Supporting Information

In Situ Redox Deposition of Palladium Nanoparticles on Oxygen-Deficient Tungsten Oxide as Efficient Hydrogenation Catalysts

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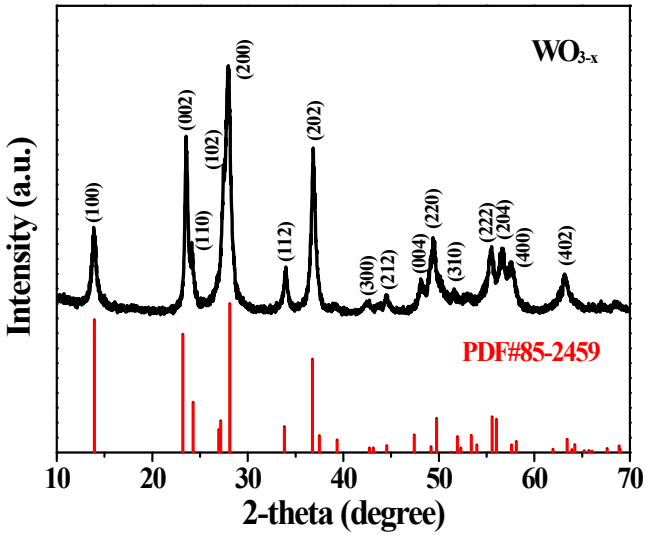

Fig. S1 XRD pattern of as-prepared WO_{3-x} nanowires. The standard card for hexagonal WO_3 (JCPDS no. 85-2459) is shown at the bottom.

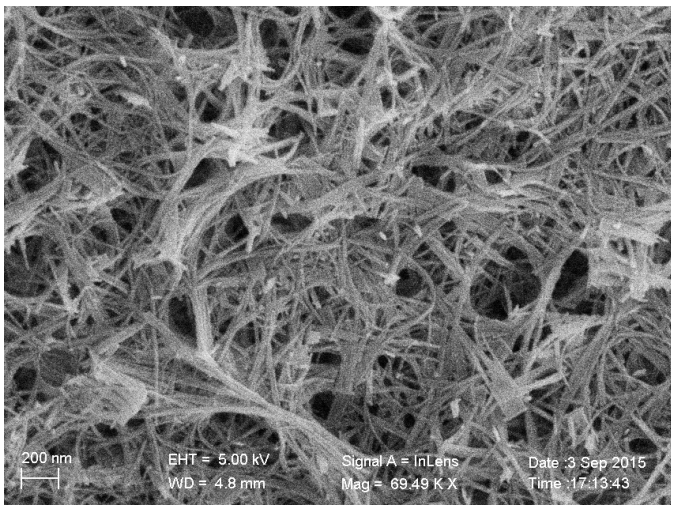

Fig. S2 SEM image of WO_{3-x} nanowires. The SEM image shows a macroporous surface morphology where nanowires (NWs) are interwoven together.

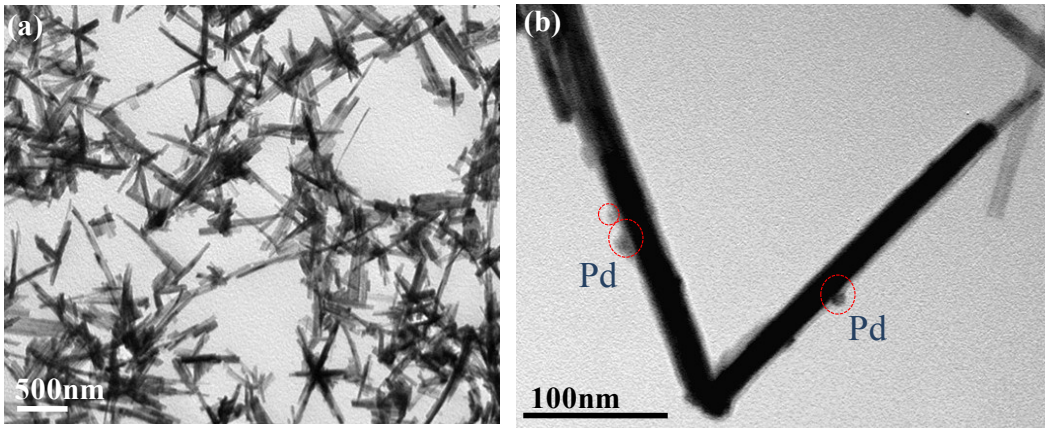

Fig. S3 TEM image of obtained (a) WO_{3-x} NWs and (b) Pd/WO_{3-x} nanocomposites.

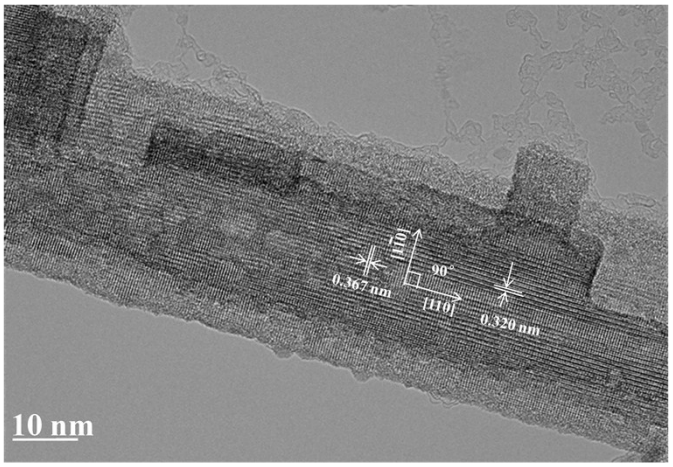

Fig. S4 HRTEM image of WO_{3-x} NWs.

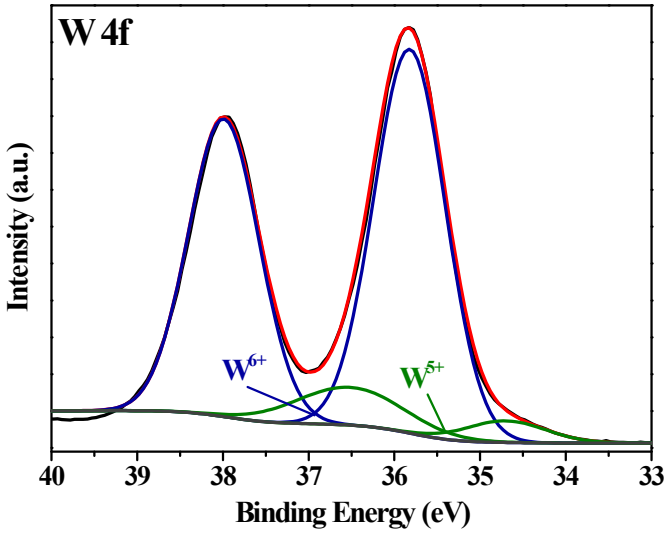

Fig. S5 The W 4f spectrum of Pd/WO_{3-x} nanocomposites. The relative content of W^{5+} is estimated to be about 11.9 % after Pd deposition.

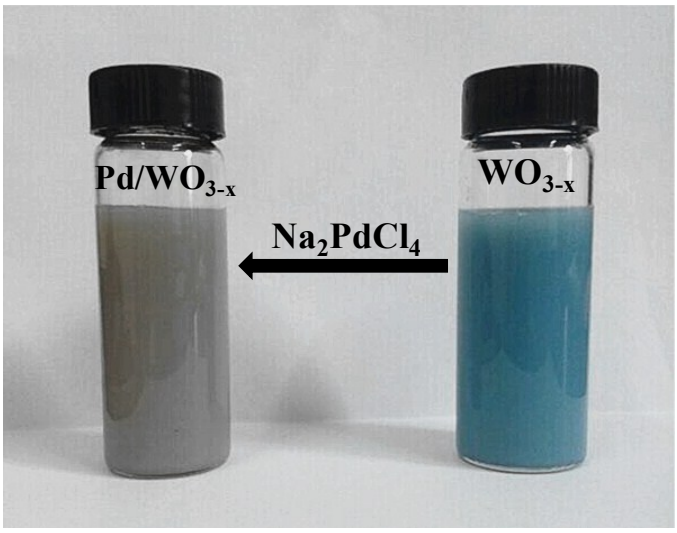

Fig. S6 Optical photographs of WO_{3-x} solutions before and after adding Na_2PdCl_4 solutions, showing the color change.

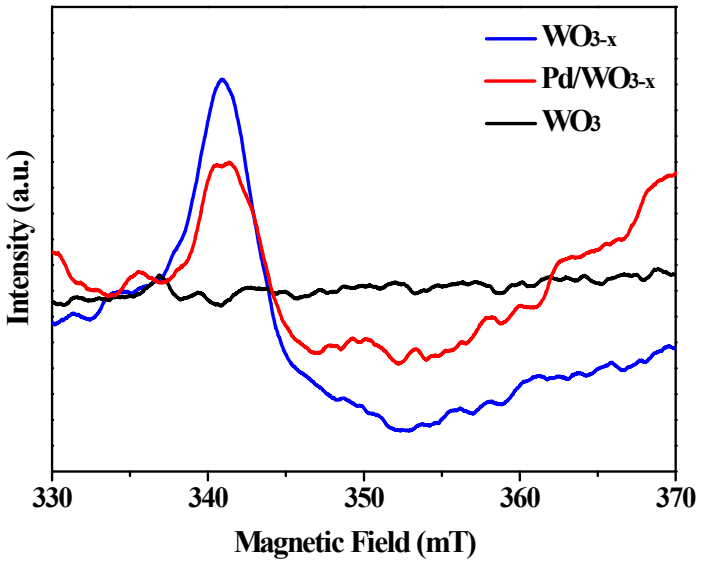

Fig. S7 The X–band EPR spectra of commercial WO_3, WO_{3-x} NWs and Pd/WO_{3-x} nanocomposites recorded at T = 298 K.

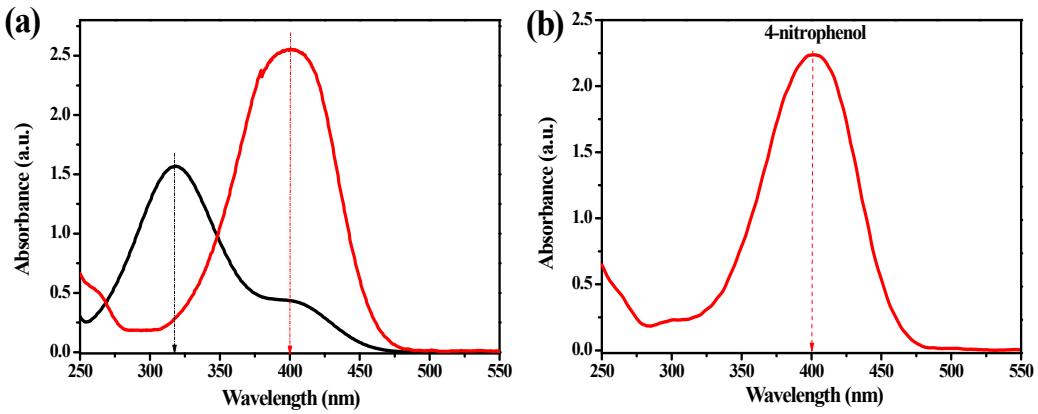

Fig. S8 (a) UV–vis absorption spectra of 4–NP before (black line) and after addition of $NaBH_4$ (red line). After adding $NaBH_4$ solution into 4–NP solution, the aqueous 4–NP solution undergoes an immediate red-shift in the UV–vis absorbance band from 317 to 400 nm. (b)UV–visible absorption spectra of 4–NP at 400 nm. The intensity of the absorption peak of 4–nitrophenol is not reduced within 30 min in the presence of $NaBH_4$.

Table S1. Comparison of the activity of 4–NP reduction over Pd/WO_{3-x} catalyst with other noble-metal loaded catalysts.

Catalyst	Metal content	Rate Constant , k (s^{-1})	References
Pd/WO_{3-x}	0.99 wt%	4.5×10^{-2}	This work
$Fe_xO_y/Pd@mSiO_2$	1.1 wt%	1.09×10^{-3}	*Nanoscale*, 2013, **5**, 5896-5904[1]
Pd/NF-CNT [a]	1.15 wt%	1.08×10^{-3}	*Nanoscale*, 2014, **6**, 6609-6616[2]
Pd/MPC [b]	5.11 wt%	1.2×10^{-2}	*J. Mater. Chem. A*, 2014, **2**, 18775-18785[3]

[a] NF-CNT: purified and oxidized carbon nanotubes. [b] MPC : magnetic porous carbon.

1 T. Yao, T. Cui, X. Fang, F. Cui and J. Wu, *Nanoscale*, 2013, **5**, 5896-5904.

2 X. Gu, W. Qi, X. Xu, Z. Sun, L. Zhang, W. Liu, X. Pan and D. Su, *Nanoscale*, 2014, **6**, 6609-6616.

3 Z. Dong, X. Le, Y. Liu, C. Dong and J. Ma, *J. Mater. Chem. A*, 2014, **2**, 18775-18785.