

Size-Controlled Silver Nanoparticles Stabilized on Thiol-Functionalized MIL-53(Al) Frameworks

*Xinquan Cheng,^a Min Liu,^{*a} Anfeng Zhang,^a Shen Hu,^a Chunshan Song,^{a,b}*

*Guoliang Zhang,^c Xinwen Guo^{*a}*

^a State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research,

School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R.

China. Fax: +86-0411-84986134; Tel: +86-0411-84986133, +86-0411-84986134; E-mail:

guoxw@dlut.edu.cn, lium@dlut.edu.cn

^b EMS Energy Institute, PSU-DUT Joint Center for Energy Research and Department of

Energy & Mineral Engineering, Pennsylvania State University, University Park,

Pennsylvania 16802, United States. Fax: 814-865-3573; Tel: 814-863-4466; E-

mail: csong@psu.edu

^c College of Biological and Environmental Engineering, Zhejiang University of Technology,

Hangzhou 310014, P. R. China. Fax: +86-0571-88320863; Tel: +86-0571-88320863; E-

mail: guoliangz@zjut.edu.cn

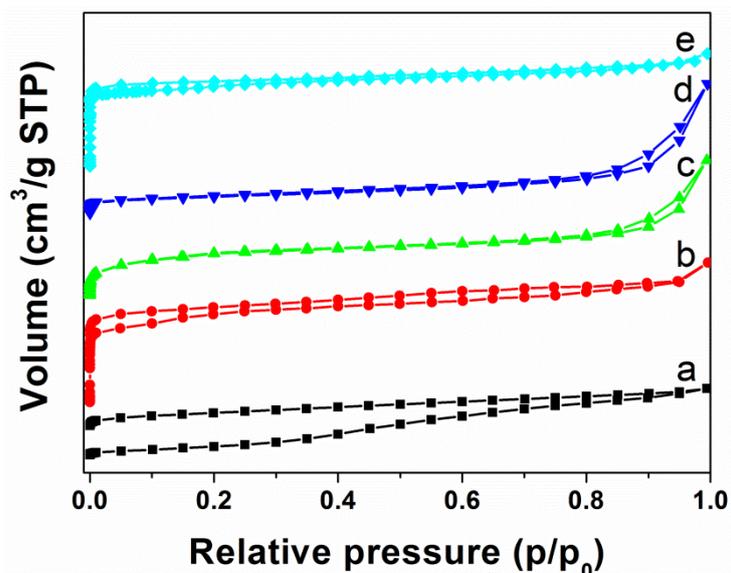


Fig. S1 N₂ adsorption/desorption isotherms of (a) **M1**; (b) **M2**; (c) 7.4 wt%-Ag@**M2**; and (d) 15.4 wt%-Ag@**M2**, (e) Argon adsorption/desorption isotherms of **M2**.

Nitrogen physisorption is a generally accepted standard method for micro- and mesopore size analysis. However, it is not very accurate for quantitative analysis of the microporosity, especially for ultramicropores (pore size less than 0.7 nm). Argon is a type of monatomic molecule and its kinetic diameter slightly smaller than nitrogen, but its adsorption behavior is quite different from nitrogen. Argon lack of a quadrupole moment, hence it is hard for argon to develop specific interactions with most functional groups on the material surface, which will give a more accurate results of micropore sorption data.¹ Therefore, we use argon as adsorptive at its boiling temperature to verify the high surface areas of matrix **M2**. In Figure S1e, the argon sorption measurement showed a similar micropore adsorption/desorption isotherm with nitrogen sorption measurement (Fig. S1b). The BET surface areas calculated from argon sorption is 2817 m²/g, which is slightly higher than the value of nitrogen sorption (2610 m²/g). This might because argon molecules are smaller than nitrogen molecules, so argon molecules can access some very small micropores that nitrogen molecules cannot.

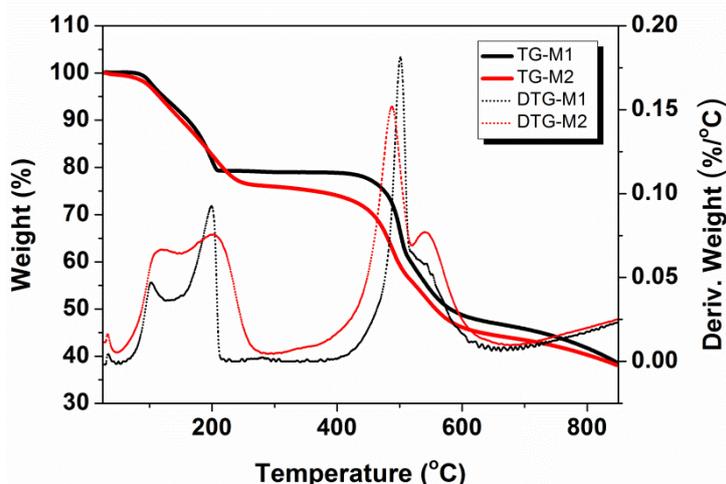


Fig. S2 TG and DTG curves of **M1** and **M2**.

The thermal behavior of these two kinds of matrices was studied by TG-DTG measurements (Fig. S2), both of them showed very similar TG and DTG curves. Both TG curves showed a two-step weight loss except a tiny weight loss (2-3%) below 80 °C which can be attributed to desorption of water. For **M1**, the first step of weight loss in the range of 80 to 220 °C corresponds to the release of the guest molecules of DMF or water within the pores, and the second weight loss started from 380 °C is due to the decomposition of the aminoterephthalic acid from the framework. For **M2**, the temperature range of weight loss is different from **M1**. The first step of weight loss was from 80 to 280 °C and the second step started from 320 °C. It looks like **M1** is more thermal stable than **M2**, but both of them have extremely high thermostability compared with other kinds of MOFs. It is worth noting that, for both matrices, the solvent-free structures are stable up to at least 320 °C. Apparently, the strong thermal stabilities of matrices will extend the application of the Ag NPs supported on these matrices.

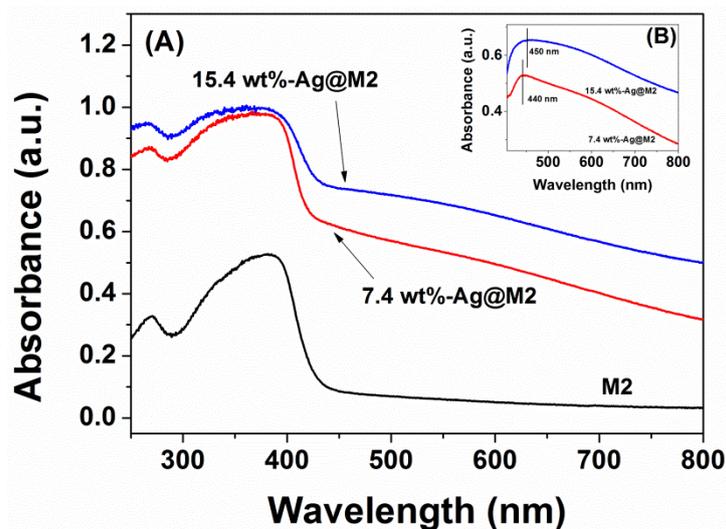


Fig. S3 UV-vis diffuse reflectance spectra of (A) **M2**, 7.4 wt%-Ag@M2, and 15.4 wt%-Ag@M2; (B) 7.4 wt%-Ag@M2 and 15.4 wt%-Ag@M2 in the visible light region by subtraction of the spectrum of **M2**.

The UV-vis DRS spectra of matrix **M2** and Ag@M2 with different amount of loading are shown in Fig. S3. As observed in Fig. S3A, the matrix **M2** only exhibited obvious absorption in the UV region with an absorption edge around 450 nm, but there was no more absorption in the visible light region. Obviously, 7.4 wt%-Ag@M2 showed significant enhancement of light absorption than the matrix **M2** both in the UV and visible light regions. The light absorption further increased with increasing the silver loading to 15.4 wt%. By subtraction of the matrix spectrum from the spectra of Ag@M2, we can see the enhanced light absorption more clearly, especially in the visible light region (Fig. S3B). In Fig. S3B, both Ag@M2 samples have strong and broad absorption at the wavelength of 400 - 800 nm, which could be attributed to the surface plasmon band of Ag NPs, as suggested in the literatures.^{2, 3} For 7.4 wt%-Ag@M2 and 15.4 wt%-Ag@M2, the broad absorption centered at around 440 nm and 450 nm, respectively. Apparently, there was a red shifted with increasing silver loading, which is because the particle size of Ag NPs increased with increasing loading.⁴ The UV-vis DRS analysis matched very well with the TEM result.

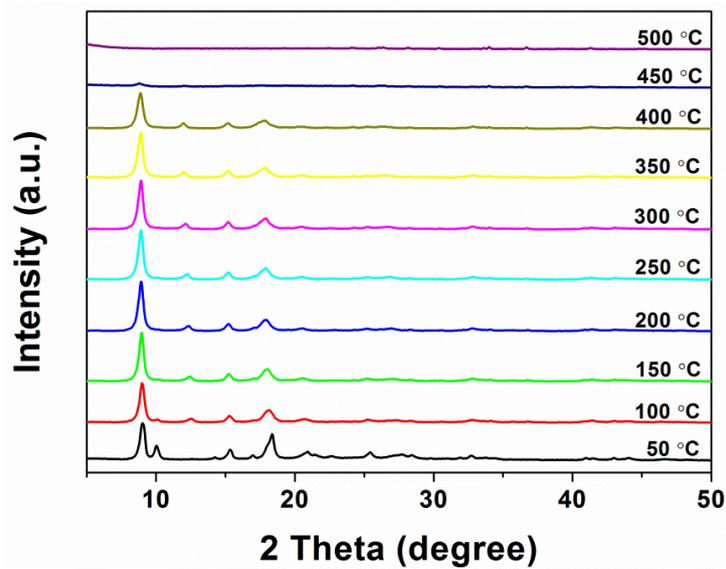


Fig. S4 TDXRD patterns of M2.

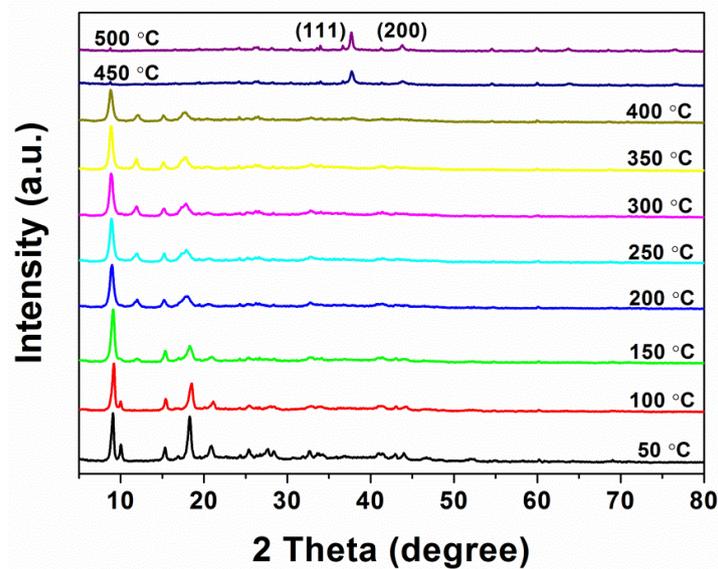


Fig. S5 TDXRD patterns of 7.4 wt%-Ag@M2.

Fig. S4 revealed that the matrix **M2** started to collapse its framework structures at around 350 °C, and completely collapsed at 450 °C. After 7.4 wt% of silver was loaded (Fig. S5), the resulting hybrid material Ag@M2 has a similar thermal stability with the matrix, but the diffraction peaks belong to the Ag NPs shown up at 450 °C. This is because the particle sizes of the Ag NPs increased as raising the temperature. This fact proved our previous assumption that the Ag NPs were formed by the aggregation of their surrounding small silver particles.

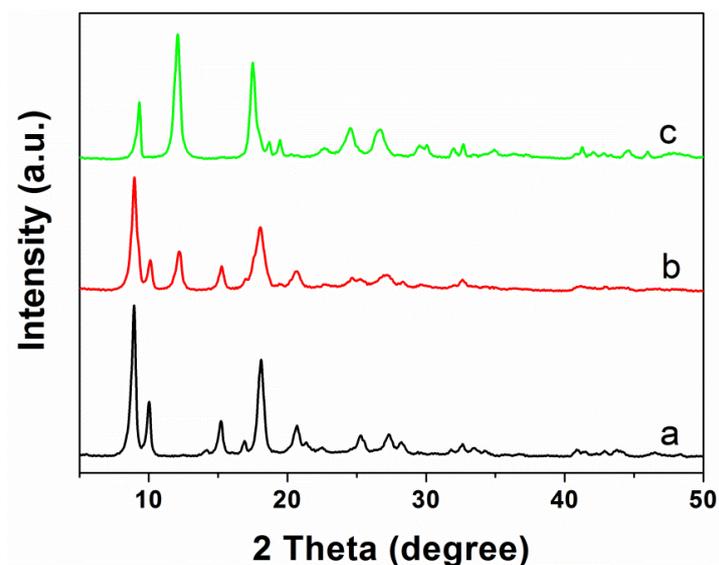


Fig. S6 XRD patterns of M2 (a) LP; (b) between LP and NP; (c) NP.

The metal organic framework MIL-53(Al) exhibits a flexible porous structure, which means guest molecules or temperature can induce a structural transition between a narrow pore (NP) and a large pore (LP) forms.⁵⁻⁷ As the porous structure changed, the X-ray powder diffraction patterns came out different. Fig. S6a and S6c are the typical XRD patterns of NH₂-MIL-53(Al) with LP and NP forms, respectively. When the temperature increased, the guest molecules were gradually detached from the frameworks of MIL-53(Al). Meanwhile, the porous structure was transformed from LP to NP. Apparently, this kind of structural transition was progressing gradually. Therefore, there must have some intermediate states between LP and NP forms. This is why the XRD pattern looks like in Fig. S6b, which contains the diffraction peaks belong to both LP and NP forms.

REFERENCES

- 1 J. Moellmer, E. B. Celer, R. Luebke, A. J. Cairns, R. Staudt, M. Eddaoudi and M. Thommes, *Microporous Mesoporous Mater.*, 2010, 129, 345-353.
- 2 D. Wang, G. Xue, Y. Zhen, F. Fu and D. Li, *J. Mater. Chem.*, 2012, **22**, 4751-4758.
- 3 P. Zhang, C. Shao, Z. Zhang, M. Zhang, J. Mu, Z. Guo, Y. Sun and Y. Liu, *J. Mater. Chem.*, 2011, **21**, 17746-17753.
- 4 E. Saion, E. Gharibshahi, K. Naghavi, *Int. J. Mol. Sci.* 2013, **14**, 7880-7896.
- 5 S. Bourrelly, B. Moulin, A. Rivera, G. Maurin, S. Devautour-Vinot, C. Serre, T. Devic, P. Horcajada, A. Vimont, G. Clet, M. Daturi, J.-C. Lavalley, S. Loera-Serna, R. Denoyel, P. L. Llewellyn and G. Férey, *J. Am. Chem. Soc.*, 2010, 132, 9488-9498.
- 6 M.-A. Springuel-Huet, A. Nossou, Z. Adem, F. Guenneau, C. Volkringer, T. Loiseau, G. Férey and A. Gédéon, *J. Am. Chem. Soc.*, 2010, 132, 11599-11607.
- 7 M. Meilikhov, K. Yusenko and R. A. Fischer, *Dalton Trans.*, 2009, DOI: 10.1039/B820882B, 600-602.