Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2021
Please do not adjust margins

COMMUNICATION

Supporting Information

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Enhanced the strong metal-support interaction between Pt and WO_{3-x} nanowires for the selective hydrogenation of *p*-chloronitrobenzene

Hongbo Yu,*[a§] Zhiyong Yu,[a§] Fan Yang,[a] Xuedong Yan,[b] and Hongfeng Yin*[a]

[a.] *Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Road, Ningbo, Zhejiang 315201, P. R. 11219 Zhongguan West Road, Ningbo, Zhejiang 315201, P. R.*
[b.] *Ningbo Polytechnic388 East Lushan Road, Ningbo, Zhejiang, 315800*

E-mail: yinhf@nimte.ac.cn; yuhongbo@nimte.ac.cn
[§] *These authors contribute equally to this work.*
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Please do not adjust margins

Please do not adjust margins

Experimental section

Chemicals.

Ammonium metatungstate (99.5%), citric acid monohydrate, chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), sodium borohydride ($NaBH_4$, 98%), tungsten trioxide (WO_3), and *p*-chloronitrobenzene (*p*-CNB) were purchased from Aladdin. Acetone (AR) and absolute ethylalcohol (AR) were purchased from Shanghai Chemical Reagent Company. Al_2O_3 and SiO_2 were purchased from Qingdao Haiyang Chemical Co., Ltd., respectively. All chemicals were used as received without further purification.

Catalyst Preparation.

Synthesis of WO_{3-x} nanowires. WO_{3-x} nanowires were synthesized by a hydrothermal method according to the literature [16]. 0.3090 mmol of ammonium tungstate hydrate and 0.8700 mmol of citric acid monohydrate were dissolved in 20 ml of distilled water under ultrasonic vibration and then the mixture was transformed into a 100 ml Teflon-lined stainless steel autoclave. The reaction was conducted in an oven at 165 ˚C for 11 h and cooled down to room temperature. The samples was collected by centrifugation and washed with acetone and ethanol several times. Finally, the samples was dried at room temperature.

Synthesis of Pt/WO_{3-x} nanocatalysts. In a typical synthesis, 0.0023 mmol $H_2PtCl_6 \cdot 6H_2O$, 0.3000 g of as-synthesized WO_{3-x} nanowires, and 30 mL ionized water were added into a 100 mL three necked round bottomed flask and kept for 3 h with vigorous magnetic stirring. Then 2.0 ml of $NaBH_4$ solution (1.25 mmol) quickly injected into the flask and kept for 8 h. After that, the products were collected by centrifugation and dried at for further use. Additionally, the as-synthesized Pt/WO_{3-x} nanocatalysts were, respectively, calcined at 300 ˚C, 400 ˚C, and 500 ˚C in air for 2 h to investigate the thermal stability. The obtained samples denoted as Pt/WO_{3-x}-300 ^oC, Pt/WO_{3-x}-400 ^oC, and Pt/WO_{3-x}-500 ^oC, respectively.

The synthetic procedure of Pt/WO_3, Pt/Al_2O_3, and Pt/SiO_2 nanocatalysts was the same as that of Pt-WO_{3-x} except that commercial WO_3, Al_2O_3, and SiO_2 powder were used instead of WO_{3-x} nanowires.

Catalyst Characterizations.

X-ray diffraction (XRD) patterns of WO_{3-x}, Pt/WO_{3-x}, Pt/WO_3, Pt/SiO_2, and Pt/Al_2O_3 nanocatalysts were obtained using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation in the 2θ range from 10° to 90°. Transmission electron microscopy (TEM) images with energy-dispersive spectroscopy (EDS) were taken with a TF20 transmission electron microscope manipulated at 200 kV. X-ray photoelectron spectra (XPS) were carried out on an AXIS ULTRA DLD multipurpose X-ray photoelectron spectroscope with an Al source, and the obtained results were verified by C1s (284.8 eV) and treated using Casa XPS software. The actual Pt loadings of the samples were determined by a PE Optima 2100DV inductively coupled plasma optical emission spectrometer (ICP-OES). H_2 temperature programmed reduction (H_2-TPR) for the Pt-based nanocatalysts were performed on a quartz microreactor (VDSorb-91i, Quzhou Vodo instrument Co. Ltd., China). For the TPR experiments, 50 mg of samples were placed in a U-type quartz reaction tube and heated to 100 ˚C in an argon flow (30 mL/ min) for 2 h. After that, the system was cooled down to 50 ^oC and then reduced in a H_2/Ar (8%v/v) flow (20 mL/min) by ramping the temperature from 50 to 920 ◦C at a rate of 15 ◦C/min. Finally, the signals were recorded by a TCD (thermal conductivity detector). The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E500 spectrometer.

Catalytic Hydrogenations.

The catalytic hydrogenation of *p*-CNB with H_2 was performed on a mild reaction conditions (30 ˚C and 0.1 MPa H_2). In a typical procedure, 0.0100 g of samples, 20.0 mL of absolute ethanol, and 0.1000 g of reactants were added into a 100 ml of three-necked bottle-bottomed flask and then the system was heated to 30 ^oC in a 0.1 MPa H_2 flow with vigorous magnetic stirring. After reactions, the liquid products were collected by centrifugation and analyzed by a gas chromatograph GC 2060 equipped with a flame ionization detector.

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Please do not adjust margins

Figure S1. The blue color sample of the hydrothermal synthesis.

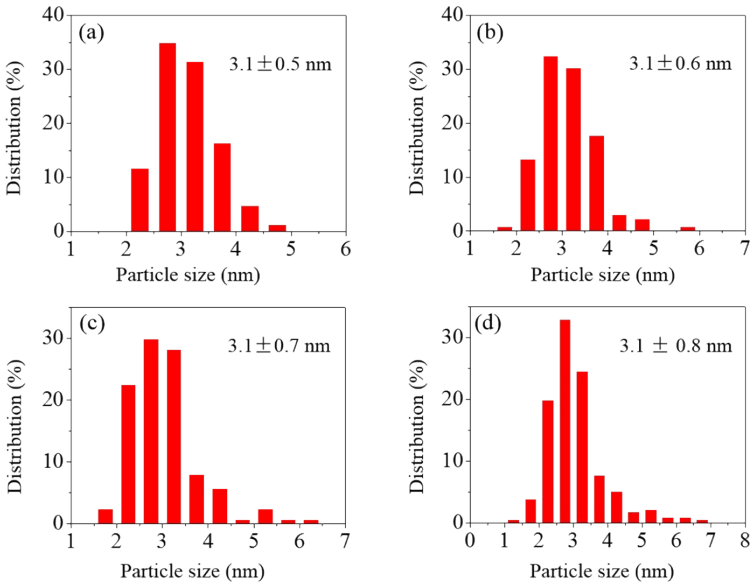

Figure S2. Size distributions of Pt NPs showing: (a) Pt/WO_{3-x}; (b) Pt/WO_{3-x} calcined at 300 °C; (c) Pt/WO_{3-x} calcined at 400 °C; (d) Pt/WO_{3-x} calcined at 500 °C.

Please do not adjust margins

Please do not adjust margins

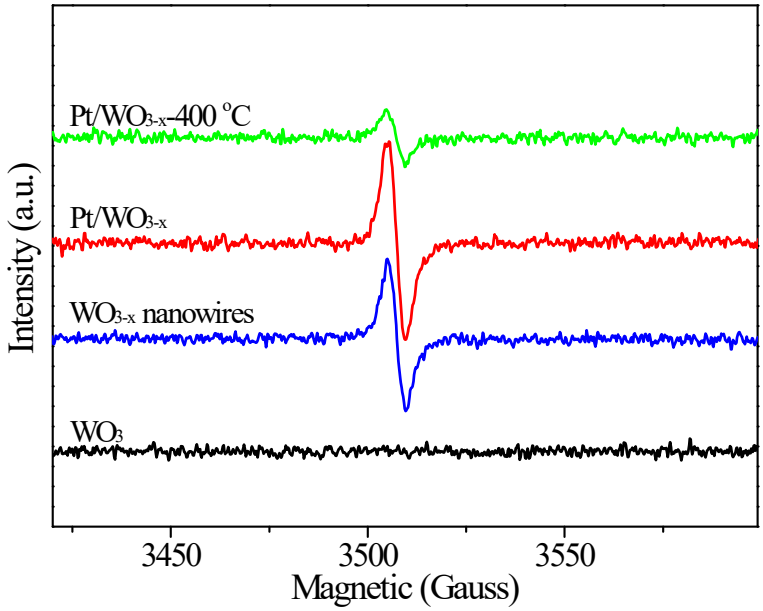

Figure S3. EPR spectra of commercial WO_3, WO_{3-x} nanowires and Pt/WO_{3-x} nanocomposites calcined at 400 °C recorded at room temperature.

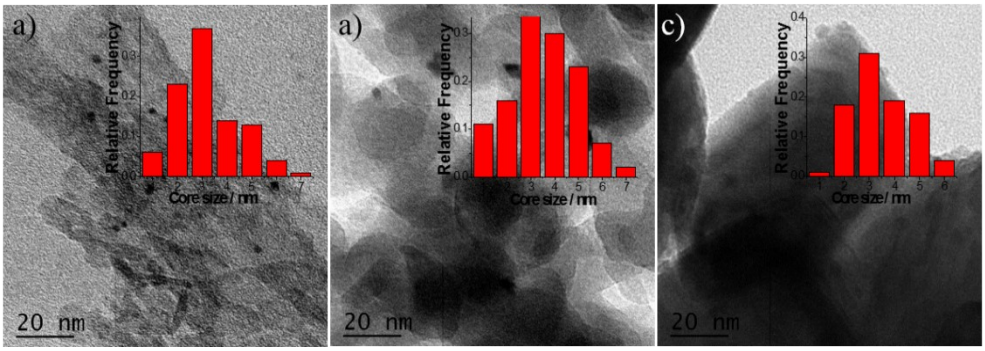

Figure S4. TEM image of the a) Pt/Al_2O_3, b) Pt/SiO_2, and c) Pt/WO_3 nanocatalyst.

Table S1. Cycle to cycle *p*-CNB hydrogenation over Pt/WO_{3-x}-400 °C catalysts.

Cycle Index[a]	Catalyst (g)	*p*-CNB (g)	Conversion (%)	*p*-CAN selectivity (%)
1	0.1000	1.0000	100.0	92.8
2	0.0777	0.777	100.0	92.6
3	0.06667	0.6670	100.0	93.7
4	0.0583	0.583	100.0	92.2

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Please do not adjust margins

[a]Reaction conditions: EtOH in cycle 1, 30.0 mL; the weight of EtOH in the following cycles decreased according to the weight of *p*-CNB at a fixed EtOH/*p*-CNB ratio; 0.10 MPa of H_2; reaction time-1.0 h; reaction temperature-30 °C; agitation speed-700 rpm.

Please do not adjust margins