Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2019

Supporting information for

Ni@PC as A Stabilized Catalyst Toward Efficient Hydrogenation of Quinoline under Ambient Temperature

Ruirui Yun,*[,a] Wanjiao Ma,[a] Lirui Hong,[a] Yang Hu,[a] Feiyang Zhan,[a] Shoujie Liu, *[,c] and Baishu Zheng*[,b]

[a] The key laboratory of functional molecular solids, Ministry of Education, College of chemistry and Materials Science, Anhui Normal University, Wuhu 214001, P. R. China. Email: ruirui58@ahnu.edu.cn

[b] Hunan Provincial Key Laboratory of Controllable Preparation and Functional Application of Fine Polymers, Hunan Provincial Key Laboratory of Advanced Materials for New Energy Storage and Conversion, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China. E-mail: zbaishu@163.com

[c] Chemistry and Chemical Engineering of Guangdong Laboratory, Shantou 515063, P. R. China. E-mail: jiesliu@ahnu.edu.cn

S1. Materials and Instrumentation

1.1 Materials and sample characterization.

All chemicals were from commercial and used without further purification: Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98.5%), starch soluble, ammonia borane (AB,90%). Powder X-ray diffraction pattern was carried out with a Bruker D8 X-ray diffractometer with monochromatized Cu Kα radiation (λ=1.5418 Å). Transmission electron microscope (TEM) and high-resolution TEM observation was acquired on JEOL-2011 with an electron acceleration energy of 200 kV. The content of Ni in the catalysts was determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES) (Table S2). X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI Quantera microscope. The surface area of the samples was estimated by method of Brunauer-Emmett-Teller (BET) and the pore size distribution was obtained from the DFT method in the Micromertics ASAP2020 software package based on the N_2 sorption at 77 K.

1.2 Sample Preparation.

For the synthesis of Ni@C/PC, Nickel nitrate hexahydrate 0.2973 g, Starch soluble 2 g, were added in 10 mL deionized water and stirred 30 min by ultrasonic. The mixture solution was heated at 100 °C for 20 min to form green sol and dried under vacuum 80 °C overnight to form green powder. The obtained green powder was placed in a tube furnace and heated to 900 °C under Ar gas atmosphere for one hour, and then naturally cooled to room temperature.

1.3 General Procedure for the Catalytic Hydrogenation Reaction.

All reactions were conducted in a 25 mL bottle and a magnetic stirrer. In a typical reaction, 0.1 mmol of substrates and 10 mg of catalyst were mixed with AB (1 mmol) in 10 mL of water and alcohol (1:1). The reaction was carried at normal pressure and room temperature. The products were analyzed using gas chromatography (GC) with an external standard of n-hexadecane and the identity of the products was further confirmed from gas chromatography-mass spectrometry (GC-MS) measurements with ndodecane as standard.

1.4 The caculate method of TOF value:

Particle size：53.6 nm
Dispersity：D=1/d=1/53.6=0.02
Loading capacity：9.98%
Catalyst amount：10 mg
Substrate amount：0.1 mmol
Catalysis time：1200s
Coversion percent：35%
TOF=N/(M*Time)   N: The conversion amount with 35% of substrates in 1200s
M: The number of the iron atoms on the catalyst surface
N=0.1*35%/1000=0.000035 mol
M=0.01*0.0998*0.02/59=$3.38*10^{-7}$
TOF=0.000035/($3.38*10^{-7}$*1200)=$0.086s^{-1}$=$309.6\ h^{-1}$

S2. Characterization Section

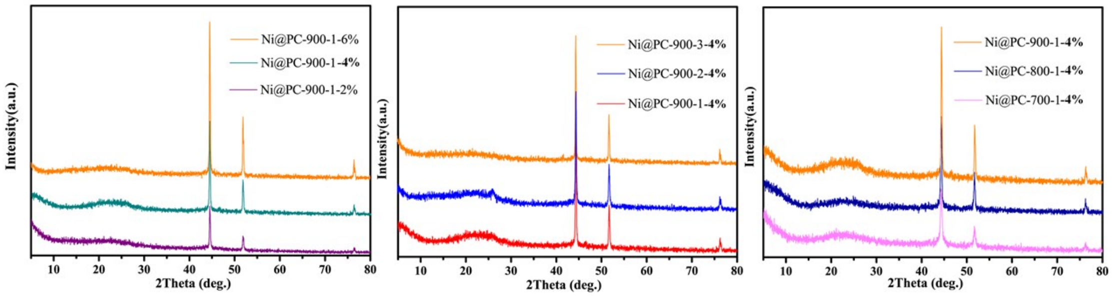

Figure S1. The PXRD of Ni@PC-T-h-x%.

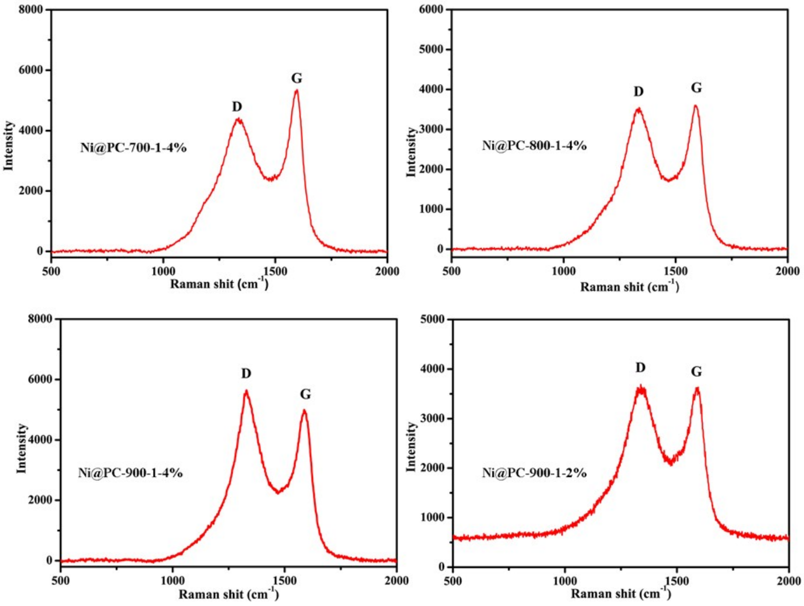

Figure S2. Raman spectrum of Ni@PC-T-h-x%.

.

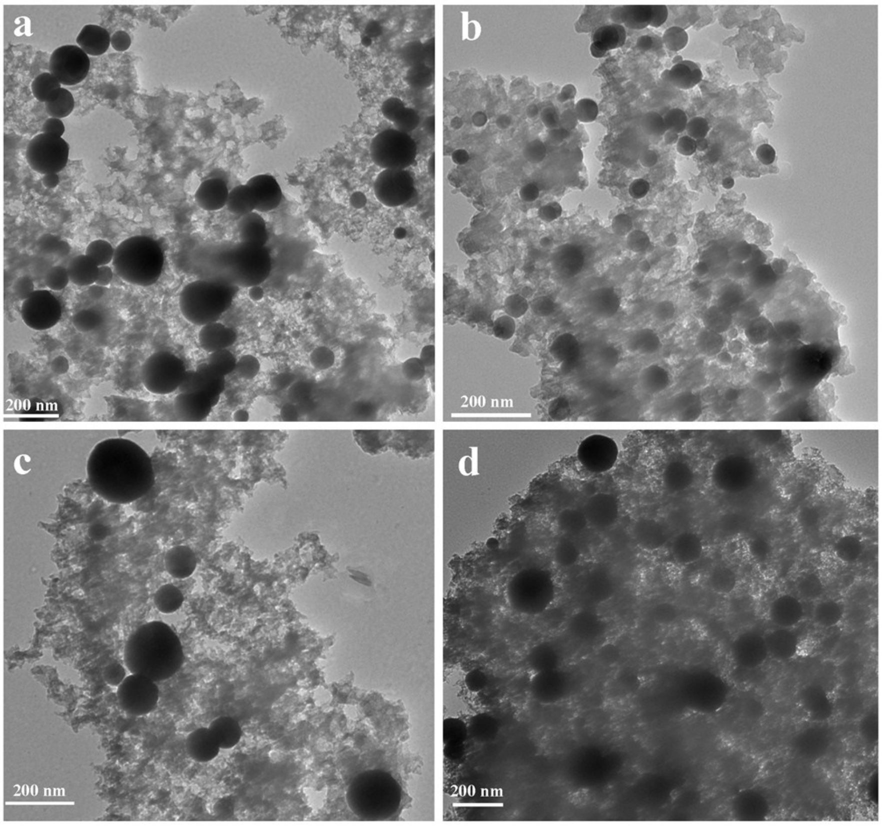

Figure S3. The TEM images of Ni@PC-T-h-x%. a): Ni@PC-900-1-6%; b): Ni@PC-800-1-4%; c) Ni@PC-900-2-4%; d): Ni@PC-700-1-4%.

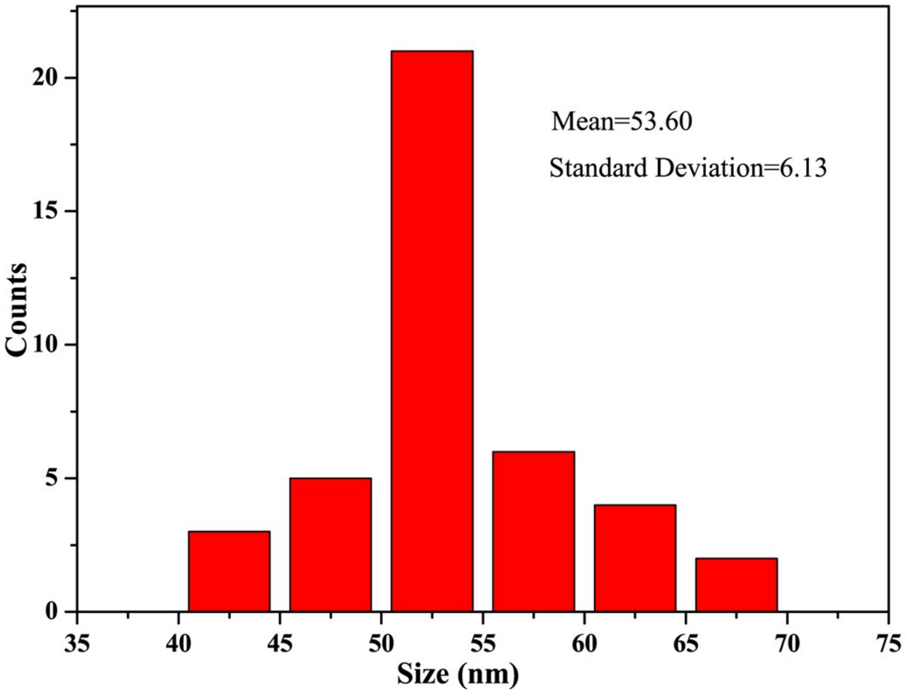

Figure S4. The particle size distribution of Ni@PC-900-1-4%.

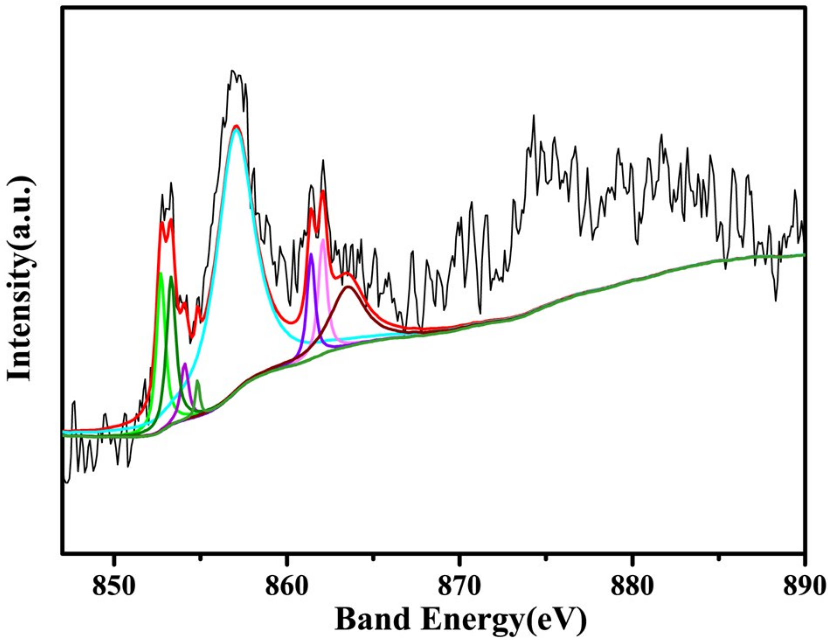

Figure S5. Ni 2p XPS spectra of Ni@PC-900-1-4%.

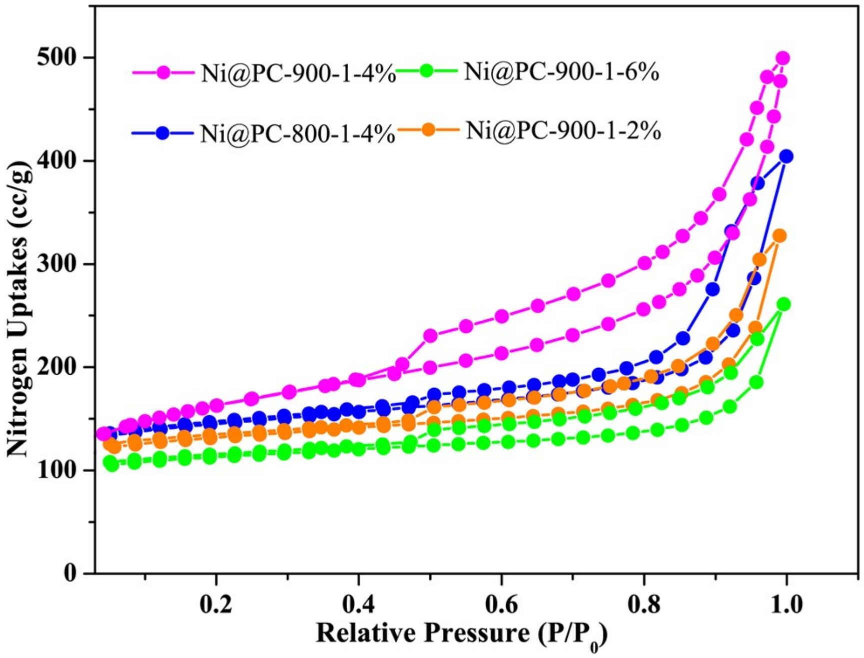

Figure S6. Nitrogen adsorption isotherms of Ni@PC-T-h-x% with the BET of 456.44 (Ni@PC-800-1-4%), 452.37 (Ni@PC-900-1-2%), 565.75 (Ni@PC-900-1-4%), and 353.08 (Ni@PC-900-1-6%) m^2/g, respectively.

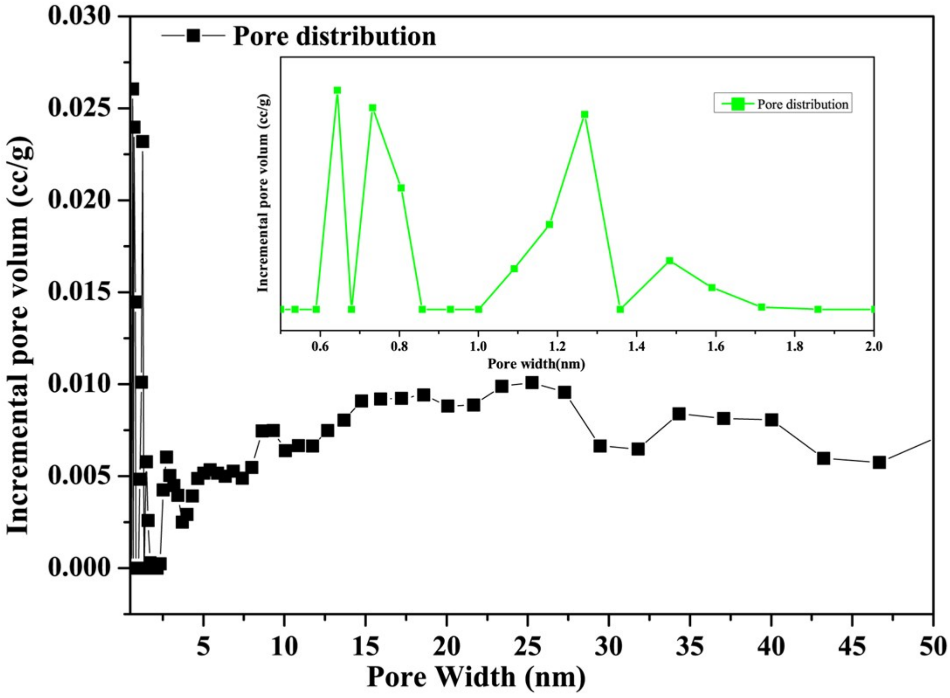

Figure S7. The pore size distribution of Ni@PC-900-1-4% (inset: the scale from 0.5-2.0 nm).

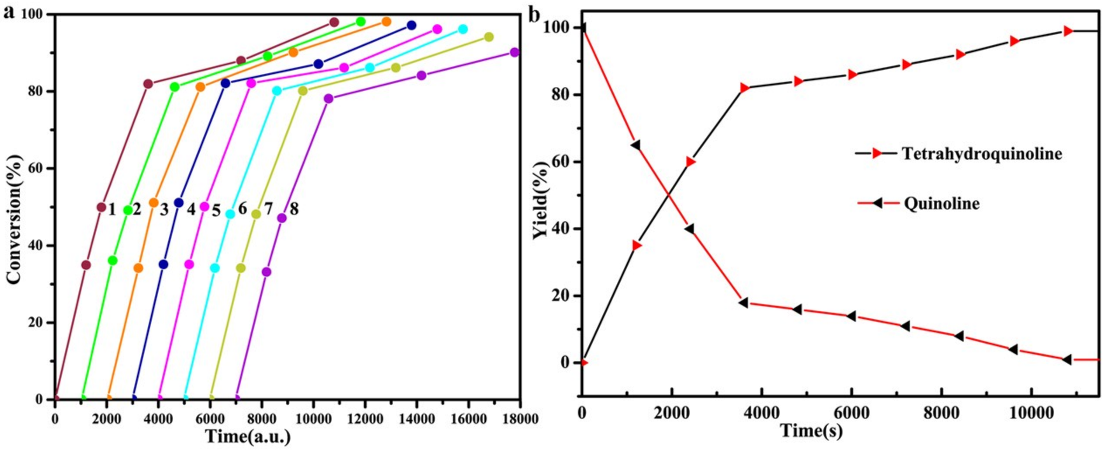

Figure S8. a: recyclability tests of Ni@PC-900-1-4%, b: the dynamics conversion curves of quinoline to THQ.

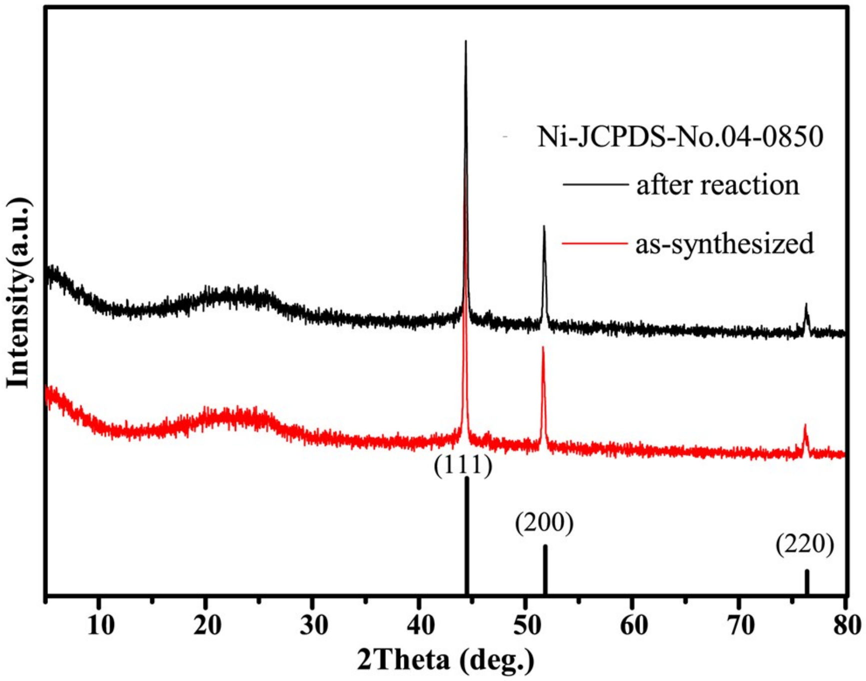

Figure S9. The PXRD of Ni@PC-T-h-x% as-synthesized and after reaction.

Table S1. ICP-AES and element analysis results for the contents of Ni in catalyst of Ni@PC doped on porous carbon.

Ni-based catalysts	The content of Ni (%)
PC-900-1	0.00
Ni@PC-700-1-4%	3.72
Ni@PC-800-1-4%	7.63
Ni@PC-900-1-4%	9.98

Ni@PC-1000-1-4%	11.32
Ni@PC-900-1-2%	5.49
Ni@PC-900-1-6%	16.10
Ni@PC-900-2-4%	7.03