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ARTICLETYPE

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

Suoying Zhang,^a Hong Liu,^a Pengfei Liu,^a Zhuhong Yang,^a Xin Feng,^a Fengwei Huo^{*b} and Xiaohua Lu^{*a}

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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.

¹⁰ 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 ¹⁵ 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

- ²⁰ 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 ²⁵ 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 ³⁰ using Prussian blue (PB) as templates^{10, 11}. Huang and co-workers
- ³⁰ using Plussian blue (PB) as templates $^{-1}$. Huang and co-workers reported Co₃O₄ hollow dodecahedra and CuO hollow octahedra by themolysis of ZIF-67 and HKUST-1^{12, 13}. Chen and coworkers prepared hollow ZnS polyhedra based on the reaction of truncated rhombic dodecahedral ZIF-8 and thioacetamide¹⁴.
- ³⁵ 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
- ⁴⁰ 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
- ⁴⁵ 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 50 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 55 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 60 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 65 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 75 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 80 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 ⁸⁵ microspheres prepared from non-uniform HKUST-1.

The strategy for preparing CuO hollow microspheres based on

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spherical aggregation and Ostwald ripening is schematically depicted in scheme 1. Firstly, HKUST-1 was synthesized from $Cu(NO_3)_2$ 3H₂O and benzene-1,3,5-tricarboxylic acid (H₃BTC) in 45 ml DMF/EtOH/H₂O (1:1:1) solvent at ambient with agitation.

- ⁵ The geometrical characteristics of the resultant were examined by Field emission scanning electron microscope (FESEM). Distinguished from the familiar octahedral shape²⁷, the crystals gained at ambient are nano-sized with a non-uniform morphology, as shown in Fig. S1A. The crystallographic structure and phase
- ¹⁰ purity were determined by powder X-ray diffraction (XRD) and clearly viewed in Fig. S1B. All of the diffraction peaks are exclusively assigned to HKUST-1 as evidenced by the good match with the stimulated PXRD patterns. Take an overview on the thermogravimetric profile in Fig. S2, a pronounced weight
- ¹⁵ loss is not found until the temperature reaches up to ~300 $^{\circ}$ C, revealing the thermal stability of the as-obtained HKUST-1 is almost identical to the crystals obtained by hydrothermal methods²⁸. Whereafter, the fresh prepared HKUST-1 was oxidated in flowing mixed gas (2 vol. % O₂ balanced with helium,
- ²⁰ 35 mL/min) at 300 °C for 1 h, 2 h, 3 h and 4 h, respectively. The hollow microspheres would be harvested during the thermal annealing process which can be illustrated by spherical aggregation and Ostwald ripening. For comparison, CuO hollow octahedra inherited from octahedral HKUST-1 was prepared as
- ²⁵ the literature reported¹³ (shown in Fig. S3).



Figure 1 FESEM images of products after oxidation in 2 % (v/v) O₂/He at 300 °C for A) 1 h; B) 2 h; C) 3 h; D) 4 h. Insets are high-magnification FESEM images of C) and D). E) and F) are ³⁰ size distributions of C) and D).



Figure 2 XRD (A) pattern and FTIR spectrum (B) of products after oxidation for for a) 1 h; b) 2 h; c) 3 h; d) 4 h.

To track the evolution of the products, the morphologies with different thermal treatment durations are monitored in Fig. 1 and the crystallizations are confirmed in Fig. 2. Distinctly, the nonuniform particles started to lose their original structure and tended to aggregate under the heat treatment in mixed gas at the 40 early stage (1 h) as shown in Fig. 1A. The phenomenon of partial oxidation of HKUST-1 can be conjectured by Fig. 2A, in which the diffraction peaks below 20 degree in pattern a are attributed to HKUST-1 and the remaining can be assigned to CuO (JCPDS card no. 45-0937) and Cu₂O (JCPDS card no. 5-0667). 45 Subsequently, copper in HKUST-1 was completely converted to CuO supported by the pattern b in Fig. 2A. The Fourier transform infrared spectroscopy (FTIR) spectrum in Fig. 2B further confirmed the chemical composition and phase change of the pyrolytical products. Four absorption peaks between 1350 to 50 1620 cm⁻¹ in Fig. 2Ba are attributed to HKUST-1²⁹. The absorption peak around 623 cm⁻¹ is reported to be the Cu (I)-O vibration³⁰. Three sharp absorption peaks around 588, 534 and 489 cm⁻¹ in Fig. 2B can be indexed to the vibrations of Cu (II)-O bonds³⁰. Residual C in the calcined samples is implied by the 55 peaks of 1634 cm⁻¹ appeared in Fig. 2B (b, c, d)¹⁵. Thus, FTIR analysis also verified the total transformation of HKUST-1 with prolonged heating. Also of note, as evident from Fig. 1B, numerous nano-sized spheres of predominantly 300 nm in diameter initially formed by the self-aggregation. In spite of the 60 fact that the formation of small size is kinetically preferred during the initial agglomeration, larger size is thermodynamically favored and predominates ultimately. Thus, the assembly of the nano-sized particles, driven by the total energy of system minimization, eventually results in uniform microspheres with an 65 average diameter of 0.87 μm as displayed in Fig. 1C, 1E. Fig. 1D demonstrates the same morphology of microsphere with Fig. 1C, but differs in size distribution, meaning the tendency of particles to grow up with the continuous heating. However, the spherical morphology is fairly reserved. Observing the inset of Fig. 1C and 70 1D carefully, the surface of microspheres turns out to be constructed by nano-sized spheres. More importantly, the size of nanospheres on the surface enlarged along with the increased time. Recrystallization of CuO should be responsible for the above-mentioned situation which has been also reported in ⁷⁵ previous researches under the liquid phase³¹. The pore appeared on the surface implies the hollow structure of the products. The detailed interior structures were identified by Transmission electron micrographs (TEM). In accordance with the observation from Fig. 1C and 1D, the hollow structure is observed 80 ambiguously in Fig. 3A. However, much larger internal space is detected by Fig. 3B, demonstrating the vacant volume inside CuO microsphere enlarged as the ripening time increased. According

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 s 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
- ¹⁰ poorly crystallized CuO in microspheres are inclined to transport to the exterior in gas phase and thermal environment, recrystalizing 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
- ¹⁵ 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
- ²⁰ 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 m² · g⁻¹ which is higher than 6 m² · g⁻¹ of CuO hollow octahedra (Fig. S5),
- ²⁵ 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 ³⁰ 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 ³⁵ respectively. Remarkably, appropriate concentration of oxy gen 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 ⁴⁰ 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 ⁴⁵ 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 ⁵⁰ 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 ⁵⁵ 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 60 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 CO_2 at 280 °C and 260 °C respectively 65 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 70 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 75 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 $^{\circ}$ C, 80 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 85 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 nonuniform HKUST-1 were finely preserved after the test shown in 70

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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 $^{\circ}$ C in pure N₂ for 5 h while the hollow octahedra would have its membels with a structure with the $(\Sigma = 0.02)$

⁵ 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

- ¹⁰ successfully fabricated from non-uniform HKUST-1 by oxidation in a mixed gas of 2 % (v/v) O_2 /He. The generation of hollow microsphere was facilitated by spherical aggregation and Ostwald ripening. Meanwhile, appropriate content of O_2 is of crucial importance in the formation. These assembled microspheres have
- 15 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 virture of tunability of
- 20 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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Notes and references

^a State Key Laboratory of Materials-Oriented Chemical Engineering, and College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, P.R. China; E-mail: xhlu@njtech.edu.cn.

- ⁴⁰ ^b Key Laboratory of Flexible Electronics (KLOFE) & Institue of Advanced Materials (IAM), National Jiangsu Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China; E-mail: fwhuo@ntu.edu.sg.
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