

Supplementary Information

Au/CNTs catalyst for highly selective hydrodeoxygenation of vanillin at the water/oil interface

Xiaomin Yang,^a Yu Liang,^a Xu Zhao,^a Yifan Song,^a Lianghai Hu,^{*b} Xiaofeng Wang,^{*a, d}

Zichen Wang^a and Jieshan Qiu^c

^a *College of Chemistry, Jilin University, Changchun 130012, China.*

^b *College of Life Sciences, Jilin University, Changchun 130012, China.*

^c *Carbon Research Laboratory, State Key Lab of Fine Chemicals, Dalian University of
Technology, Dalian 116023, China*

^d *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of
Chemistry, Jilin University, Changchun 130012, China*

**Correspondence:*

E-mail: lianghaihu@jlu.edu.cn; wangxf103@jlu.edu.cn.

Experimental

Materials

CNTs with a diameter of 10–20 nm, a length of 1–2 μm , and a N_2 surface area of 151 m^2/g were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). The carbon nanotubes are MW, which were prepared by chemical vapor deposition (CVD) method. The purity of pristine CNT is higher than 97%. Before use, pristine CNTs were refluxed in a mixture of HNO_3 , H_2SO_4 , and deionized water (volume ratio of 2:1:1) at 120 $^\circ\text{C}$ for 4 h, then filtered and washed with deionized water until the pH value of the filtrate reached 7, then dried under vacuum. The modification method of AC was the same as that described above. All reagents used in this work were of analytical grade.

Catalyst preparation and characterization

The Au/CNTs catalyst was synthesized via the sol immobilization technique using polyvinyl alcohol (PVA) as protective agent and NaBH_4 as reducing agent. Briefly, 3.7 mL of HAuCl_4 (24.28 mmol/L) was dissolved in 690 mL of H_2O , and 1.6 mL of PVA (0.2 wt.%) was added under stirring. NaBH_4 (4 mL, 0.1 M) was added to the yellow solution under vigorous magnetic stirring. Within a few minutes of sol generation, the colloid was immobilized by adding oxidized carbon nanotubes under fast stirring. After 4 day magnetic stirring, the suspension was filtered. The catalyst was washed thoroughly with distilled water until the filtrate was free of chloride (checked by the AgNO_3 test) and dried at 110 $^\circ\text{C}$ for 12 h. The organic scaffold was removed from the support by a heat treatment under nitrogen flow for 3 h at 350 $^\circ\text{C}$,

and then, the catalyst was activated by reduction under hydrogen flow for 3 h also at 350 °C. For Au/AC catalyst, the same preparation method was adopted as described above.

The crystalline structure of Au/CNTs was analyzed by X-ray powder diffraction (XRD, Rigaku D/MAX-2550VB, Japan) using Cu-K α radiation with a scanning rate of 2° min⁻¹. Transmission electron microscopy (TEM) examination was conducted using a JEOL JEM-2010F equipped with a CCD camera operated at 200 kV.

The gold loading of the prepared Au/CNTs catalyst was determined by inductively coupled plasma-optical emission spectroscopy (ICP/OES) using an Optima 3300 DV spectrometer. The sample preparation and methodology for ICP analysis are as following. 10 mg of Au/CNTs was calcined at 800 °C for 2 h in muffle furnace. After calcination, the residual solid was dissolved in a proper amount of aqua regia. The obtained solution was diluted with deionized water to produce a 100 mL solution. The concentration of gold was determined by ICP/OES.

Particle size distributions were obtained by the measurement of at least 200 particles, and the average diameter was calculated by $d_M = \sum d_i n_i / \sum n_i$, where n_i and d_i are the number and diameter of Au nanoparticles, respectively.

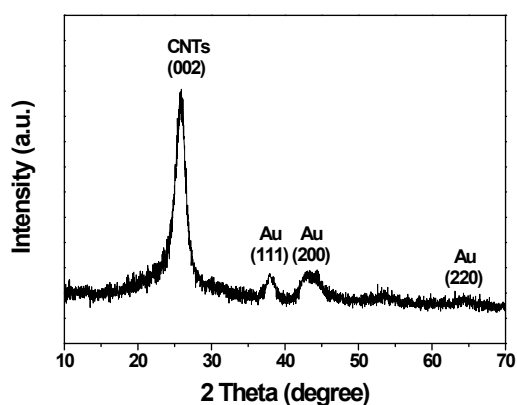


Fig. S1 XRD pattern of Au/CNTs via sol immobilization method.

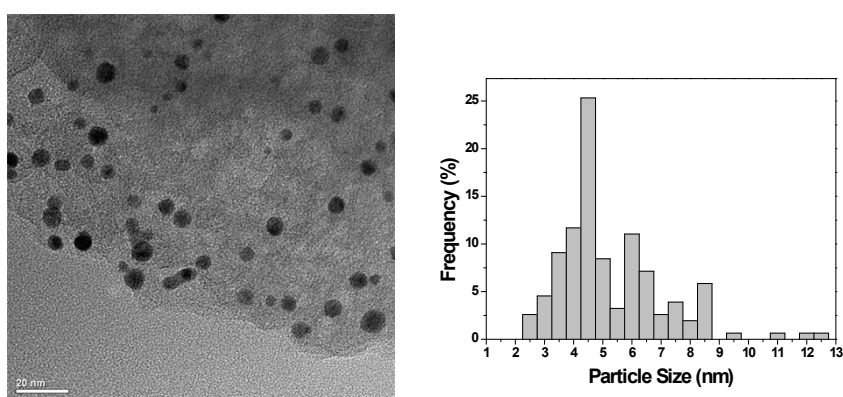


Fig. S2 TEM image and particle size distribution of the Au/AC catalyst via sol immobilization method.

Preparation of fluorescently labeled probes (Au/CNTs-P)

Procedures for the preparation of FITC-labeled Au/CNTs are schematically shown in Fig. S3. The Au/CNTs catalyst was reacted with hexamethylenediamine in the presence of EDC to afford a linker between the CNTs and the subsequent fluorescent probe. Briefly, 2 mg Au/CNTs was mixed with 5 mg hexamethylenediamine and 1 mg EDC in 0.1 mol L⁻¹ MES buffer (pH=6.0). The mixed solution was stirred at room temperature for 2 h. The CNTs conjugated to hexamethylenediamine (CNTs–CONH(CH₂)₆NH₂) were obtained by centrifuging at 25,000 rpm. Subsequent reaction of the CNTs–CONH(CH₂)₆NH₂ with FITC resulted in the formation of fluorescently

labeled Au/CNTs-P. Excess FITC was removed by rinsing with 500 μL PBS and centrifuging three times at 25,000 rpm.

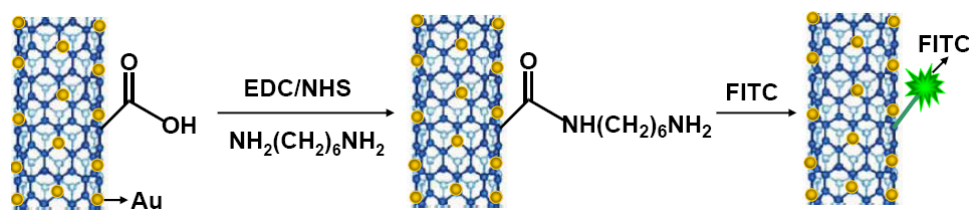


Fig. S3 Schematic representation of the synthesis of fluorescently labeled Au/CNT.

Hydrogenation of vanillin

The hydrogenation reactions were performed in a 100 mL autoclave under stirring. For a typical run, the reaction was carried out with 0.1 mmol vanillin, 0.68 mol% Au/CNTs, 20 mL decalin and 20 mL water as solvents, and 1 MPa H₂ at 150 °C for 8 h. For the blank experiment, the reaction was performed with 0.1 mmol vanillin, 30 mg CNTs, 20 mL decalin and 20 mL water as solvents, and 1 MPa H₂ at 150 °C for 8 h. After each reaction, the emulsion was broken by filtering out the catalyst particles. The two liquid phases were separated and analyzed individually by means of GC (2014C, SHIMADZU) and GC-MS (2010 Plus, SHIMADZU).