RSC Advances

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

Journal Name

COMMUNICATION

Preparation and enhanced catalytic activity of amphiphilic rambutan-like micro-reactors

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

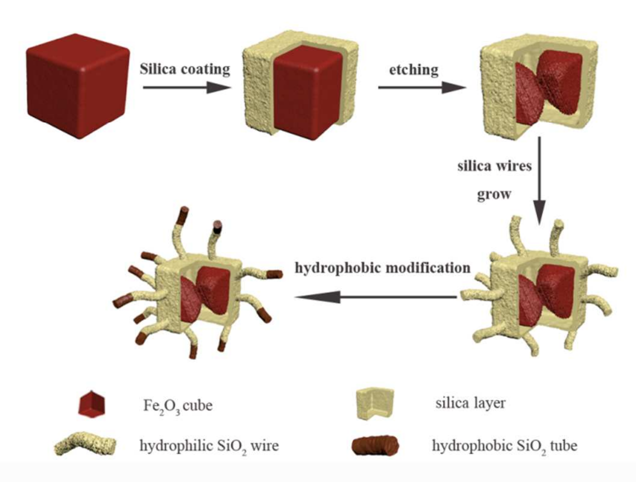
Dongzhi Li,[ac†] Bin Zhao,[ac†] Yue Long,*[b] Guoqiang Yang,[a] Chen-Ho Tung[a] and Kai Song*[b]

Through a novel wet-chemical and selectively etching stratagy, amphiphilic micro-reactors with mesocrystal core as catalytic activity center and rambutan-like structure were prepared and showed enhanced catalytic activity in biphasic environment.

Yolk-shell particles, due to the hybrid of core-shell and hollow structures, have attracted a great deal of interest and provide powerful platforms for controlled release, confined nanocatalysis, and energy storage and conversion.[1] With the tailorability and functionality in both the cores and hollow shells, much research work focus on nanoparticles as functional materials encapsulated by a protecting shell.[2] As miniaturized reaction systems, micro-reactors are usually fabricated by using the methods of microtechnology and precision engineering,[3] and are generally used to describe a great number of devices that have small dimensions. In virtue of the void space within the shell, yolk-shell materials can be seen as micro-reactors for catalytic reactions and several reports have shown that yolk-shell particles had high catalytic activities in certain reactions, such as oxidation of aerobic alcohol, reduction of nitrophenol, and Fenton-like reaction.[4] However, in most situations, the micro-reactors can only carry out catalytic reactions in a single-phase system because of the same composition on the interior and exterior surfaces of the shell. The conversion and selectivity can be greatly enhanced in a biphasic environment.[5] Until now, the reported biphasic reactions were usually carried out in emulsions (especially Pickering emulsions) which is too weak to tolerate strong stirring.[6] It remains an interesting challenge to synthesize amphiphilic micro-reactors which can selectively capture the desired compounds from biphasic environment which little work has been reported.[7]

Recently, Bahng et al. reported an anomalous dispersion phenomenon of 'hedgehog' particles due to their unusual geometrical and topographical effect.[8] That is, hydrophobic hedgehog particles can disperse in a hydrophilic solvent for the enhanced colloidal stability by the presence of trapped air shell in the spikes layer. Inspired by this work, we designed and synthesized a smart rambutan-shaped micro-reactor consists of a catalytic active mesocrystal hematite core and a layer of amphiphilic silica spikes, which are composed of a hydrophilic body and hydrophobic tails. The as-synthesized rambutan-like particles, with their hydrophobic silica tails, can form stable dispersions in hydrophobic solvents such as heptane, hexane and tetrachloroethylene. And the hydrophilic part forms a 'buffer zone', which allows water and contained pollutants to stay temporarily before entering the mesocrystal 'reaction zone' in a biphasic environment. The smart micro-reactor revealed selective capture and highly efficient catalytic activity from their liquid surroundings.

These composite amphiphilic particles were synthesized through a series of steps as shown in scheme 1. Firstly, uniform hematite pseudocubes were prepared through a facile and scalable method by aging a condensed ferric hydroxide gel at 100 ⍰ for eight days.[9] The cubic hematite were then used as seeds for



Scheme 1 Synthesis procedure of amphiphilic rambutan-like micro-reactors.

---

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
[b] Laboratory of Bio-Inspired Smart Interface Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Science, Beijing 100190, China. E-mail: longyue@mail.ipc.ac.cn; songkai@mail.ipc.ac.cn.
[c] University of the Chinese Academy of Sciences, Beijing 100049, China.

† These authors contributed equally to this work.

‡ Electronic Supplementary Information (ESI) available: Experimental details, XRD, N_2 sorption isotherm and pore size distribution, TEM images.

mesoporous silica coating in a heterogeneous oil–water biphase stratification reaction system as reported by Zhao et al. This is a general method to prepare functional core-shell materials with different cores (such as Au and Ag nanoparticles).[10] After a selective acid treatment, the cubic hematite core was etched into hierarchical microcones,[11] which played a role of catalytic activity site in the amphiphilic micro-reactor. Subsequently, the as-synthesized primary micro-reactor was endowed with hydrophilic silica wires, followed by addition of a second organo-silica precursor to obtain hydrophobic silica tails. This micro-reactors can act as micelle-like containers which the amphiphilic spikes of the micro-reactors can therefore selectively capture the hydrophilic pollutant in a biphasic environment. Due to the catalytic ability of mesocrystal hematite core and amphiphilic spikes, the micro-reactors can be a promising candidate for hydrophilic pollutant adsorbents in the biphasic environment. The scanning electron microscopy (SEM) images shown in Fig.1a suggest that the as-prepared α-Fe_2O_3 microcubes are well-defined pseudocubes with an edge length of 1.9 ± 0.2 μm. Moreover, the X-ray diffraction (XRD) pattern of the microcubes (Fig. S1) suggests that the product is pure hematite crystals with a rhombohedral structure. Fig.1b presents a typical SEM image of α-Fe_2O_3@mesoporous SiO_2 (HMS) composite structure obtained from a heterogeneous oil–water biphase stratification reaction. It can be seen from the inset of Fig. 1b and 1c that the composite has a core-shell structure and the silica shell possesses meso-channel with average pore diameter 3.4 nm calculated by BJH (Barrett-Joyner- Halenda methods), which is critically important for mass transfer of desired compounds. The N_2 absorption-desorption isotherm and pore size distribution of the HMS are shown in Fig.S2. Notably, in a conventional mesoporous silica coating process, a sacrificial layer of non-mesoporous silica coating for elevated affinity is necessary before the mesoporous silica coating. It is time-cost and not eco-friendly. Here the mesoporous silica layer was fabricated directly according to a modified oil–water biphase stratification approach.[10]

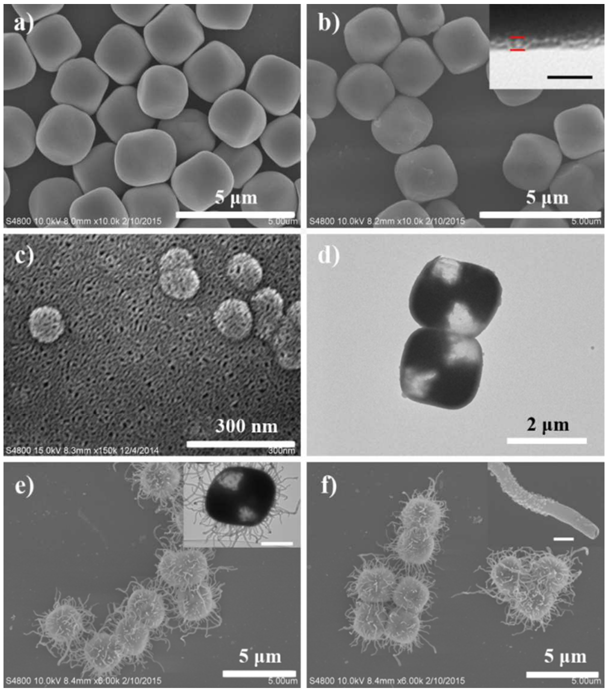


Fig. 1 SEM images of (a) α-Fe_2O_3 microcubes; (b) α-Fe_2O_3 @mesoporous SiO_2; the inset shows the mesoporous SiO_2 layer, and the scale bar is 50 nm; (c) the surface of α-Fe_2O_3@mesoporous SiO_2; (d) TEM image of the α-Fe_2O_3 @mesoporous SiO_2 etched for 1.5 h; (e) SEM image of HMS@hydrophilic silica wires, the inset shows the corresponding TEM image and the scale bar is 1 μm; (f) SEM image of the final amphiphilic rambutan-like micro-reactors, the inset shows the detail of the amphiphilic silica wires and the scale bar is 200 nm.

Selective etching is a key fabrication step for the micro-reactor, which results in a highly efficient catalytic activity center while the cubic shape can be maintained. To investigate the effect of hematite etching on the catalytic efficiency, the as-prepared α-Fe_2O_3@mesoporous SiO_2 cubes were etched for different time scales with hydrochloric acid. After etching for 1h, obvious gaps were seen on the hematite core, which was resulted from etching along the [001] direction and the direction perpendicular to the [001] direction around the equatorial regions.[9] Further increasing the etching time to 1.5 h, the gap enlarged and a dumbbell-like structure appeared in the mesoporous silica box. The TEM images in Fig. S3 suggest that the connecting point of the dumbbell becomes smaller when increasing the etching time.

In order to adapt to the biphasic environment, the micro-reactor was designed to have an amphiphilic structure. Here we demonstrate a facile strategy to synthesize amphiphilic silica wires with two segmented components by using a novel wet-chemical method.[12] After obtaining the hydrophilic silica wires from the hydrolysis of tetraethoxysilane (TEOS), an organo-silica precursor octadecyltrimethoxysilane (OTMS) was added to the system for the growth of the hydrophobic silica part. The introduction of octaedecyl groups leads to the hydrophobic exterior segment. Therefore, the amphiphilic micro-reactor contains three sections: the first section is the mesocrystal hematite core, and it would be used as functional domain, where catalytic reaction performs. The second section is the mesoporous silica wall and the hydrophilic silica wires. It would be used as buffer zone, where aqueous solution containing pollutants stays temporarily and then passes through the mesoporous silica wall for degradation. The third section is the hydrophobic silica wires, which enables the micro-reactor to be dispersible in a hydrophobic environment. Fig.1e shows the SEM and TEM images of the micro-reactors without the hydrophobic silica wires. In the low magnificaion image the exterior surface of the micro-reactros with or without the hydrophobic silica wires show no difference, but in high magnification (inset image of Fig.1f) it can be seen that the surface of the hyphophilic part is rough, and the surface of the hydrophobic part is smooth. This different surface morphology is believed to be due to the different hydrolysis rates of perspective precursor.

To test the catalytic efficiency of the rambutan-like structured mesocrystal α-Fe_2O_3@mesoporouse SiO_2 amphiphilic micro-reactors, Fenton-like reaction, i.e. a widely used method for degradation of organic pollutants by oxidation the waste water based on ferrous ions and H_2O_2, was chosen as a model reaction. In this study, the Fenton-like reaction was carried out in a biphasic environment (heptane/water, v/v= 8:2) to degrade methylene blue (MB, 3.33

ppm). All the experiments were performed in the dark to avoid the influence of light, and no extra acid or base was added to adjust the pH value of the reaction system.

The rambutan-like amphiphilic micro-reactors dispersed easily in organic phase such as heptane and hexane, while HMS and HMS@hydrophilic silica wires aggregated. In the catalytic reaction, the water contained pollutant was captured in the buffer zone of the amphiphilic micro-reactors first. Confocal laser scanning microscope (CLMS) verified this hypothesis, as a water soluble FITC-dextran dye was added in the system, bright green fluorescence can be observed in the buffer zone of the amphiphilic micro-reactors (Fig. 2b). The meso-channel of the silica shell ensures mass transfer of the desired compounds and stirring accelerates this process. During the reaction process, stirring enhances the exchange of water, reagents and products between free water droplets and captured water in buffer zone. With the amphiphilic structure, permeable mesoporous shell and unique structure of catalytic cores, the resulted amphiphilic micro-reactors show outstanding catalytic efficiency.

As shown in Fig.2c, HMS and HMS@hydrophilic silica wires showed relatively low efficiency that about 35% of the MB was degraded after 180 min. The rate of degradation of the MB with the above two micro-reactors was nearly the same indicating that the presence of the hydrophilic wires had barely effect in the catalytic activity. However, the catalytic activity of the as-synthesized amphiphilic structured micro-reactors showed significant etching time prolonged, more MB molecules were degraded in the same period of time. Nearly 65% and 85% of the MB molecules were degraded with the micro-reactors etched with 1 h and 1.5 h, respectively.

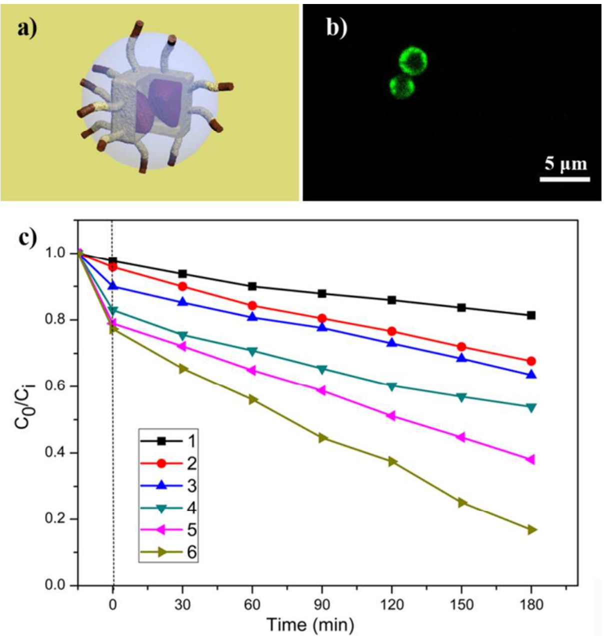


Fig.2 (a) Schematic of the amphiphilic rambutan-like micro-reactor in biphasic system; (b) Confocal laser scanning microscopy image and the corresponding fluorescence intensity contours of the final amphiphilic micro-reactors after being labeled with FITC-dextran; (c) Feton-like degradation of MB in the dark as a function of time, respectively with the blank (line 1), α-Fe_2O_3@mesoporous SiO_2 (line 2), HMS@hydrophilic silica wires (line 3), and the final amphiphilic micro-reactors with the cores etched for different time (line 4 for 0 h, line 5 for 1 h; line 6 for 1.5 h).

The amphiphilic structure makes the micro-reactors disperse in the biphasic system or even more complex environment. And as shown in Fig. 2c, it is noteworthy that comparing with HMS (line 2), the amphiphilic structure plays better in capturing MB from the surrounding and enriching them in the buffer zone (line 4-6). The mesocrystal morphology of the amphiphilic micro-reactors contributed to the outstanding activity of the catalyst in the biphasic environment. The degradation reactions were confined in the inner of the micro-reactors, where the mesocrystal α-Fe_2O_3 core was more accessible.

In summary, we developed a novel and facile method to synthesize amphiphilic micro-reactor with rambutan-like structure, which has a mesocrystal core acting as highly efficient catalytic site. Depending on the amphiphilic rambutan-like structure and the mesocrystal core, the micro-reactors show excellent activity toward MB degradation in biphasic environment. We believe that this method can be developed into an important and general strategy for other kinds of amphiphilic micro-reactors with diverse catalytic cores (such as Au and Ag). The amphiphilic micro-reactor opens a door to selectively capture the desired species for further reaction and would be a promising candidate to be used in biphasic or even more complicated system.

Acknowledgement

We are grateful for funding from the National Basic Research Program (No. 2013CB834505) and the National Natural Science Foundation of China (No. 21273248).

Notes and references

1 H. C. Zeng, *J. Mater. Chem.*, 2006, **16**, 649; J. Liu, S. Y. Bai and Q. H. Yang, *J. Phys. Chem. C*, 2010, **114**, 953; J. Liu, F. T. Fan and C. Li, *J. Phys. Chem. C*, 2008, **112**, 16445; J. Liu, Q. H. Yang and C. Li, *Chem. Mater.*, 2008, **20**, 4268; J. Liu, S. Z. Qiao and G. Q. M. Lux. *Angew. Chew. Int. Ed.*, 2010, **49**, 4981; J. Liu, S. Z. Qiao and G. Q. M. Lux, *Small*, 2011, **7**, 425.

2 S. Joo, J. Park and G. Somorjai, *Nat. Mater.*, 2009, **8**, 126; M. Kim, K. Sohn and T. Hyeon, *Nano Lett.*, 2002, **2**, 1383; Y. H. Deng, Y. Cai and D. Y. Zhao. *J. Am. Chem. Soc.*, 2010, **132**, 8466; C. C. Huang, W, Huang and C. S. Yeh, *Biometerial*, 2011, **32**, 556; C. Graf, D. Vossen and A. van Blaaderen, *Langmuir*, 2003, **19**, 6693; K. S. Chou and C. C. Chen, *Microporous Mesoporous Mater.*, 2007, **98**, 208; V. Calderone, J.Schuetz-Widoniak and A. Philipse, *Catal. Lett.*, 2010, **137**, 132.

3 W. Ehrfeld, V. Hessel and H. Löwe. Microreactors: new technology for modern chemistry. Wiley-VCH, Weinheim, 2005.

4 T. Harada, S. Ikeda and M. Matsumura, *Langmuir*, 2010, **26**, 17720; S. N. Wang, M. C. Zhang and W. Q. Zhang, *ACS Catal*, 2011, **1**, 207; Z. M. Cui, Z. Chen and W.-G. Song, *Chem. Commun.*, 2013, **49**, 2332.

5 S. Crossley, J. Faria and D. E. Resasco, *Science*, 2010, **327**, 68; V. Yesilyurt, R. Ramireddy and S. Thayumanavan, *Angew. Chem., Int. Ed.*, 2011, **50**, 3038.

6 H. Q. Yang, T. Zhou and W. J. Zhang, *Angew. Chem., Int. Ed.*, 2013, 52, 1; J. P. Huang and H. Q. Yang, *Chem. Commun.*, 2015, **51**, 7333.
7 L. L. Zhao, L. J. Zhu and Z. Z. Yang, *Chem. Commun.*, 2013, **49**, 6161.
8 J. H. Bahng, B. Yeom and N. Kotov, *Nature*, 517, **29**, 596.
9 T. Sugimoto, M. Khan, A. Muramatsu, *Colloids Surf., A*, 1993, **70**, 167.
10 D. K. Sheng, J. P. Yang and D. Y. Zhao, *Nano Lett.*, 2014, **14**, 923.
11 J. G. Cai, S. Y. Chen and L. M. Qi, *CrystEngComm.*, 2013, **15**, 6284.
12 A. Kuijk, A. van Blaaderen and A. Imhof, *J. Am. Chem. Soc.*, 2011, **133**, 2346; J. He, B. Y. Yu and Z. H. Nie, *Angew. Chem., Int. Ed.*, 2012, **51**, 3628.