Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


**Supporting information**

# Hierarchical porous carbon stabilized atomically dispersed Au catalyst for acetylene hydrochlorination

Guojun Lan, Jinlong Zhou, Qingfeng Ye, Di Lin, Yiyang Qiu, Zaizhe Cheng, Xiucheng Sun, Ying Li*

Institute of Industrial Catalysis, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Zhejiang University of Technology, *Corresponding authors E-mail address: liying@zjut.edu.cn (Y. Li)

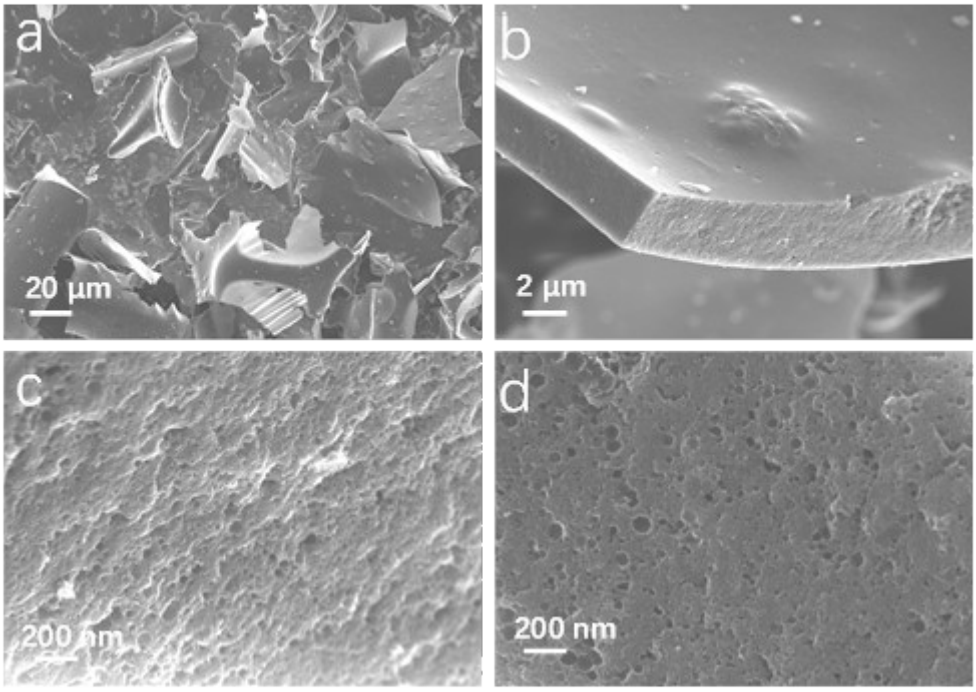


**Figure S1** SEM images of Au-CSC-850 catalyst.

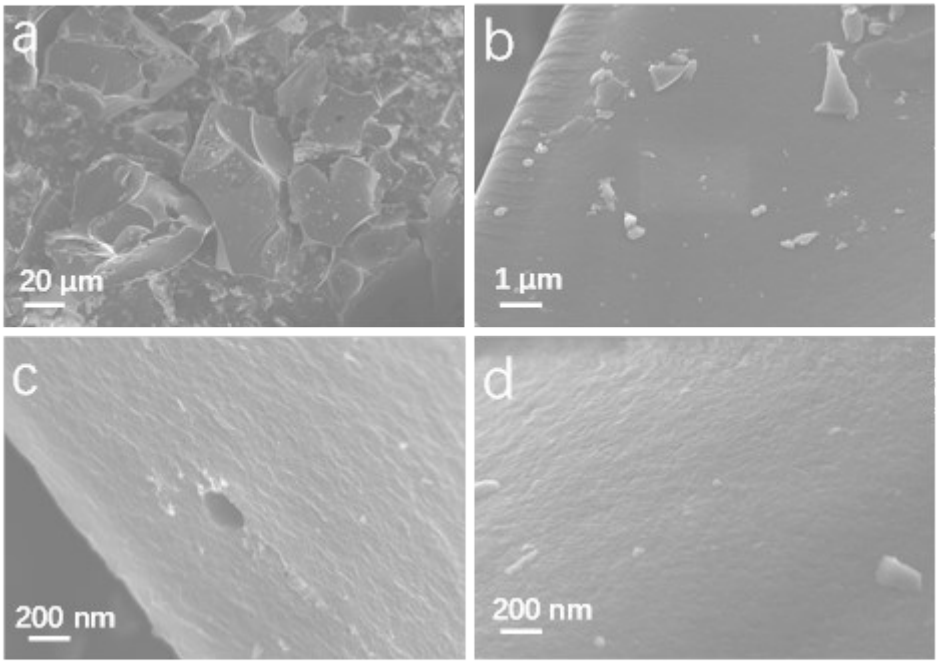


**Figure S2** SEM images of Au-SC-850 catalyst.

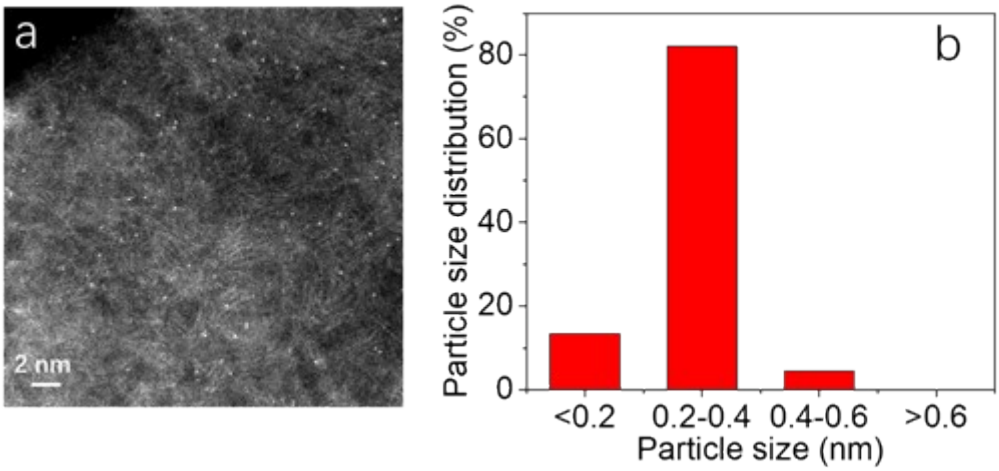


**Figure S3** (a) The representative aberration-corrected high-angle annular dark field-scanning transmission electron microscopy images of Au-CSC-850 catalyst, and (b) histogram of Au particle size distribution over Au-CSC-850 catalyst.

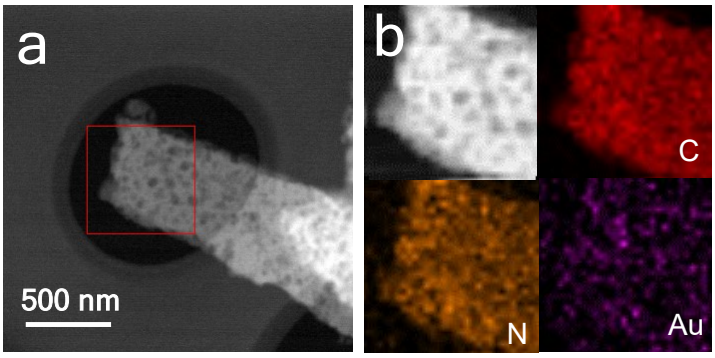


**Figure S4.** STEM image (a) and EDX elemental mapping (b) of Au-CSC-850 catalyst.

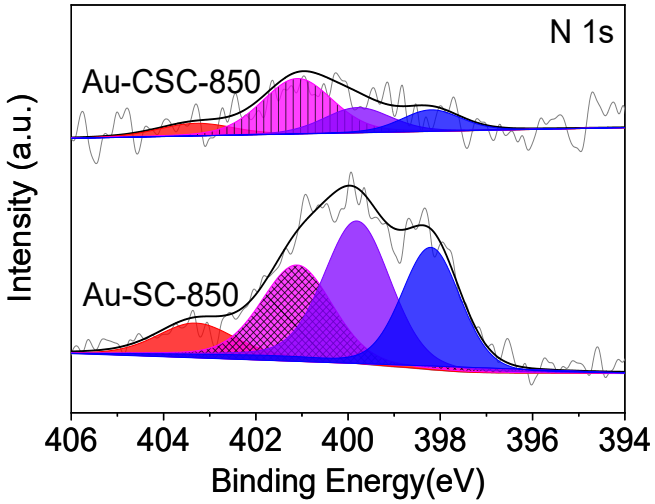


**Figure S5** Deconvolution of N 1s XPS spectra for Au-CSC-850 and Au-SC-850 catalysts.

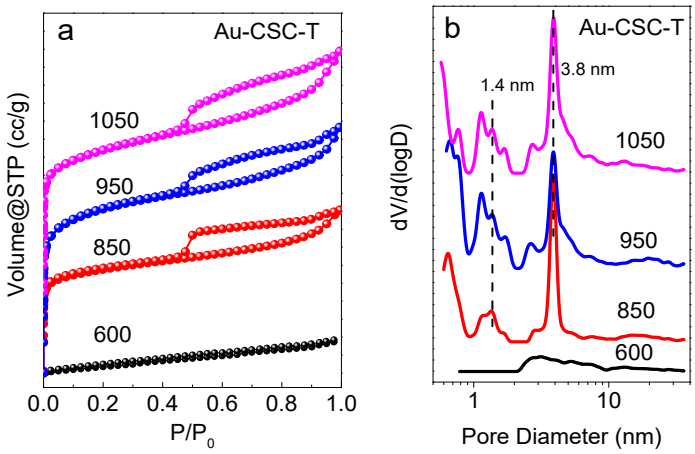


**Figure S6** $N_2$ adsorption isotherms (a) and pore size distribution (b) of Au-CSC-T catalysts

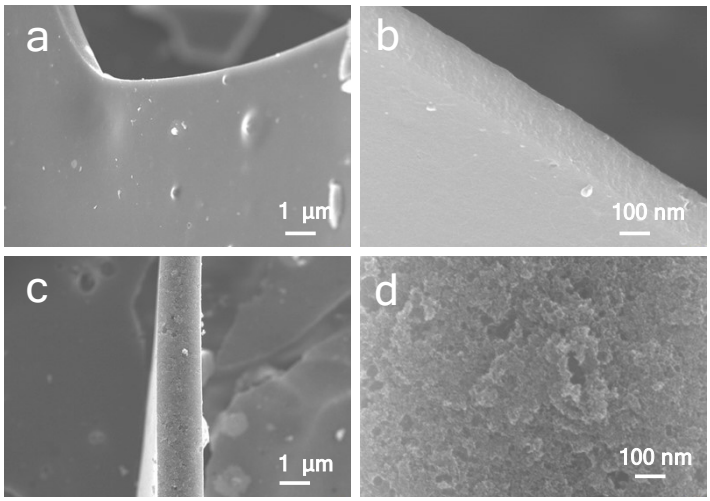


**Figure S7** SEM images of (a, b) Au-CSC-600 and (c, d) Au-CSC-1050 catalysts.

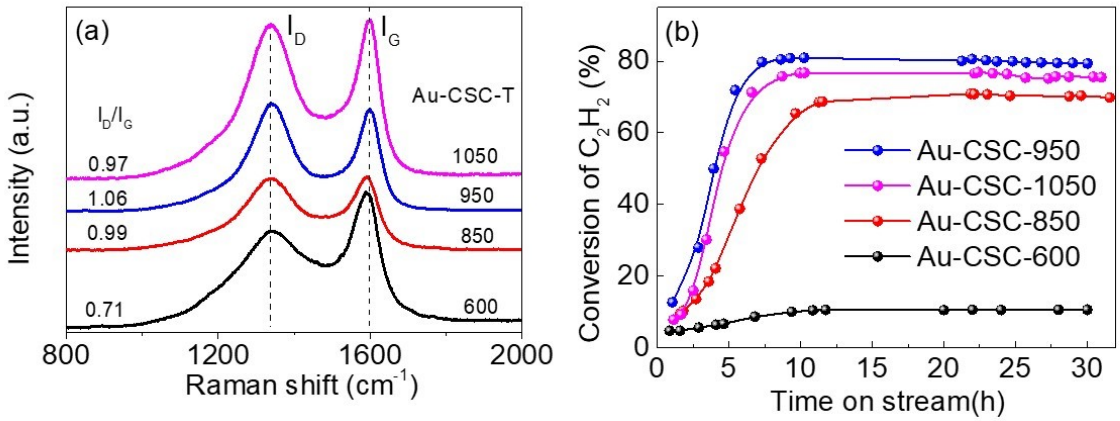


**Figure S8** Raman spectra (a) and conversion of acetylene (b) for Au-CSC-T catalysts in acetylene hydrochlorination. Temperature: 180 °C; $V_{C2H2}$:$V_{HCl}$ = 1.10; GHSV of $C_2H_2$ = 600 $h^{-1}$.

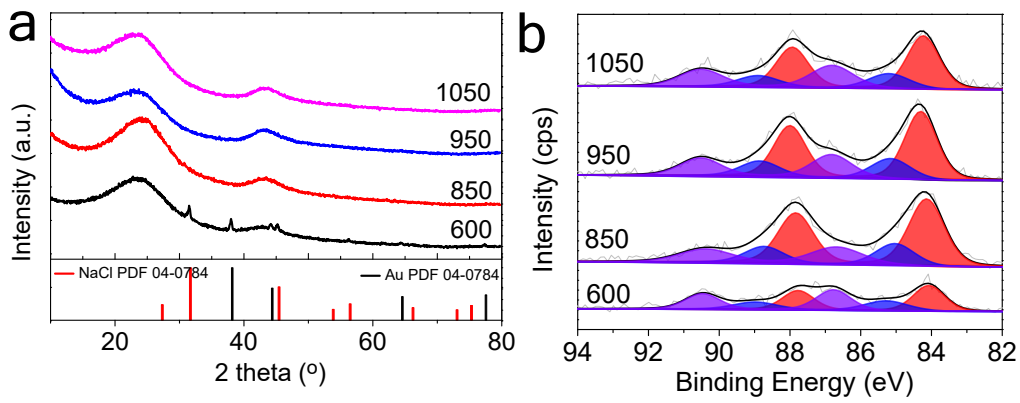


**Figure S9** (a) XRD patterns and (b) deconvolution of Au 4f XPS spectra for Au-CSC-T catalysts.

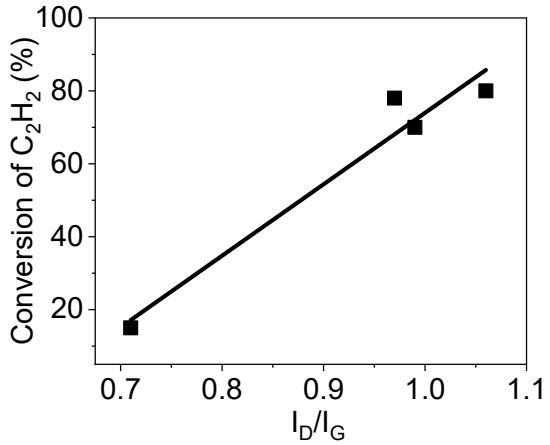


**Figure S10** The relationship between the conversion of acetylene and defects (ratio of $I_D/I_G$) for Au-CSC-T catalysts in acetylene hydrochlorination.

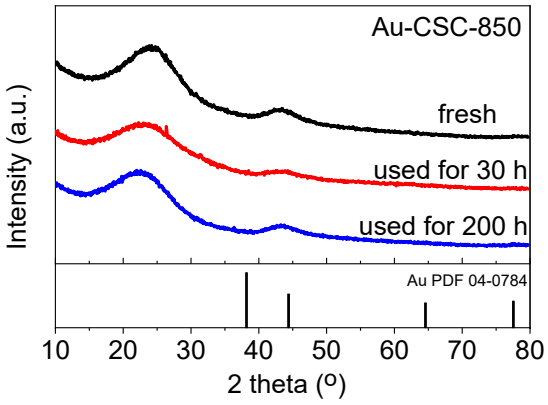


**Figure S11** XRD patterns of used Au-CSC-850 catalyst.

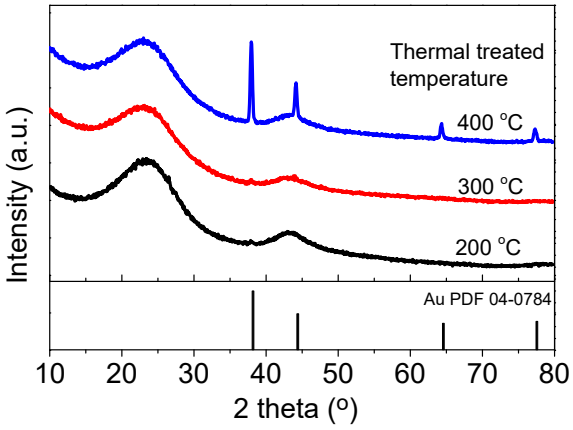


**Figure S12** XRD patterns of Au-CSC-850 catalyst thermal treated at elevated temperature.

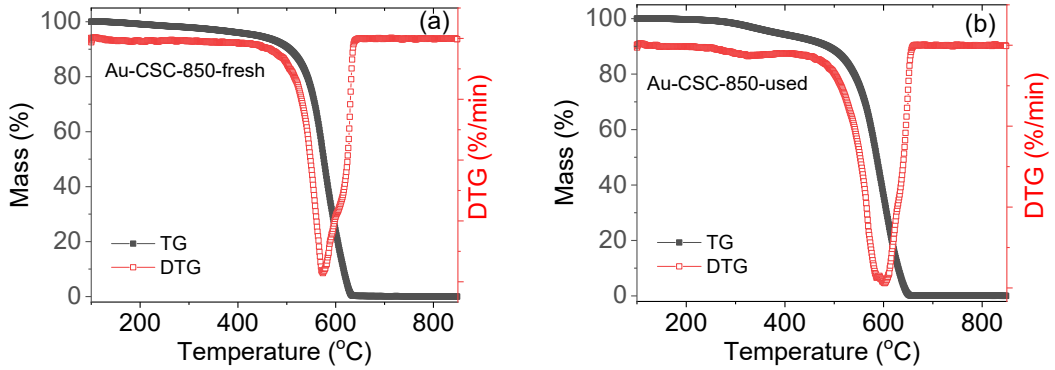


**Figure S13** TG and DTG curves of (a) fresh and (b) used Au-CSC-850 catalysts under air flow.

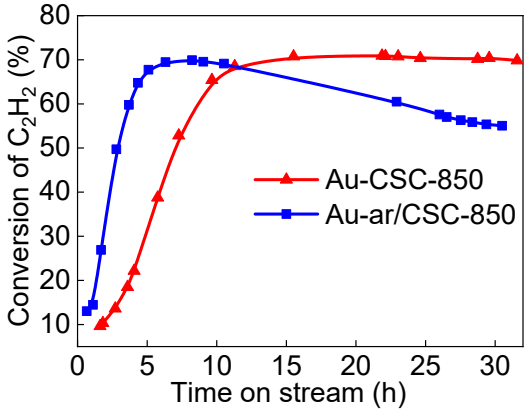


**Figure S14** Catalytic performance for Au-CSC-850 and Au/CSC-850 catalysts
Reaction condition: T = 180 °C, P = 0.1 MPa, GHSV($C_2H_2$) = 600 $h^{-1}$, $V_{(HCl)}/V_{(C2H2)}$ = 1.1

**Table S1.** The comparison of catalyst performance for various Au/C Catalysts in acetylene hydrochlorination.

| Catalysts | Notes/precursors | Au (wt%) | Temp. (°C) | $C_2H_2$ GHSV ($h^{-1}$) | $C_2H_2$ Conversion (%) | VCM Productivity (mol $kg_{cat}^{-1}$ $h^{-1}$) | References |
|---|---|---|---|---|---|---|---|
| Au-CSC-850 | $HAuCl_4/H_2O$ | 0.31 | 180 | 600 | 70.6 | ~169.6 | This work |
| Au-CSC-950 | $HAuCl_4/H_2O$ | 0.55 | 180 | 600 | 80.6 | ~193.6 | This work |
| Au-CSC-1050 | $HAuCl_4/H_2O$ | 0.34 | 180 | 600 | 76.8 | ~184.5 | This work |
| Au/AC-D | $HAuCl_4/H_2O$ | 0.25 | 180 | 1000 | 55 | ~55.8 | Ref [1] |
| Au/AC-D | $HAuCl_4/H_2O$ | 0.5 | 180 | 1000 | 72 | ~73.1 | Ref [1] |
| Au/AC | $(NH_4)_3Au(S_2O_3)_2$ | 0.3 | 180 | 227 | ~97 | ~24.7 | Ref [2] |
| Au/AC | $HAuCl_4$/Aqua regia | 0.5 | 180 | 227 | ~95 | ~106.0 | Ref [2] |
| Au-Cu/AC | SCN: Au = 20:1/Aqua regia | 0.25 | 180 | 1200 | ~60 | ~73.0 | Ref [3] |
| Au-Cu/AC | SCN: Au = 20:1/Aqua regia | 0.5 | 180 | 1200 | ~70 | ~85.2 | Ref [3] |
| Au/AC | $HAuCl_4/H_2O$ | 1.0 | 200 | 650 | ~75 | ~56.9 | Ref [4] |

**Table S2** The XPS spectra fitting results of N 1s for Au-SC-850 and Au-CSC-T catalysts.

| Catalysts | N content (%) | Relative content of different N species /% | | | |
|---|---|---|---|---|---|
| | | Oxidized N (403.3 eV) | Graphitic N (401.0 eV) | Pyrrolic N (399.8 eV) | Pyridinic N (398.2 eV) |
| Au-SC-850 | 2.3 | 9.20 | 25.63 | 37.05 | 28.12 |
| Au-CSC-600 | 1.4 | 11.98 | 25.45 | 50.05 | 12.53 |
| Au-CSC-850 | 0.7 | 12.04 | 50.13 | 21.56 | 16.28 |
| Au-CSC-950 | 0.7 | 20.99 | 33.42 | 34.89 | 10.70 |
| Au-CSC-1050 | 0.9 | 7.55 | 41.70 | 33.87 | 16.88 |

**References**


[1] Lan, G.J.; Ye, Q.F.; Zhu, Y.H.; Tang, H.D.; Han, W.F.; Li, Y., Single-Site Au/Carbon Catalysts with Single-Atom and Au Nanoparticles for Acetylene Hydrochlorination. *ACS Appl. Nano Mater.* 2020, 3(3), 3004-3010.

[2] Johnston, P., Carthey, N., and Hutchings, G.J. Discovery, Development, and Commercialization of Gold Catalysts for Acetylene Hydrochlorination. *J. Am. Chem. Soc.* **2015**, 137, 14548-14557.

[3] Zhou, K., Jia, J., Li, C., Xu, H., Zhou, J., Luo, G., and Wei, F., A low content Au-based catalyst for

hydrochlorination of $C_2H_2$ and its industrial scale-up for future PVC processes. *Green Chem.* **2015**, 17, 356-364.

[4] Kaiser S. K., Fako E., Manzocchi G., et al. Nanostructuring unlocks high performance of platinum single-atom catalysts for stable vinyl chloride production. *Nat. Catal.*, **2020**, 3(4): 376-385.