Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers

Electronic supplementary information

Broadband Photocatalysis using Z-scheme Heterojunctions of $Au/NaYF_4$: Yb, Er/$WO_3 \cdot 0.33H_2O$-$W_{18}O_{49}$ via a Synergetic Strategy of Plasmonic/Upconversion

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Supplemental experimental section

Synthesis of $W_{18}O_{49}$: $W_{18}O_{49}$ was synthesized via solvothermal method according to previous report.[1, 2] 1.6 g of WCl_6 as the precursor was dissolved in 80 mL of absolute ethanol, forming a clear yellow solution. After continuous stirring for 1 h, the solution was transferred into a 100 mL Teflon-sealed autoclave, sealed and heated at 160 °C for 24 h. After cooling down to room temperature, the blue product was obtained by collecting, washing with deionized water and ethanol for several times and drying at 60 °C for 10 h.

Synthesis of NYYE/WW with different mass ratios: 4.30 mmol $Na_2WO_4{\cdot}2H_2O$ was dissolved in 60 mL of deionized water under vigorous stirring for 30 min at room temperature. Then, different masses of NYYE, such as 0.25 g, 0.43 g, 0.67 g and 1.00 g, were added to the above solution under stirring, adjusting the pH of the whole solution to 1.0 with nitric acid. After stirring for another 1 h, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. the obtained products were collected washed with deionized water and ethanol for several times and dried at 60 °C for 10 h, which were marked as NYYE (20)/WW, NYYE (30)/WW, NYYE (40)/WW and NYYE (50)/WW, respectively.

Synthesis of Au/NYYE/WW with loading different masses of Au NPs, 1% Au/$WO_3{\cdot}0.33H_2O$ and 1% Au/$W_{18}O_{49}$: Au/NYYE/WW with loading different masses of Au NPs samples were prepared by a photo-reduction method, taking $HAuCl_4{\cdot}4H_2O$ as the Au precursor. Typically, 1.00 g of as-synthesized NYYE (40)/WW was thoroughly dispersed in 50 mL deionized water for 30 min under vigorous stirring. And then, different volumes of $HAuCl_4{\cdot}4H_2O$ solution (9.7 mM), such as 2.638 mL, 5.275 mL, 7.913 mL and 10.550 mL, were added in the above dispersion, especially, taking 20 mL of methanol as sacrificial agent. The whole reaction was carried out under 300 W UV lamp irradiation for 3 h in a stirring condition. The obtained samples (about 0.5%, 1.0%, 1.5% and 2.0% mass ratio loading) were washed several times with deionized water and ethanol, and dried in vacuum oven at 60 °C for 10 h. And the 1% Au/$WO_3{\cdot}0.33H_2O$ and 1% Au/$W_{18}O_{49}$ were prepared by the same method with changing NYYE (40)/WW to $WO_3{\cdot}0.33H_2O$ or $W_{18}O_{49}$, where the volume of $HAuCl_4{\cdot}4H_2O$ solution is 5.275 mL.

1. Z. F. Huang, J. Song, X. Wang, L. Pan, K. Li, X. Zhang, L. Wang and J. J. Zou, *Nano Energy*, 2017, **40**, 308-316
2. Y. Yao, M. Yin, J. Yan and S. F. Liu, *Appl. Surf. Sci.,* 2018, **441**, 277-284.

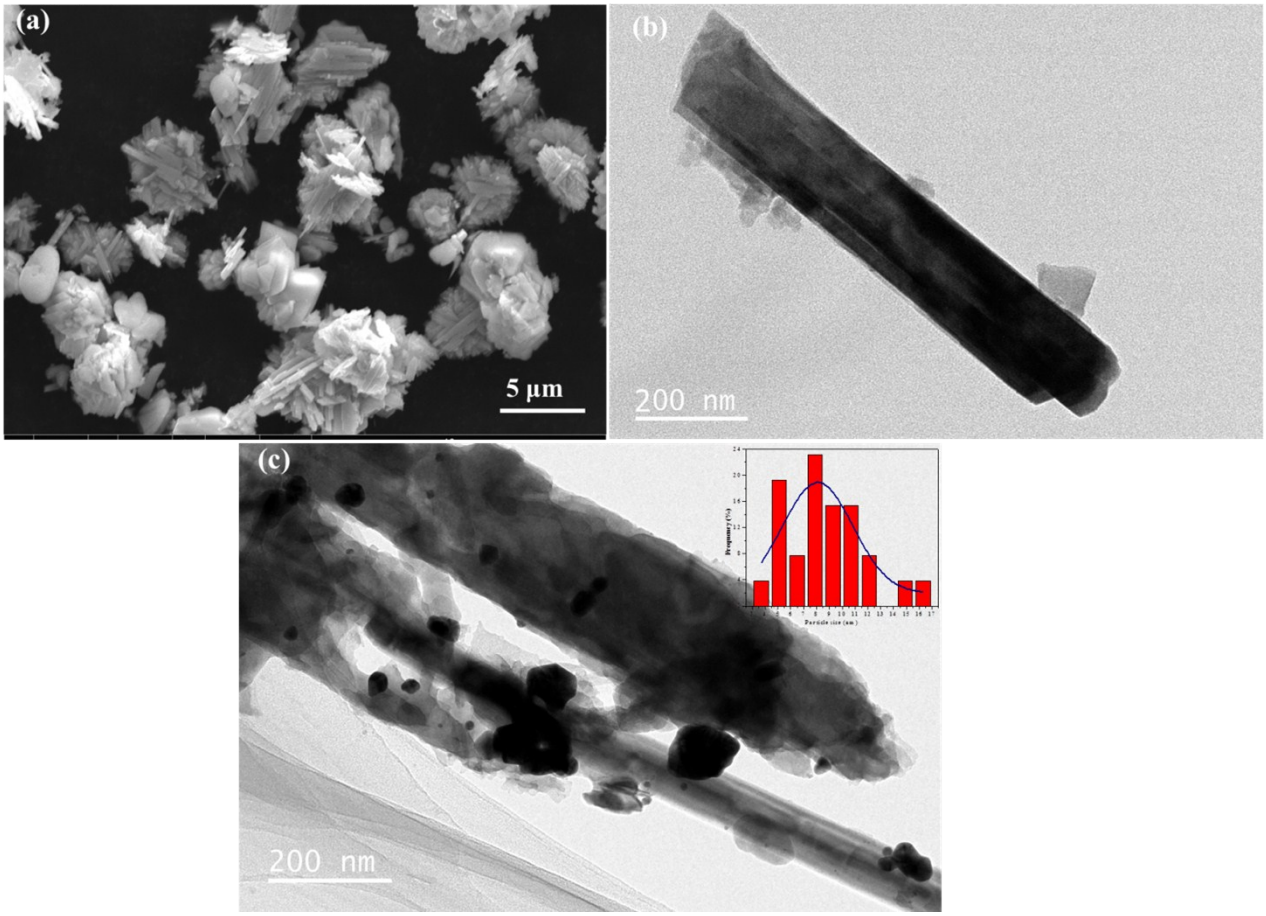

Fig. S1 (a) SEM images of NYYE/WW, TEM images of (b) $WO_3.0.33H_2O$ and (c) A/NYYE/WW with the corresponding particle size distribution (inset).

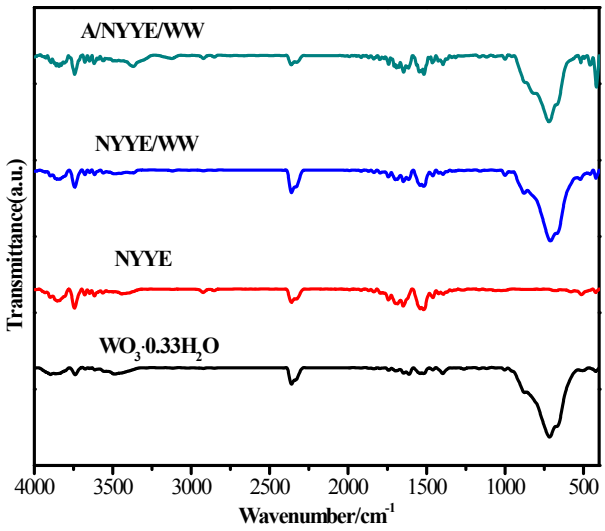

Fig. S2 FT-IR spectra of the obtained samples.

The chemical bonds could be identified in the photocatalysts from FT-IR spectra. As shown in Fig.S2, FT-IR spectra were registered in the region 4000–400 cm^{-1}. The strong absorption peaks centered at 650-900 cm^{-1} are attributed to the characteristic O-W-O stretching vibration [3]. As we know, the bands at 3730 $cm^{-1}$and 2350 cm^{-1} are assigned to OH stretching vibration of H_2O, indicating the existence of water absorbed on the surface of the catalysts .The peaks at 1530 cm^{-1} and 1650 cm^{-1} correspond to C=O stretching vibration due to CO_2 in air adsorbed on samples[4].

3. Z. Chen, J. Wang, G. Zhai, W. An and Y. Men, *Appl. Catal., B*, 2017, **218**, 825-832.

4. M. Saranya, R. Ramachandran, E. J. J. Samuel, S. K. Jeong and A. N. Grace, *Powder technology*, 2015, **279**, 209-220.

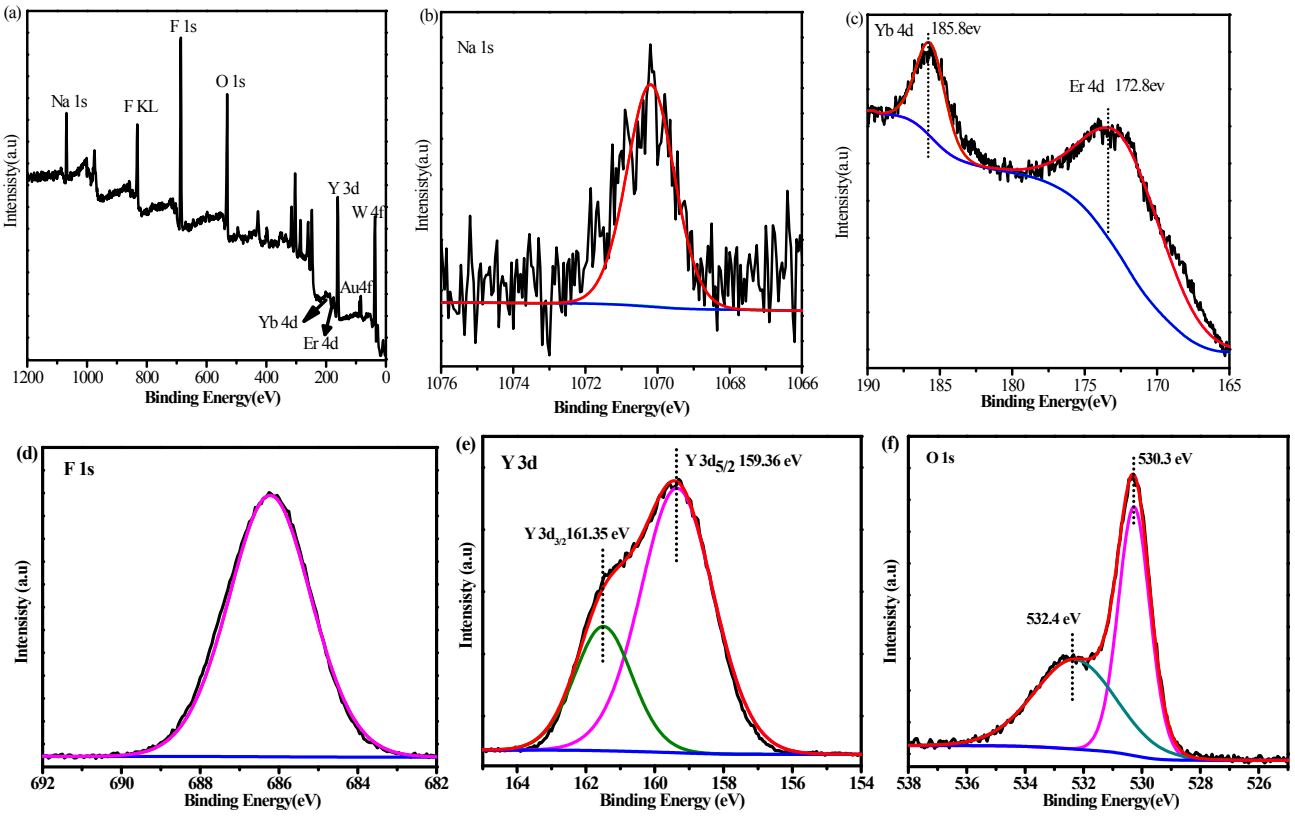

Fig. S3 XPS spectra of A/NYYE/WW (a) survey spectrum, (b)Na 1s, (c) Yb 4d and Er 4d,(d) F 1s, (e)Y 3d, (f) O 1s.

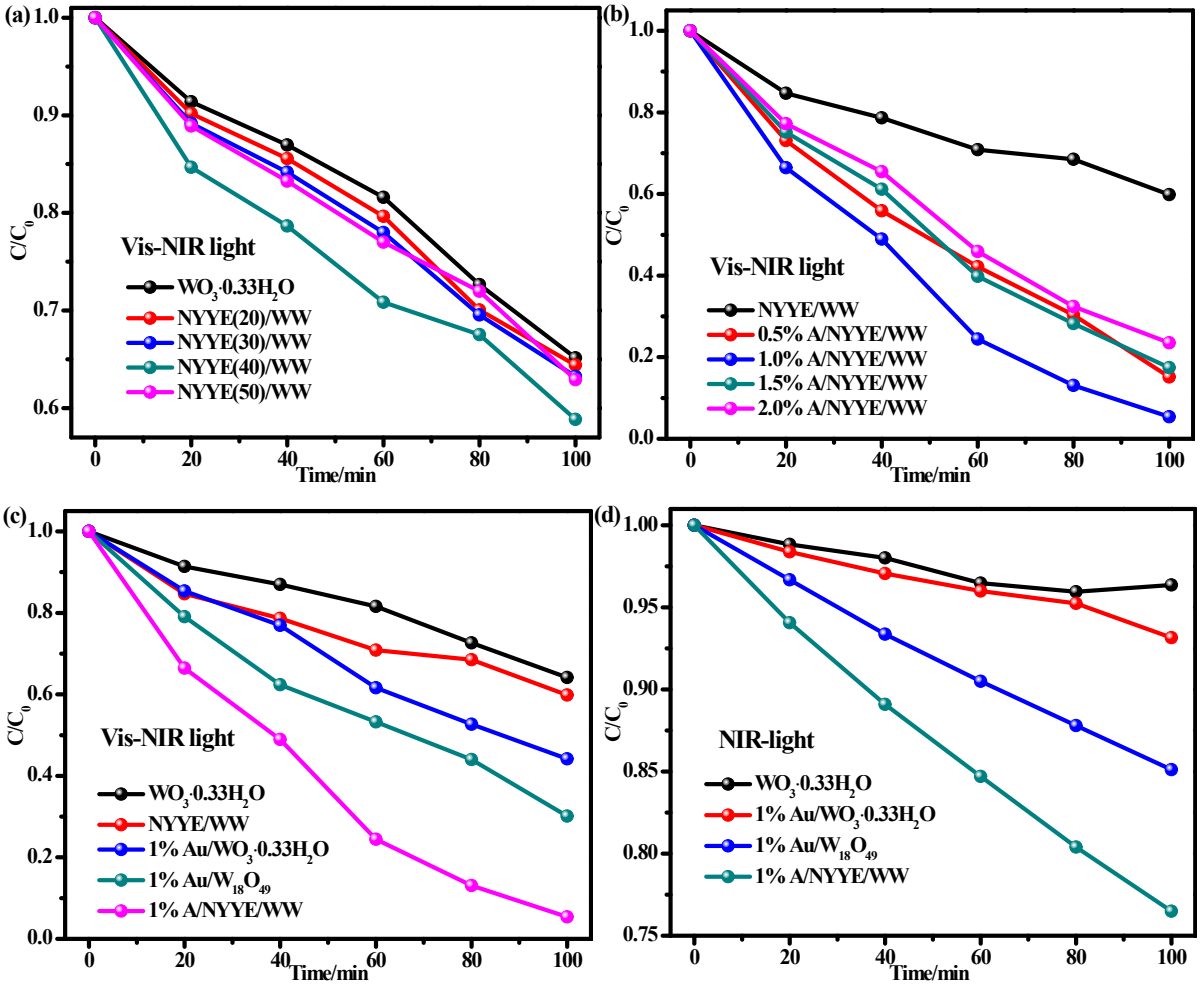

Fig. S4 Photocatalytic activities of (a) the NYYE/WW composites with different mass ratios (NYYE for 20, 30, 40 and 50 wt %) under Vis-NIR light, (b) Au/NYYE (40)/WW with different mass fraction amounts of Au NPs loading under Vis-NIR light, (c, d) activities of the 1% Au/ $WO_3 \cdot 0.33H_2O$, 1% Au/$W_{18}O_{49}$ and 1% A/NYYE/WW under Vis-NIR light and NIR light, respectively.