

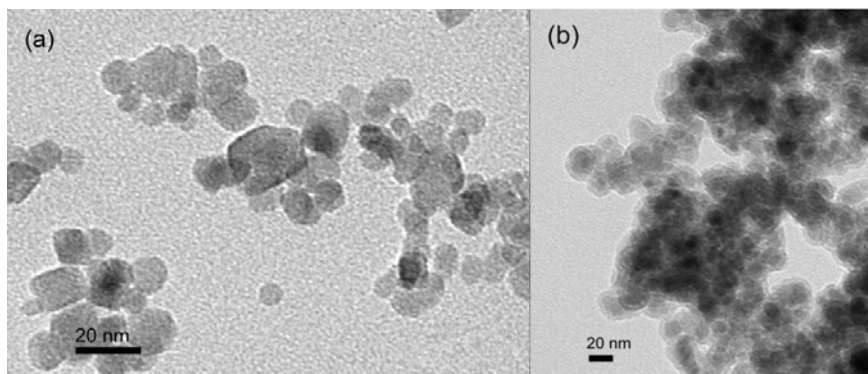
## Supplementary Material

### Efficient hydrolytic breakage of $\beta$ -1,4-glycosidic bond catalyzed by a difunctional magnetic nano catalyst

*Ren-Qiang Yang<sup>A</sup>, Ni Zhang<sup>A</sup>, Xiang-Guang Meng<sup>A,B</sup>, Xiao-Hong Liao<sup>A</sup>, Lu Li<sup>A</sup> and Hong-Jin Song<sup>A</sup>*

<sup>A</sup>Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China.

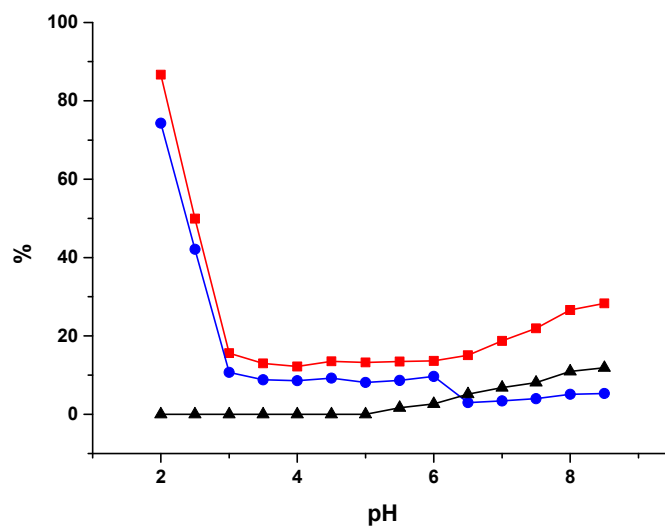
<sup>B</sup>Corresponding author. Email: [mengxgchem@163.com](mailto:mengxgchem@163.com)



**Fig. S1** TEM images of Fe<sub>3</sub>O<sub>4</sub> (a) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (b)

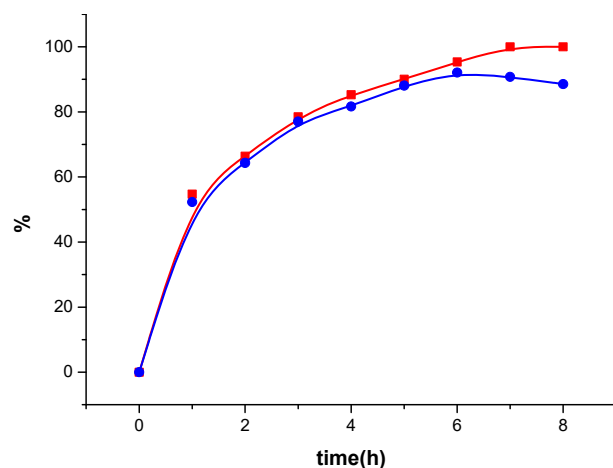


**Fig. S2** Separation of DMNC by using an outer magnet.

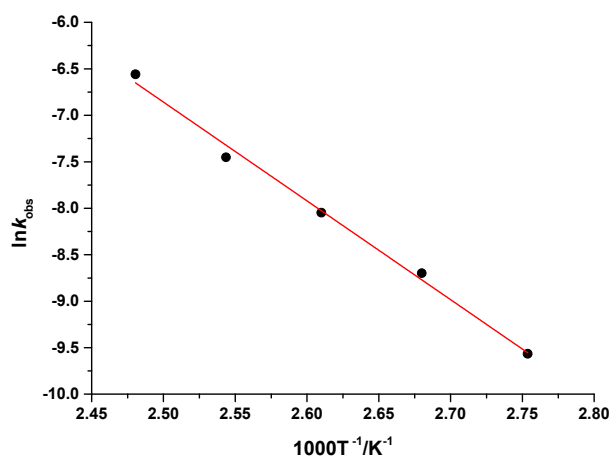


**Fig. S3** Plots of conversion of cellobiose (■), yield of glucose (●) and yield of sucrose (▲)

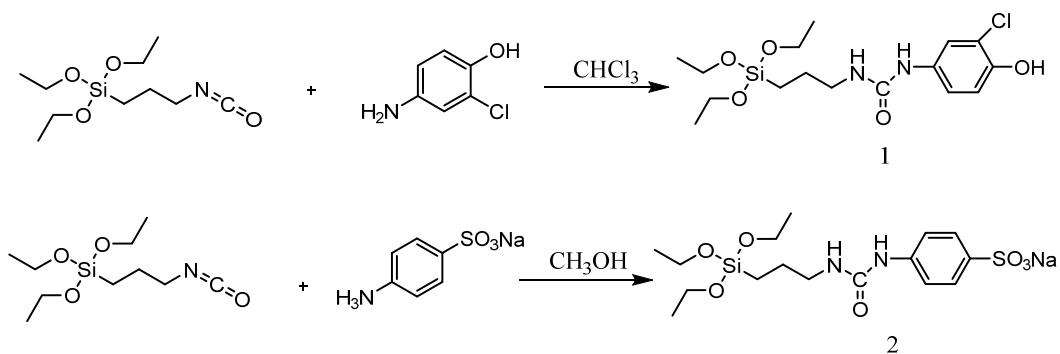
with pH. [Cellobiose] = 0.02 mol·L<sup>-1</sup>, 130 °C, 6 h



**Fig. S4** Plots of conversion of cellobiose (■) and yield of glucose(●) versus reaction time at pH 4.0 and 130 °C.



**Fig. S5** Plots of  $\ln k_{\text{obs}}$  vs.  $1/T$  for cellobiose conversion



**Scheme S1** syntheses of Compound 1 and Compound 2

## **Preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles**

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by chemical coprecipitation method. The procedure was as follows: FeCl<sub>3</sub>·6H<sub>2</sub>O (0.6826 g) and FeSO<sub>4</sub>·7H<sub>2</sub>O (1.5094 g) were added into 40 mL of deionized water containing sodium citrate (0.1188 g) in a three neck glass flask. Before sealing, N<sub>2</sub> gas was passed into the solution for 30 min. The mixture was stirred and heated to 80 °C. Then, the pH of solution was adjusted to 10 by adding 25% aqueous ammonia dropwise. The black solution was stirred for 30 min and then kept at 80 °C for 30 min. After it was cooled to room temperature, the solid was separated by magnet adsorption. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained by washing alternately with deionized water (3×10 mL) and ethanol (3×10 mL), and drying in a vacuum drying oven at 60 °C for 12 h.

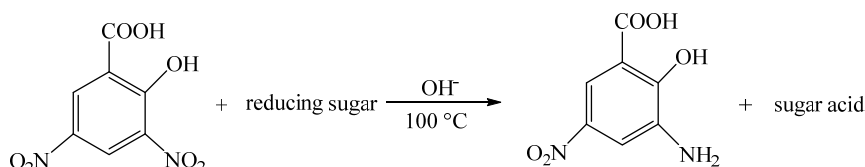
## **Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles**

The core-shell type Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> composite nano particles were prepared by the sol-gel method. The procedure was as follows: 0.5 g of the prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles were ultrasonically dispersed in a mixed solution of 60 mL of ethanol and 20 mL of water. Then, 1.0 mL of TEOS in 15 mL of ethanol was added into the solution and stirred for 15 min at room temperature. After aqueous ammonia (2 mL) was added dropwise to the solution, the solution was stirred and kept at room temperature for 8 h. The solid was separated by magnetic adsorption. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were obtained by washing with ethanol (3×20 mL) and then drying in a vacuum drying oven at 60 °C for 12 h.

## **DNS Analysis method for the detection of total reducing sugars**

The DNS method is a commonly used for the detection of total reducing sugars<sup>[1-3]</sup>. The mechanism is as follows: 3,5-dinitrosalicylic acid (DNS) undergoes redox reactions with the aldehyde groups of reducing sugars under heating and alkaline conditions, and 3,5-

dinitrosalicylic acid is reduced to red-brown 3-amino-2-hydroxy-5-nitrobenzoic acid, which has infrared absorption at 520 nm. Therefore, the concentration of total reducing sugars (TRS) is proportional to the absorbance at 520 nm. The reaction is illustrated as Scheme S2.

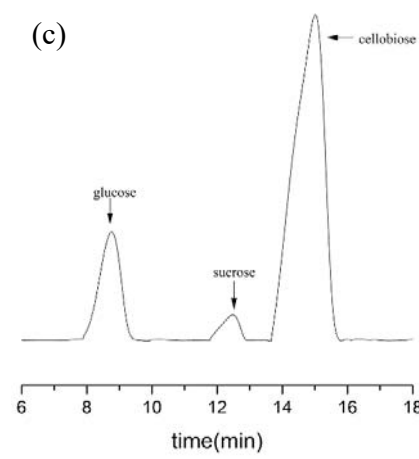
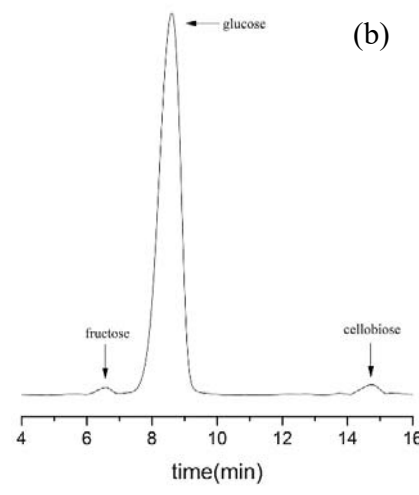
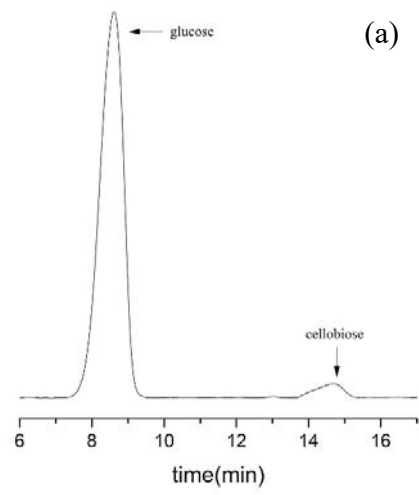


**Scheme S2** The DNS method for the detecting total reducing sugar

Preparation of DNS reagent: 91 g potassium sodium tartrate was dissolved in 250 mL of deionized water, and then 3.15 g of 3,5-dinitrosalicylic acid and 131 mL of 2 mol·L<sup>-1</sup> sodium hydroxide were added into the solution. After the 3,5-dinitrosalicylic acid was completely dissolved, 2.5 g of phenol and 2.5 g of sodium sulfite were added, respectively. The solution was stirred and sonicated. Then, the solution was transferred to a 500 mL brown volumetric flask, deionized water was added the volumetric flask, the solution was well-mixed, and the volumetric flask was placed in a dark place for a week.

The DNS method was used for the determination of total reducing sugars (TRS). The detailed procedures are as follows: 0.4 mL supernatant was transferred to a tube with stopper and 1.5 mL DNS reagent was added into the sample. The solution was heated in boiling water for 5 min and then the test tube was quickly cooled by flowing water to room temperature. The solution was diluted with deionized water to 25 mL. The absorbance was tested by a UV-5300 spectrophotometer at 520 nm, and the concentration of TRS was calculated based on a standard curve obtained with glucose.

## HPLC chromatographs of reaction solution



**Fig. S6** HPLC chromatographs of reaction solution of cellobiose hydrolysis at 130 °C 6 h: (a) pH 4.0, (b) pH 4.5 (c) pH 8.0

## References

- [1] K. Zhuo, J. Wang, Q. Du, G. Bai, C. Wang, Y. Chen, *Carbohydr. Polym.* **2015**, *115*, 49.
- [2] J. Wang, M. Zhou, Y. Yuan, Q. Zhang, X. Fang, S. Zang, *Bioresour. Technol.* **2015**, *197*, 42.
- [3] L. Hu, Z. Li, Z. Wu, L. Lin, S. Zhou, *Ind. Crops Prod.* **2016**, *84*, 408.