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A template-free method for stable CuO hollow microspheres fabricated from metal organic framework (HKUST-1)

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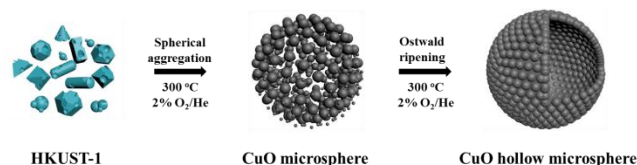
Uniform CuO hollow microspheres were successfully achieved from non-uniform metal organic framework by a template-free method. The process mechanism has been revealed to be spherical aggregation and Ostwald ripening. When tested in CO oxidation and heat treatment, these assembled microspheres exhibited an excellent catalytic performance and show a much better stability than the inherited hollow structure from MOFs.

Metal organic frameworks (MOFs), with the reticular architecture built by the bonding of metal-containing units and multidentate organic linkers, have garnered considerable attention in gas separation¹, catalysis², drug delivery³ and sensor⁴, for their distinguishable properties such as large surface areas, tailorable cavities, precise functionalities and flexible structures¹⁻⁷. At present, the exploitation of MOFs as prominent sacrificial templates or precursors has been pursued intensively, propelling them further into new synthetic field where hollow metal oxides or complexes with special geometrical features could be accessed^{8, 9}. Since MOFs are extensive in the variety and structural tunability, simply annealing would yield multivariate hollow materials with novel architectures and mixed components¹⁰⁻¹⁴. Lou and co-workers synthesized Fe₂O₃ hollow microboxes and multifarious complexes (Fe₂O₃/SnO₂, Fe₂O₃/SiO₂, Fe₂O₃/GeO₂, Fe₂O₃/Al₂O₃ and Fe₂O₃/B₂O₃) hollow microboxes using Prussian blue (PB) as templates^{10, 11}. Huang and co-workers reported Co₃O₄ hollow dodecahedra and CuO hollow octahedra by themolysis of ZIF-67 and HKUST-1^{12, 13}. Chen and co-workers prepared hollow ZnS polyhedra based on the reaction of truncated rhombic dodecahedral ZIF-8 and thioacetamide¹⁴. Despite the multiplicity and tailorability, these structures inherited from MOFs usually suffered from poor stability. For example, Huang et al. reported Co₃O₄ hollow dodecahedra and CuO hollow octahedra were lack of thermal stability, proved by the collapse of the hollow structures when exposed to high temperature^{12, 13}. Additionally, although CuO hollow octahedra and CuO/Cu₂O hollow polyhedron exhibited excellent performance in lithium ion batteries with stable cycling behavior and good rate capability, the inherited structure was serious damaged after 100 cycles measurement^{13, 15}. To maximize the structural advantages of MOFs in hollow particles fabrication, it is highly desirable to develop facile methods for the construction of MOFs derived materials with high stability.

On the other hand, hollow inorganic micro- and nanostructures

with controllable size, shape, composition, and shell/internal structure have long been paid considerable attention due to their distinguished structure-dependent properties and promising applications in catalysis, drug delivery, lithium ion batteries and so forth¹⁶⁻¹⁸. Traditionally, there are two synthetic strategies for preparing hollow structures. The first one is template-assisted synthesis, where sacrificial templates such as colloids and MOFs^{10, 19}, hard templates such as monodispersed silica and polymer latex spheres^{20, 21}, or soft templates such as surfactant micelles and gas bubbles^{22, 23} have been utilized. Although templating methods have been considered as the most representative and straightforward approach, such strategy practically has some disadvantages related to high cost and tedious synthetic procedures. Thus the template-free technique emerged as required. Various known physical phenomena such as aggregation¹⁷, oriented attachment²⁴, Ostwald ripening²⁵, and Kirkendall effect²⁶ have been employed to create interior space in many wet fabrications of hollow inorganic nanostructures. Despite the fundamental supported evidence of this mechanism is lacking¹⁶, by this efficient method many hollow metal oxide and sulfide with high stability have been fabricated.

Inspired by the template-free method, herein, we propose a facile synthetic approach to obtain stable CuO hollow microspheres. HKUST-1, one of the most famous and commercial available MOFs, was prepared with non-uniform morphology and then properly calcinated to harvest the uniform CuO hollow particles. Apart from the excellent thermostability, catalytic stability has been demonstrated compared to the regular hollow structures inherited from MOFs. Spherical aggregation and Ostwald ripening are deduced to facilitate the formation of the desired product. Note that in our example, the construction by this template-free approach based on aggregation and Ostwald ripening, which is usually applied in liquid phase, as far as we know, has been realized in gas phase for the first time.



Scheme 1 Schematic illustration of uniform stable CuO hollow microspheres prepared from non-uniform HKUST-1.

The strategy for preparing CuO hollow microspheres based on

to Ostwald ripening in liquid phase, this process always involves “the growth of larger crystals from those of smaller size which have a higher solubility than the larger ones”²⁵. It is also comprehensible for three-dimensional colloidal aggregation that some interior space would be eventually generated within the solids, as larger particles are essentially immobile while smaller ones are undergoing mass transfer through dissolving and growing²⁵. From the above analysis, it can be speculated that, so as to further lower the total energy of the system, amorphous or poorly crystallized CuO in microspheres are inclined to transport to the exterior in gas phase and thermal environment, recrystallizing and generating the vacancies inside. It is just analogous to recrystallization in liquid phase which can be validated by the coarser surface and more unambiguous particle gaps of samples shown in Fig. 1D and Fig. S4. High-resolution (HR)-TEM images in Fig. 3 well certify the crystalline nature of the microspheres. The lattice distances of the selected area in Fig. 3C and D are both calculated to be 0.137 nm, corresponding to the (-220) crystal lattice plane of CuO. The surface area of hollow products was evaluated by the nitrogen adsorption-desorption isotherms (Fig. S5). The hysteresis loop in the curve ascertains the presence of porous structures. Although the two kinds of microspheres show a similar surface area of about $8 \text{ m}^2 \cdot \text{g}^{-1}$ which is higher than $6 \text{ m}^2 \cdot \text{g}^{-1}$ of CuO hollow octahedra (Fig. S5), they have a different pore size distribution. Exactly consistent with the observation in TEM, with longer ripening time microspheres facilitate a wider pore size distribution.

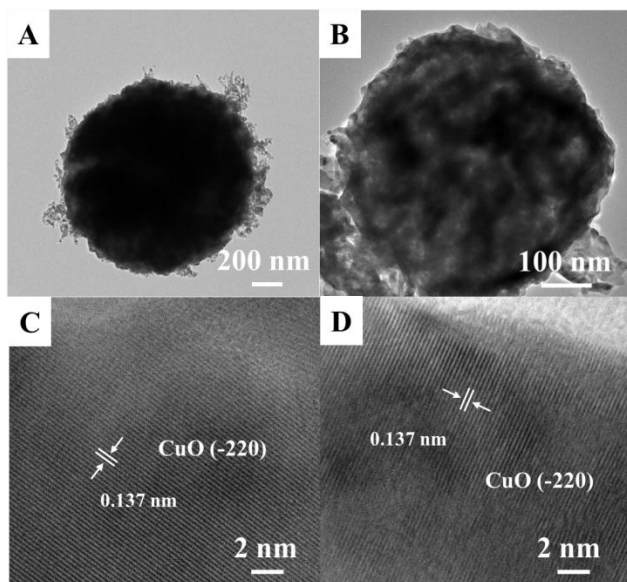


Figure 3 TEM and HRTEM images of products after oxidation for A), C) 3 h; B), D) 4 h.

The effect of gas concentration on the morphology of products is studied to delve further into the formation mechanism of hollow microspheres. Hence, for comparison, the as-prepared HKUST-1 was calcined under the pure He and air at 300 °C respectively. Remarkably, appropriate concentration of oxygen in mixed gas is of great significance to the generation of the uniform microspheres judged by the topographies in Fig. S6 and Fig. S7. The HKUST-1 particles were gradually decomposed and accumulated at random in the pure gas of He, producing no

appreciable microspheres. While in pure air, they tended to form nanospheres preliminarily under the influence of oxidation. Subsequently a few microspheres were found and finally the majority would collapse. As shown in Fig. S8, HKUST-1 particles were totally oxidated to CuO after only 1 hour, hinting sufficient oxygen can accelerate the oxidation process. However, as it is well known, low reaction rate is indispensable to develop symmetrical microspheres³². Thus, the formation of uniform microspheres is greatly hindered. Meanwhile the excess oxygen may also accelerate mass transfer, incurring the rapid recrystallization on the external surface and collapse of the existed microspheres.

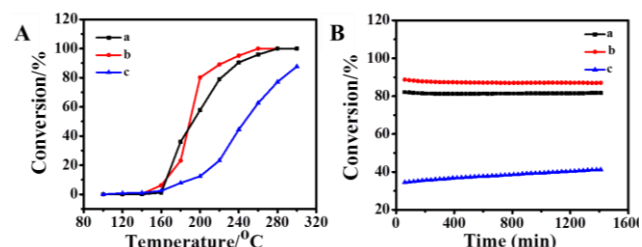


Figure 4 CO conversion (A) and catalytic stability (B) of products: CuO hollow microspheres obtained by 3 h (a) and 4 h oxidation; (c) CuO hollow octahedra.

The catalytic activity and stability of as-obtained CuO hollow microspheres and CuO hollow octahedra have been evaluated in CO oxidation. The measurements were conducted in a fixed-bed flow reactor with 25 mg catalysts. The flow gas was composed of CO (1.5 ml/min), O₂ (30 ml/min), and He (60 ml/min). The conversion curve with increasing temperatures plotted in Fig. 4 declares the better catalytic performance of CuO hollow microspheres compared to the hollow octahedra. CO can be completely converted to CO₂ at 280 °C and 260 °C respectively by hollow microspheres. Actually, all of the three samples have shown a better performance than commercial and normally calcined CuO particles reported before^{33, 34}. The high activity may be mainly originated from the unique hollow structures, creating larger surface area which plays an important role in CO oxidation³³. When reactions were kept at 200 °C for 24 h respectively after the activity test, the conversion rates of two hollow microspheres maintained at about 81% and 87%. While CuO hollow octahedra showed an apparently increasing activity from 34% to 41%. It may be caused by the gradual collapse of the hollow structure (Fig. S9), resulting smaller sized CuO particles which have been proved to be efficient in CO oxidation³⁴. The slightly enhanced performance appeared in the stability test compared with the original samples can be ascribed to the activation of the samples³⁴. After the activity test to 300 °C, samples were heated to release guest molecules adsorbed completely, exposing more surface area and endowing the catalyst more active site, thus bring about the improvement in the performance. Negligible decline in activity happened during the test of stability indicating a highly stable catalytic performance of hollow microspheres, while the hollow octahedra showed a poor one. More importantly, compared to the totally collapsed structure inherited from octahedral HKUST-1, the morphology and interior structure of microspheres assembled from non-uniform HKUST-1 were finely preserved after the test shown in

Fig. S10 and Fig. S11, suggesting the assembled structure had a higher stability. Impressively, the bulk of microspheres can also retain the original morphology even when they were further treated at 500 °C in pure N₂ for 5 h while the hollow octahedra would lose its morphology after only 1 h (Fig. S9 and Fig. S10). These aggregated microspheres, in a word, have exhibited good stability in terms of thermal and catalytic capability compared to the inherited octahedral structure.

In summary, uniform CuO hollow microspheres were successfully fabricated from non-uniform HKUST-1 by oxidation in a mixed gas of 2 % (v/v) O₂/He. The generation of hollow microsphere was facilitated by spherical aggregation and Ostwald ripening. Meanwhile, appropriate content of O₂ is of crucial importance in the formation. These assembled microspheres have exhibited excellent CO oxidation activity with high stability. Additionally, the assembled microspheres obtained by this approach have demonstrated much more stable performances in heat treatment and stability test when compared to the structures inherited from MOFs. Importantly, by the virtue of tunability of MOFs and composites, the facile methodology introduced here can be versatile and easily extended, providing a novel path for the fabrication of various hollow metal oxides and multifarious core/shell composites, catering to the multipurpose applications. Related work is in progress.

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- Q. Y. Yang, D. H. Liu, C. L. Zhong and J. R. Li, *Chem. Rev.*, 2013, **113**, 8261-8323.
- D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chem. Int. Ed.*, 2009, **48**, 7502-7513.
- J. Zhuang, C.-H. Kuo, L.-Y. Chou, D.-Y. Liu, E. Weerapana and C.-K. Tsung, *ACS Nano*, 2014, **8**, 2812-2819.
- L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105-1125.
- P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232-1268.

- Y. Liu and Z. Tang, *Adv. Mater.*, 2013, **25**, 5819-5825.
- M. Du and X. H. Bu, *Prog. Chem.*, 2009, **21**, 2458-2464.
- L. Hu and Q. Chen, *Nanoscale*, 2014, **6**, 1236-1257.
- Z. Zhang, Y. Chen, X. Xu, J. Zhang, G. Xiang, W. He and X. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 429-433.
- L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng and X. W. Lou, *J. Am. Chem. Soc.*, 2012, **134**, 17388-17391.
- L. Zhang, H. B. Wu and X. W. Lou, *J. Am. Chem. Soc.*, 2013, **135**, 10664-10672.
- R. Wu, X. Qian, X. Rui, H. Liu, B. Yadian, K. Zhou, J. Wei, Q. Yan, X. Q. Feng, Y. Long, L. Wang and Y. Huang, *Small*, 2014, **10**, 1932-1938.
- R. B. Wu, X. K. Qian, F. Yu, H. Liu, K. Zhou, J. Wei and Y. Z. Huang, *J. Mater. Chem. A*, 2013, **1**, 11126-11129.
- Z. Jiang, H. Sun, Z. Qin, X. Jiao and D. Chen, *Chem. Commun.*, 2012, **48**, 3620-3622.
- L. Hu, Y. Huang, F. Zhang and Q. Chen, *Nanoscale*, 2013, **5**, 4186-4190.
- X. W. D. Lou, L. A. Archer and Z. Yang, *Adv. Mater.*, 2008, **20**, 3987-4019.
- J. J. Teo, Y. Chang and H. C. Zeng, *Langmuir*, 2006, **22**, 7369-7377.
- J. S. Chen, C. M. Li, W. W. Zhou, Q. Y. Yan, L. A. Archer and X. W. Lou, *Nanoscale*, 2009, **1**, 280-285.
- Y. Sun and Y. Xia, *Science*, 2002, **298**, 2176-2179.
- S.-W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, **124**, 7642-7643.
- M. Yang, J. Ma, C. Zhang, Z. Yang and Y. Lu, *Angew. Chem. Int. Ed.*, 2005, **44**, 6727-6730.
- C. I. Zoldesi and A. Imhof, *Adv. Mater.*, 2005, **17**, 924-928.
- Q. Peng, Y. Dong and Y. Li, *Angew. Chem. Int. Ed.*, 2003, **42**, 3027-3030.
- B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2004, **126**, 8124-8125.
- B. Liu and H. C. Zeng, *Small*, 2005, **1**, 566-571.
- H. J. Fan, M. Knez, R. Scholz, D. Hesse, K. Nielsch, M. Zacharias and U. Gösele, *Nano Lett.*, 2007, **7**, 993-997.
- S. S.-Y. Chui, S. M.-F. Lo, J. P. Chamant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.
- A. Ozgur Yazaydin, Annabelle I. Benin, Syed A. Faheem, Paulina Jakubczak, John J. Low, Richard R. Willis and R. Q. Snurr, *Chem. Mater.*, 2009, **21**, 1425-1430.
- J. L. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304-1315.
- M. Kooti and L. Matouri, *Transaction F: Nanotechnology*, 2010, **17**, 73-78.
- H. G. Yu, J. G. Yu, S. W. Liu and S. Mann, *Chem. Mater.*, 2007, **19**, 4327-4334.
- Y. Chang, J. J. Teo and H. C. Zeng, *Langmuir*, 2004, **21**, 1074-1079.
- H. Huang, L. Zhang, K. Wu, Q. Yu, R. Chen, H. Yang, X. Peng and Z. Ye, *Nanoscale*, 2012, **4**, 7832-7841.
- J. M. Zamaro, N. C. Pérez, E. E. Miró C. Casado, B. Seoane, C. T. delz and J. Coronas, *Chem. Eng. J.*, 2012, **195-196**, 180-187.