Supporting Information

Ultra-small Rh nanoparticles supported on WO$_{3-x}$ nanowires as efficient catalysts for visible-light-enhanced hydrogen evolution from ammonia borane

Xiao Li, Yucong Yan, Yi Jiang, Xingqiao Wu, Shi Li, Jingbo Huang, Junjie Li, Yangfan Lin, Deren Yang and Hui Zhang*

“State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People’s Republic of China. Email: msezhanghui@zju.edu.cn"
Fig S1. Size distribution of the Rh nanoparticles in the Rh/WO$_{3-x}$-2 hybrid nanowires.
Fig S2. (a, c) TEM images and (b, d) corresponding size distributions for the Rh nanoparticles of Rh/WO$_{3-x}$-1 and Rh/WO$_{3-x}$-3 hybrid nanowires, respectively.
Fig S3. (a) TEM image and (b) corresponding size distribution of the Rh nanoparticles.
Fig S4. (a) TEM image and (b) XRD pattern of the $\text{WO}_{3-x}$ nanowires.
**Fig S5.** (a) TEM and (b) HRTEM images of the Rh/C catalysts prepared by dispersing the Rh nanoparticles on carbon black supports.
Fig S6. (a) TEM and (b) HRTEM images of the mixed Rh nanoparticles and WO$_{3-x}$ nanowires (Rh+WO$_{3-x}$).
Fig S7. (a) Time courses for hydrogen production from AB over Rh/WO$_3$-x-1, Rh/WO$_3$-x-2, and Rh/WO$_3$-x-3 catalysts and (b) their corresponding TOF values under dark condition.
Fig S8. UV-Vis-NIR absorption spectra of Rh/WO$_{3-x}$ hybrid nanowires and WO$_{3-x}$ nanowires.
Fig S9. Plots of time versus volume of hydrogen generated from the hydrolysis of AB catalyzed by Rh/WO$_{3-x}$ and corresponding Arrhenius plots under (a, b) dark condition and (c, d) visible light irradiation at different temperatures in the range of 298–328 K, respectively.
**Fig S10.** (a) Plots of time versus volume of hydrogen generated from the hydrolysis of AB catalyzed by Rh/WO$_3$-x and (b) the corresponding TOF values under visible light irradiation with different powers of Xe lamp.
**Fig S11.** Digital photograph of Rh/WO$_3$ suspension under different conditions: (a) before catalytic reaction, (b) after catalytic reaction and the flask was kept sealed, (c) after catalytic reaction and the flask was exposed to the air for a little while.
Fig S12. Plots of dV/dt vs. t by using Rh/WO$_{3-x}$ as the catalysts under dark condition and visible light irradiation, respectively. The dV/dt is the differential of H$_2$ production volume (V) to H$_2$ generation time (t).
**Fig S13.** (a) Plots of time versus volume of hydrogen generated from the hydrolysis of AB catalyzed by Rh/WO$_{3-x}$ for ten cycles and (b) the corresponding TOF values.
Fig S14. (a) TEM image and (b) size distribution of Rh nanoparticles of the Rh/WO$_3$ catalysts after the fifth cycle.
**Fig S15.** (a) XRD patterns and (b) XPS spectra for Rh 3d orbitals of the Rh/WO$_{3-x}$ catalysts before and after the fifth cycle.