## **Supporting Information**

## Ultra-small Rh nanoparticles supported on WO<sub>3-x</sub> nanowires as efficient catalysts for visible-light-enhanced hydrogen evolution from ammonia borane

Xiao Li,<sup>a</sup> Yucong Yan,<sup>a</sup> Yi Jiang,<sup>a</sup> Xingqiao Wu,<sup>a</sup> Shi Li,<sup>a</sup> Jingbo Huang,<sup>a</sup> Junjie Li,<sup>a</sup> Yangfan Lin,<sup>a</sup> Deren Yang<sup>a</sup> and Hui Zhang<sup>a,\*</sup>

<sup>a</sup>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<sub>3-x</sub>-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  $WO_{3-x}$  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<sub>3-x</sub>).



**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<sub>3-x</sub> hybrid nanowires and WO<sub>3-x</sub> 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 diderent powers of Xe lamp.



**Fig S11.** Digital photograph of  $Rh/WO_{3-x}$  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<sub>3-x</sub> 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<sub>3-x</sub> catalysts after the fifth cycle.



**Fig S15.** (a) XRD patterns and (b) XPS spectra for Rh 3*d* orbitals of the Rh/WO<sub>3-x</sub> catalysts before and after the fifth cycle.