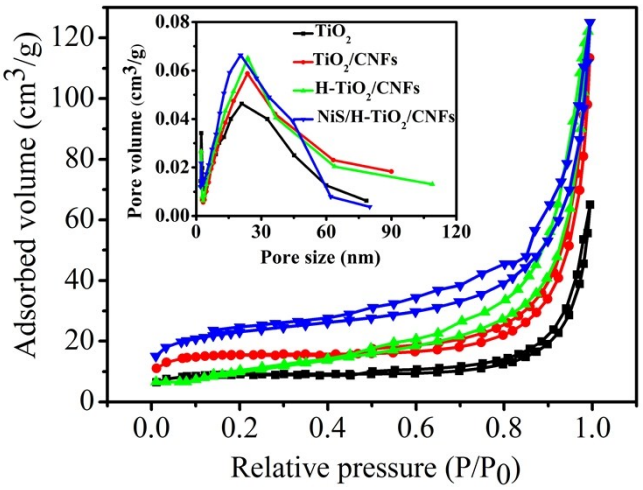

Fig. S6. Nitrogen adsorption–desorption isotherms and the pore size distribution plots (inset) of TiO_2, TiO_2/CNFs, H-TiO_2/CNFs, and NiS/H-TiO_2/CNFs.

Table S1 Summary of the photoluminescence decay time (τ) and their relative intensities of the different samples.

sample	τ_1(ns)	τ_2(ns)	I_1 (%)	I_2 (%)	Average lifetime (τ, ns)
NiS/H-TiO_2/CNFs	3.93	8.07	35.52	64.48	7.19
H-TiO_2/CNFs	3.75	7.41	36.95	63.05	6.57
TiO_2/CNFs	3.50	6.33	38.27	61.73	5.61
TiO_2	3.64	5.96	39.99	60.01	5.29

The average lifetime was calculated using equation: $<\tau>=(I_1\tau_1^2 + I_2\tau_2^2)/(I_1\tau_1 + I_2\tau_2)$

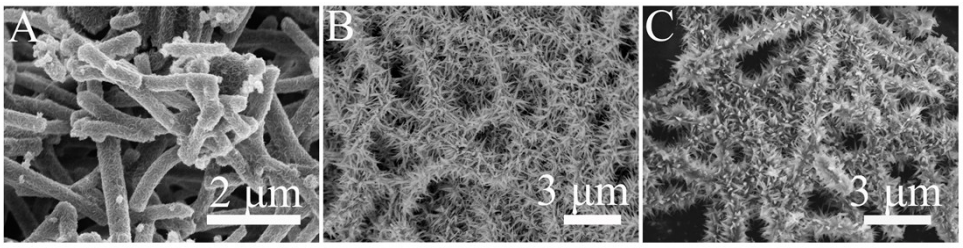

Fig. S7. (A), (B), and (C) are SEM images of TiO_2/CNFs prepared from 30, 20, and 10 mg carbon fibers, respectively.

We control the relative content of TiO_2 and CNFs according to the dosage of carbon fiber (CNFs) under the fixed 0.5 mL tetrabutyl titanate. The TiO_2/CNFs prepared from 10, 20, 30 mg CNFs were obtained. The SEM images were shown in Fig. S7. When the CNFs content is high, there are fewer TiO_2 nanothorns grown on the surface of CNFs. With the decrease of CNFs amount, more TiO_2 nanothorns can be found.

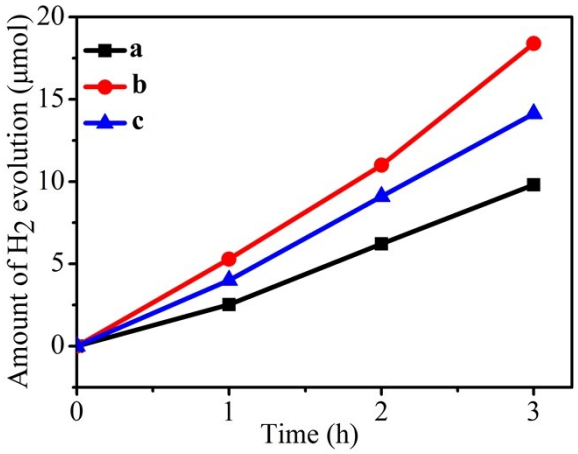

Fig. S8. The photocatalytic H_2 evolution activities of TiO_2/CNFs prepared from 10 (a), 20 (b), and 30 mg (c) carbon fibers, respectively.

The relative content of TiO_2 and CNFs also influence the photocatalytic activity (Fig. S8). Only proper content of TiO_2 and CNFs can exhibit optimal photocatalytic activity. When the content of CNFs is too high, there would have strong shading effect of CNFs. Meanwhole, the amount of TiO_2 catalyst is relatively low (Fig. S7A). So the photocatalytic hydrogen evolution activity is relative low. When the content of CNFs is too low, additional TiO_2 separated from CNFs can exist (Fig. S7C). There would have relatively weak interaction between TiO_2 and CNFs, not contributing to the photogenerated charge transfer and separation, leading to the decrease of photocatalytic hydrogen evolution activity.

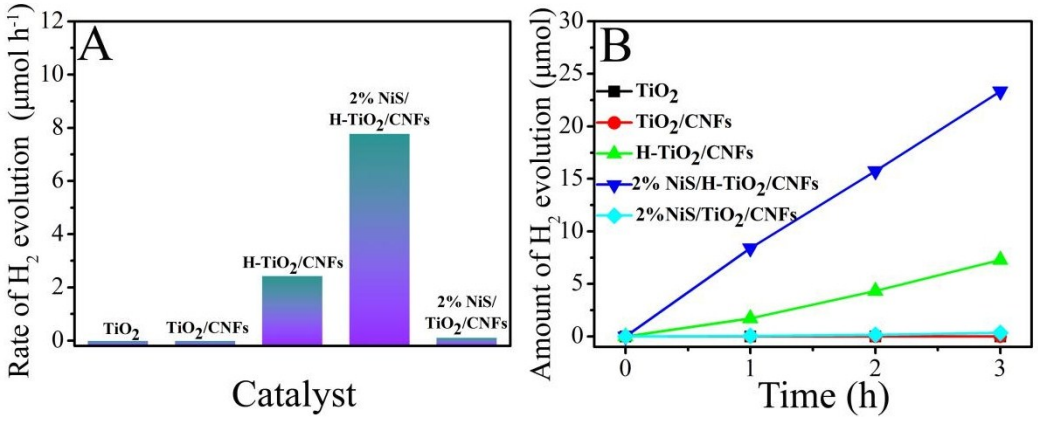

Fig. S9. The photocatalytic H_2 evolution activities of these catalysts under visible light irradiation ($\lambda > 420$ nm).

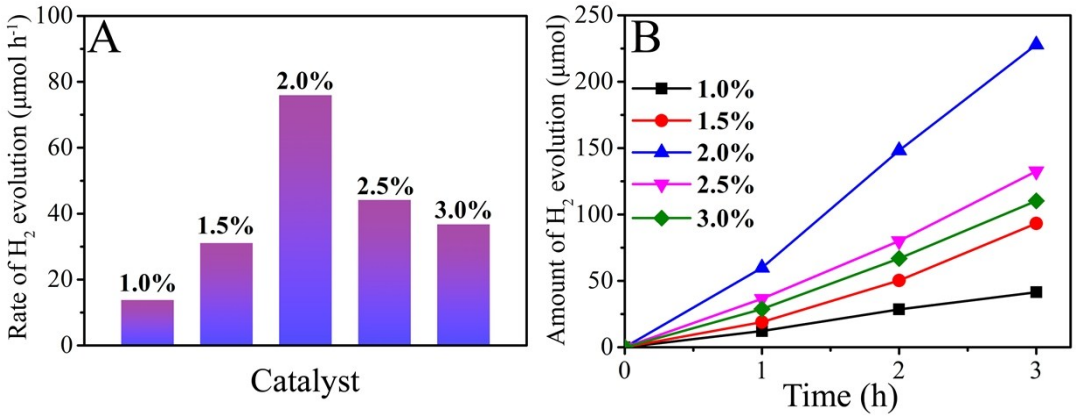

Fig. S10. The photocatalytic H_2 evolution rates of the NiS/H-TiO_2/CNFs with different NiS contents (A). The amounts of photocatalytic H_2 evolution plotted against AM1.5 irradiation time.

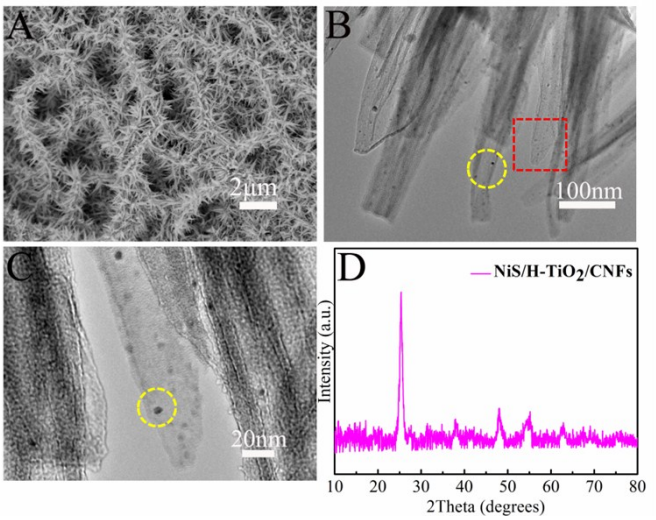

Fig. S11. SEM image (A), TEM images (B, C), and XRD pattern of the NiS/H-TiO_2/CNFs after photocatalytic H_2 evolution reaction.

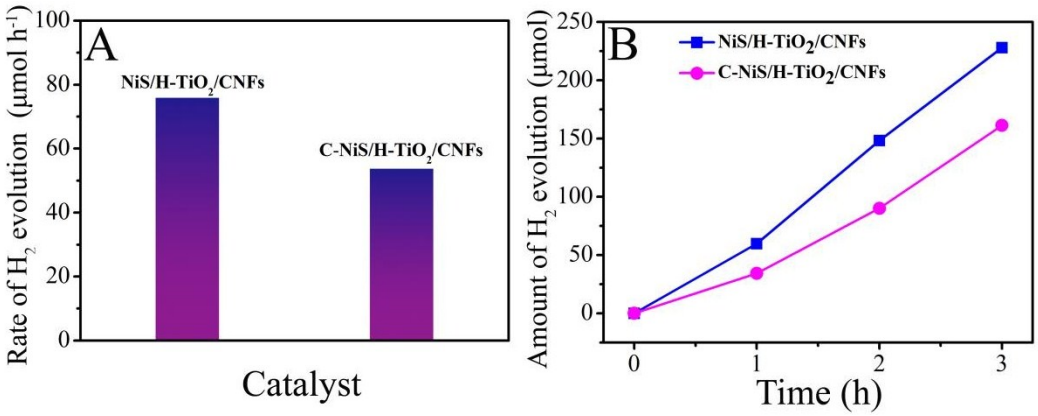

Fig. S12. Comparison of the photocatalytic H_2 evolution rate of NiS/H-TiO_2/CNFs and the crushed NiS/H-TiO_2/CNFs (C-NiS/H-TiO_2/CNFs) (A), and corresponding amounts of photocatalytic H_2 evolution plotted against AM1.5 irradiation time (B).

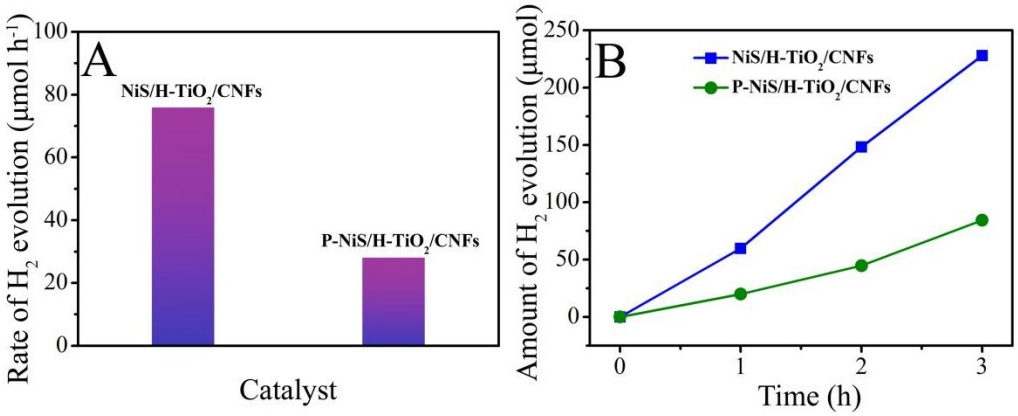

Fig. S13. Comparison of the photocatalytic H_2 evolution rate of NiS/H-TiO_2/CNFs (a) and the physically mixed NiS/H-TiO_2 and CNFs (b) (A), and corresponding amounts of photocatalytic H_2 evolution plotted against AM1.5 irradiation time (B).