Electronic Supplementary Information

In situ Assembly of Well-dispersed Gold Nanoparticles on Hierarchical Double-Walled Nickel Silicate Hollow Nanofibers as An Efficient and Reusable Hydrogenation Catalyst

Renxi Jin, [a] **Yang Yang,** [a] **Yunfeng Li,**[a] **Lin Fang,**[a] **Yan Xing*** [a] **and Shuyan Song***[b]

[a] *College of Chemistry, Northeast Normal University, Changchun, 130024, China; E-mail: xingy202@nenu.edu.cn; Tel: +86-431-85099657*
[b] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130012, China; E-mail: songsy@ciac.ac.cn*

Experimental section:

Synthesis of SiO_2 hollow nanofibers (SHNFs): The SHNFs were prepared through a single capillary electrospinning method. 0.95 g of polyvinylpyrrolidone (PVP) powder (Mn = 90000) was dissolved in 10 mL of ethanol. Then, 1.6 mL of tetraethyl orthosilicate (TEOS) was slowly dropped into the above PVP solution to obtain the precursor. After that, the precursor was transferred into a plastic syringe for electrospinning under the voltage of 9.5 kV. The products were collected at a distance about 20 cm to the syringe tip. Finally, the above composites of PVP/TEOS were calcined at a rate of 0.5 °C min^{-1} and remained for 2 h at 550 °C. Thus, the SHNFs were obtained.

Synthesis of hierarchical double-walled nickel silicate hollow nanofibers (NSHNFs): The NSHNFs were prepared through a simple hydrothermal process. In a typical synthesis, nickel acetate tetrahydrate (0.1 mmol), ammonia chloride (2 mmol), and $NH_3 \cdot H_2O$ (0.2 mL, 28%) were added under stirring to 10 mL of distilled water, the resulting solution and the as-prepared SHNFs (0.01 g) were transferred into a 15 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 100 °C for 10 h. After the autoclave was cooled down to room temperature, the resulting light-green precipitates were collected and washed several times with distilled water and absolute ethanol. The final products were dried under vacuum at 60 °C for 4 h.

Synthesis of AuNPs/NSHNFs: 0.01 g of $SnCl_2$ was dissolved in 20 mL of HCl (10 mM) solution. Then, 0.01 g of the obtained NSHNFs was added to the above solution and stirred for 2.5 h at room temperature. After this, the precipitates were collected by sedimentation followed by washing with distilled water for five times. Thus, the activated NSHNFs were obtained. The activated NSHNFs were mixed with 20 mL of distilled water, then 32.3 μm of $HAuCl_4$ solution (0.0486 M) was added to the above mixture. After stirring for 10 min, AuNPs/NSHNFs were obtained and washed for several times with distilled water and absolute ethanol.

Catalytic property of AuNPs/NSHNFs: 1 mg of the as-prepared AuNPs/NSHNFs was added to 30 mL of aqueous 4-NP solution (0.12 mM). Then, 30 mL of fresh $NaBH_4$ solution (12 mM) was rapidly injected into the above mixture under stirring. The color of the mixture vanished gradually. Parts of the mixture were taken out after appropriate time intervals for the determination with UV-vis absorption spectra. Recycle catalysis experiments were conducted in order to study the reusability of the catalysts. Similar to the above reduction process, a given amount of the as-prepared AuNPs/NSHNFs (1 mg) was used to catalyze 4-NP (c (4-NP) = 1.2×10^{-4} mol L^{-1}, c ($NaBH_4$) = 1.2×10^{-2} mol L^{-1}). After 10 min of reaction, the catalyst was separated by centrifugation, and the supernatant was measured by using UV–vis spectroscope. Then the same procedures were repeated four times.

Characterization: X-ray powder diffraction (XRD) analysis was measured on a Siemens D5005 Diffractometer with Cu Kα radiation (λ = 1.5418Å). Field-emission scanning electron microscopy (FE-SEM) images were obtained with a XHITACHI S-4800 microscope. Transmission electron microscopic (TEM) images, high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEM-2100F microscope with an accelerating voltage of 200 kV. Brunauer-Emmett-Teller (BET) surface area was measured on a Micromeritics Tristar 3000 analyzer at 77.4 K. A Thermo ESCALAB 250 X-ray photoelectron spectroscope (XPS) equipped with a standard and monochromatic source (Al *Kα hv* = 1486.6 eV) was employed for surface analysis. UV-Vis absorption spectra were measured at room temperature with a UV–vis–NIR (Purkinje General, TU-1900) spectrophotometer.

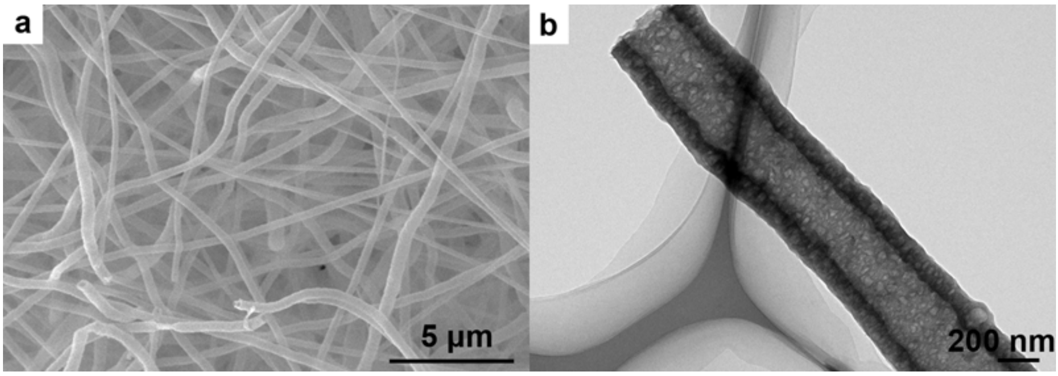


Fig. S1 Typical FESEM (a) and TEM (b) images of SiO_2 hollow nanofibers.

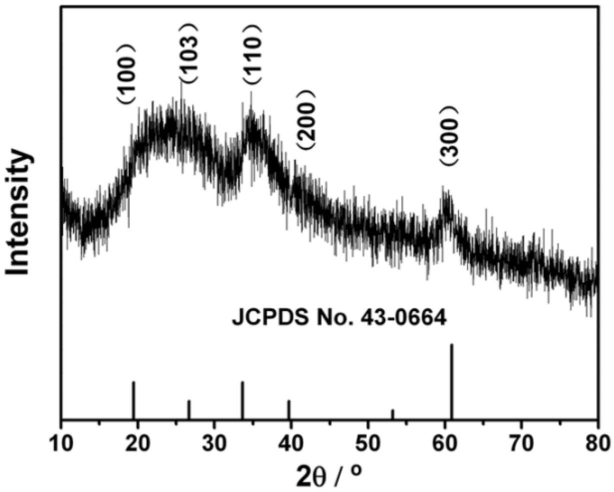


Fig. S2 XRD patterns of NSHNFs.

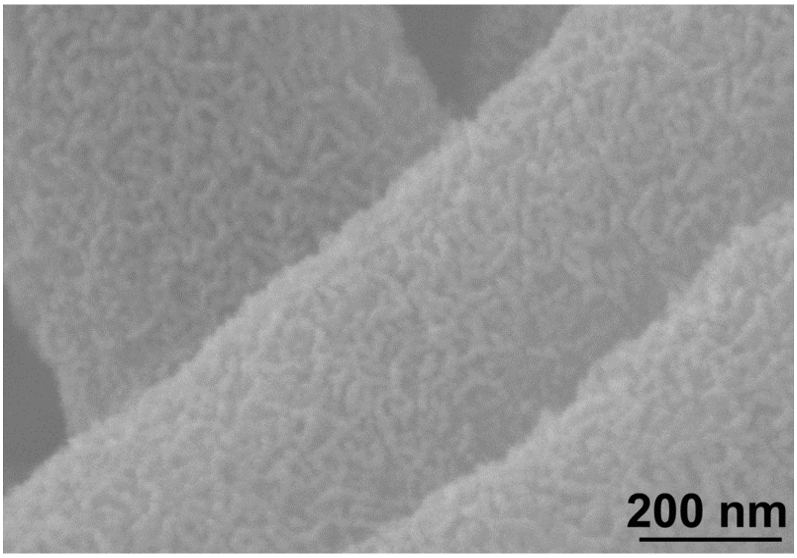


Fig. S3 Typical FESEM of NSHNFs.

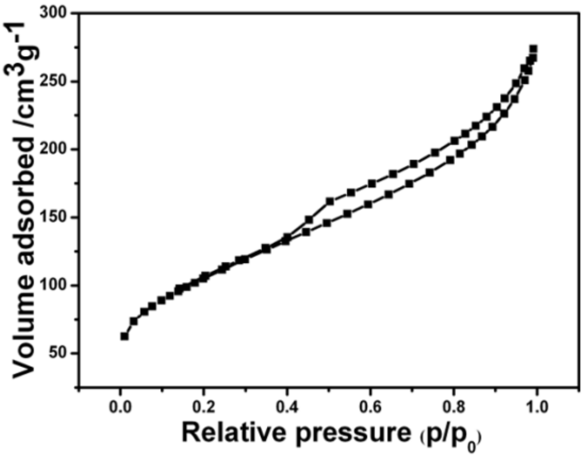


Fig. S4 Nitrogen adsorption-desorption isotherm of the as-prepared NSHNFs.

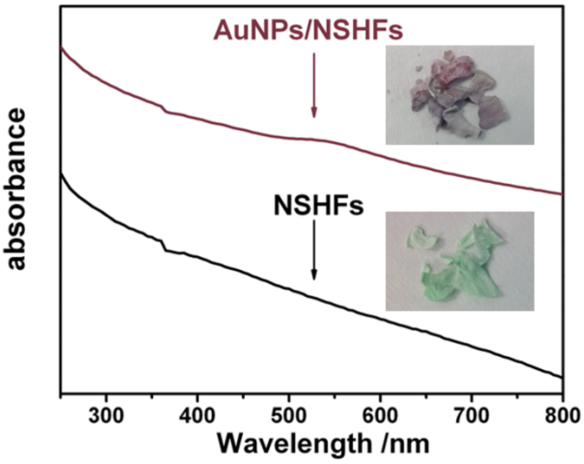


Fig. S5 UV-Vis absorption spectra of aqueous suspensions of NSHNFs and AuNPs/NSHNFs; insert is the optical images of NSHNFs and AuNPs/NSHNFs, respectively.

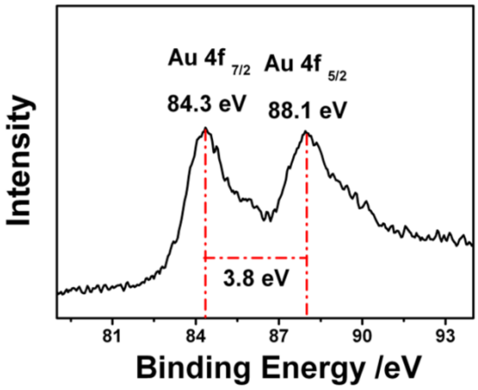


Fig. S6 Au 4f XPS spectrum of the as-prepared AuNPs/NSHNFs.

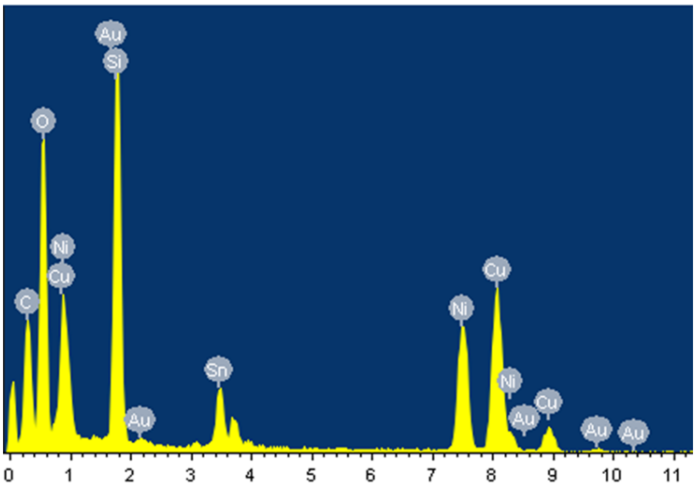


Fig. S7 The EDX spectrum of the as-prepared AuNPs/NSHNFs.

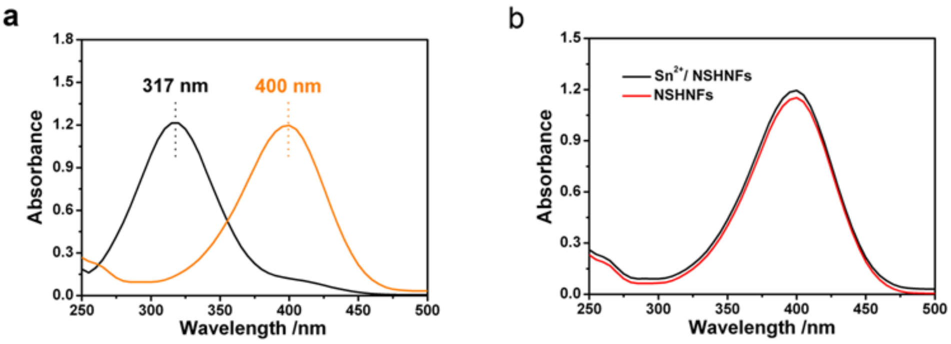


Fig. S8 (a) UV-Vis spectra of 4-NP before and after the addition of an aqueous solution of $NaBH_4$; (b) UV-Vis absorption spectra of 4-NP in the presence of $NaBH_4$ and Sn^{2+}/NSHNFs; $NaBH_4$ and NSHNFs for 2.5 h.

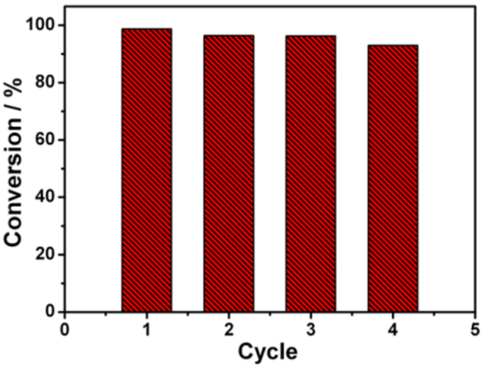


Fig. S9 The reusability of the as-prepared AuNPs/NSHNFs.

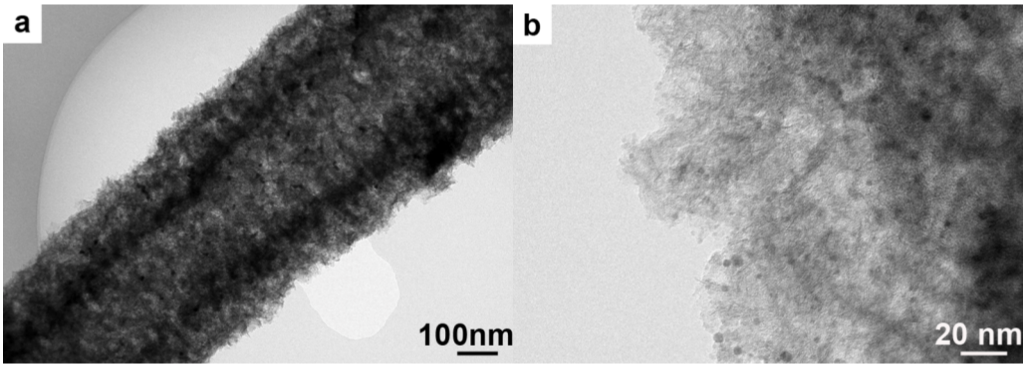


Fig. S10 TEM image of AuNPs/NSHNFs after four cycles of the catalytic reduction reactions.

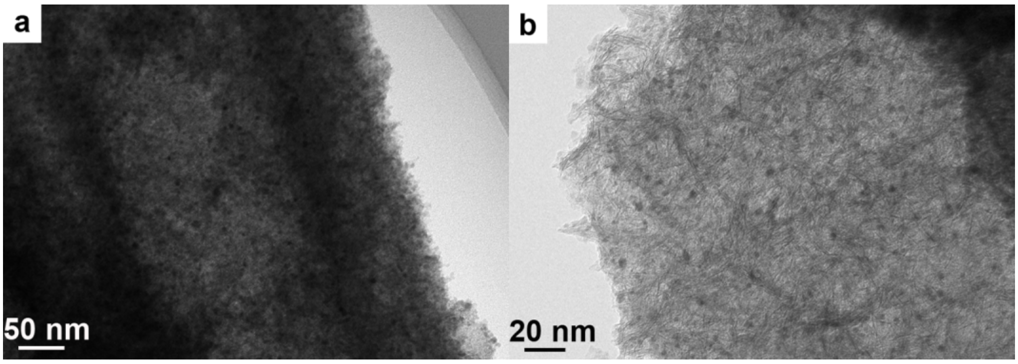
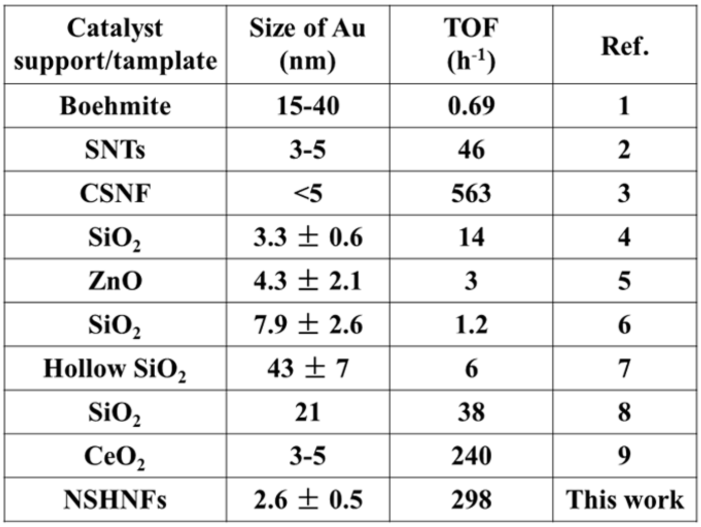


Fig. S11 Typical TEM images of the as-prepared AuNPs/NSHNFs after calcination at 500 °C for 2 h.



Catalyst support/tamplate	Size of Au (nm)	TOF (h^{-1})	Ref.
Boehmite	15-40	0.69	1
SNTs	3-5	46	2
CSNF	<5	563	3
SiO_2	3.3 ± 0.6	14	4
ZnO	4.3 ± 2.1	3	5
SiO_2	7.9 ± 2.6	1.2	6
Hollow SiO_2	43 ± 7	6	7
SiO_2	21	38	8
CeO_2	3-5	240	9
NSHNFs	2.6 ± 0.5	298	This work

SNTs: silica nanotubes; CSNF: cellulose single nanofibers

Table S1. Recent studies on the reduction of 4-NP over Au nanocatalysts.

1 D. Jana, A. Dandapat and G. De, *Langmuir*, 2010, **26**, 12177.

2 Z. Zhang, C. Shao, P. Zou, P. Zhang, M. Zhang, J. Mu, Z. Guo, X. Li, C. Wang and Y. Liu, *Chem. Commun.*, 2011, **47**, 3906.

3 H. Koga, E. Tokunaga, M. Hidaka, Y. Umemura, T. Saito, A. Isogai and T. Kitaoka, *Chem. Commun.*, 2010, **46**, 8567.

4 S. H. Wu, C. T. Tseng, Y. S. Lin, C. H. Lin, Y. Hung and C. Y. Mou, *J. Mater. Chem.*, 2011, **21**, 789.

5 H. Koga and T. Kitaoka, *Chem. Eng. J.*, 2011, **168**, 420.

6 H. Wang, J. G. Wang, H. J. Zhou, Y. P. Liu, P. C. Sun and T. H. Chen, *Chem. Commun.*, 2011, **47**, 7680.

7 J. Lee, J. C. Park and H. Song, *Adv. Mater.*, 2008, **20**, 1523.

8 S. Wang, M. Zhang and W. Zhang, *ACS Catal.*, 2011, **1**, 207.

9 B. Liu, S. Yu, Q. Wang, W. Hu, P. Jing, Y. Liu, W. Jia, Y. Liu, L. Liu and J. Zhang, *Chem. Commun.*, 2013, **49**, 3757.