Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

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Novel Hollow and Yolk-Shell Structured Periodic Mesoporous Polymer Nanoparticles

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The pioneered construction of novel monodisperse hollow and yolk-shell structured periodic mesoporous polymer nanoparticles was reported by development of an efficient reactive interface-guided co-assembly approach.

Hollow and yolk-shell structured nanoparticles have been one of the most active areas in materials science because of their potential in various applications, such as adsorption, controlled delivery, catalysts and nanoreactors.[1] Within this family of zero-dimensional (0D) nanomaterials, it is well recognized that control over shell structure, core size, permeability and functionality is critical for elevating their performance in targeted applications.[1f, 2] Particularly, incorporation of nanopores into the shell structure not only provides large surface area for dispersion of active sites, but also serves as a favorable pathway for guest molecules to enter the void space.[3] Consequently, integration of rational porous structure into the shell of hollow and yolk-shell structured nanoparticles, which may lead to unconventional properties, is highly desirable and important for their practical applications.

Periodic porous polymers form an important class of nanomaterials, due to their intrinsic porous nature that avoids mass transport limitations of disordered pores by providing a highly ordered pore structure for fast movement of guest molecules throughout the material.[4] These features are of great interest for a broad spectrum of applications. The past two decades have witnessed the rapid growth of interest in periodic porous polymers with various morphologies including solid nanoparticles,[5] one-dimensional nanofiber,[6] two-dimensional films,[7] three-dimensional network.[8] Nonetheless, the incorporation of periodic mesoporous polymeric

architectures into hollow and yolk-shell structured nanoparticles has not been realized so far. The shell of the current reported hollow and yolk-shell polymer nanoparticles always possess quasi-nonporous or small-sized (< 2 nm) and highly disordered porous characteristics (Fig. S1). The main reason for this limitation is that the co-assembly of the building blocks of ordered mesostructures is very challenging to attain on a high-curvature 0D nanosurface of core templates, especially when further decreasing the substrate size to a nanometer scale. Therefore, it has been very difficult, if not impossible, to obtain hollow and yolk-shell structured periodic mesoporous (> 2 nm) polymer nanoparticles.

Herein, for the first time, we report the design and fabrication of a novel class of monodisperse hollow and yolk-shell structured periodic mesoporous polymer nanoparticles by a conceptually different approach using reactive interface-assisted co-assembly. In a model study, SiO_2 and $Au@SiO_2$ nanoparticles containing aldehyde groups were designed and employed as the core templates with reactive functional groups (Fig. S2). The aldehyde groups of these nanoparticles reacted with resol of the self-assembly system to *in-situ* form stable covalent bonds at their interface (Fig. 1a). Such very strong interactions acted as the driving force to assist the successful self-assembly of resol and triblock copolymer F127 directly onto the high-curvature surface of SiO_2 or $Au@SiO_2$ nanoparticles. Removal of the F127 from the as-made polymeric/inorganic hybrid materials created a highly periodic mesoporous polymeric shell coated on the inorganic nanoparticles. Novel classes of monodisperse hollow and yolk-shell structured periodic mesoporous polymer nanoparticles with a caged cubic mesostructure were generated after selectively etching the silica component (Fig. 1). The polymer nanoparticles discussed in this article possess novel and intriguing periodic large-sized (*ca.* 5 nm) mesoporous shell structures, different from the current hollow and yolk-shell polymer nanoparticles with quasi-nonporous or highly disordered microporous shell structures. This class of materials provides opportunities for broadening the scope of their applications. For example, the resulting hollow periodic

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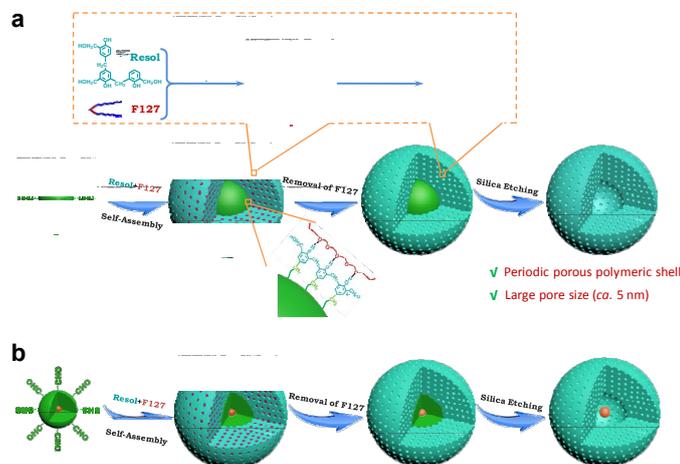
Fig. 1 Schematic illustration of preparation of novel (a) hollow periodic mesoporous polymer nanoparticle and (b) yolk-shell structured Au@periodic mesoporous polymer nanoparticle by developing an approach of reactive interface-assisted co-assembly.

mesoporous polymer nanoparticle (HPMPNP) demonstrated much faster mass transport, providing excellent adsorption performance.
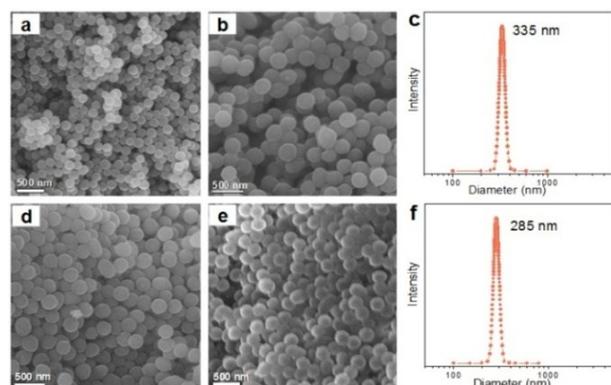
Fig. 2 SEM images of (a) SiO_2 nanoparticles with functional aldehyde groups, (b) as-made SiO_2@polymer nanoparticles, (d) SiO_2@PMPNP and (e) HPMPNP. DLS curves of (c) as-made SiO_2@polymer nanoparticles and (f) HPMPNP.

SiO_2-CHO nanoparticles were designed as a proof-of-concept demonstration and used as the core template for synthesizing hollow nanostructures (Fig. 2a). The surface of the SiO_2 nanoparticles were functional by reaction of the conventional SiO_2 nanoparticle with (3-aminopropyl)triethoxysilane to introduce an amine functionality onto the surface, followed by transformation of the amine to an aldehyde terminal group through chemical coupling with glutaraldehyde (Fig. S2~S4). The validity of the functionalization treatment was supported by the Fourier-transform infrared spectrum (Fig. S5).
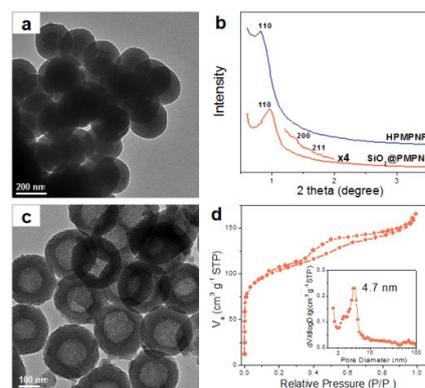
Fig. 3 TEM images of (a) SiO_2@PMPNP and (c) HPMPNP. (b) Low-angle XRD patterns of SiO_2@PMPNP and HPMPNP. (d) Nitrogen adsorption-desorption isotherm and DFT pore size distribution curve (inset) for HPMPNP.

After thermosetting of resol resin, the as-made SiO_2@polymer nanoparticles with a diameter of *ca.* 293 nm and a low polydispersity index (PDI) of 0.005 were obtained (Fig. 2b, 2c and S6), indicating a uniform polymeric shell was successfully coated onto the SiO_2 nanoparticle. Subsequently, heating the as-made SiO_2@polymer nanoparticle at 350 °C under nitrogen atmosphere resulted in decomposition of the F127 and formation of uniform core-shell structured SiO_2@periodic mesoporous polymer nanoparticle, denoted as SiO_2@PMPNP (Fig. 2d and S7). Transmission electron microscopy (TEM) image clearly demonstrated that SiO_2@PMPNP had a uniform core-shell structure, where a dark core was encapsulated in a gray layer; and their shell exhibited a periodic mesoporous structure (Fig. 3a). The low-angle X-ray diffraction (XRD) pattern of SiO_2@PMPNP displayed a well-

resolved diffraction peak and two weak diffraction peaks with a *d* spacing ratio of $1/\sqrt{2}/\sqrt{3}$, which could be indexed as 110, 200, and 211 diffractions of an ordered body-centered cubic mesostructure (Fig. 3b).[9]

The SiO_2 core was then removed to form a spherical macropore, leading to formation of a totally new targeted HPMPNP. The original perfect spherical morphology, nanoparticle diameter and smooth surface were perfectly retained in the resulting HPMPNP (Fig. 2e and S8). The typical core size and shell thickness of HPMPNP were calculated to be around 110 and 75 nm, respectively (Fig. 3c). DLS curve in Fig. 2f clearly showed that the as-prepared HPMPNP were very highly monodispersed with a PDI of 0.005. In addition, the HPMPNP with phenolic resin network possessed periodic structures with regular and dense mesopores in the shell regions, corresponding well with the XRD data (Fig. 3b and S9). The presence of these mesopores was confirmed by a typical type-IV curve with an obvious H2-type hysteresis loop in the nitrogen adsorption-desorption isotherm (Fig. 3d). The size of these mesopores was calculated to be as large as 4.7 nm. A Brunauer-Emmett-Teller (BET) calculation gave the surface area for HPMPNP equal to 359 $m^2 g^{-1}$.

For comparison, control samples were prepared using the conventional unreactive SiO_2 nanoparticles as the substrate (Fig. S3). The resulting control polymer/SiO_2 composites were mainly composed of irregular polymeric particles and spherical SiO_2 nanoparticles (Fig. S10a). Further etching silica component from the control polymer/SiO_2 composites, the as-obtained control polymer samples were totally solid nanoparticles and did not show any hollow structure (Fig. S10b and S10c). These results clearly confirmed that resol and F127 indeed could not co-assemble onto the unreactive SiO_2 nanoparticles to form core-shell organic/inorganic hybrid nanoparticles (Fig. S11).

The above observations confirmed the existence of the SiO_2-CHO nanoparticle with a reactive surface played a crucial role in the formation of a hollow periodic mesoporous particle structure. In general, one basic condition must be met in order to obtain hollow polymer nanoparticles with a periodic mesoporous shell structure, *i.e.*, a sufficiently strong interaction between the building blocks of the ordered mesostructures, *e.g.*, resol-F127 composite, and core template, *e.g.*, SiO_2 nanoparticle. In contrast, the traditional SiO_2 nanoparticle interacted with the building blocks through weak interactions such as hydrogen bonding and electrostatic interaction. As a result, the resol and triblock copolymer F127 failed to self-assemble on the bare SiO_2 nanoparticles to form core-shell organic/inorganic hybrid particles, eventually failing to construct hollow nanostructures (Fig. S10~S11). However, unlike the unreactive surface of the raw SiO_2 nanoparticles, the aldehyde groups on the functionalized SiO_2 surface can react with phenolic groups of the PF resol to form stable covalent bonds (Fig. 1a). Such additional but necessary covalent bonds greatly enhanced the interaction between the resol and SiO_2 nanoparticles, and thus provided active SiO_2/resol interfacial sites for the accumulation and subsequent self-assembly of resol and F127 onto the surface of SiO_2 nanoparticles. Thus, uniform SiO_2@F127/resol

composite core-shell nanoparticles were successfully constructed. After successive removal of F127 and SiO_2, hollow periodic mesoporous polymer nanoparticles with an ordered cubic mesoporous shell were obtained.
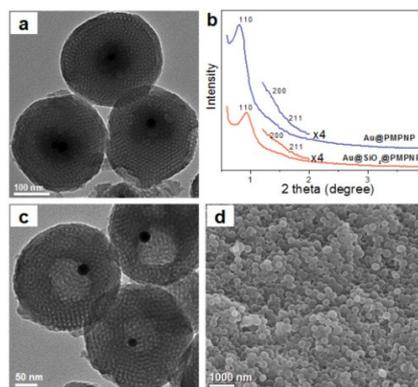
Fig. 4 (a) TEM image of Au@SiO_2@PMPNP. (b) Low-angle XRD patterns of Au@SiO_2@PMPNP and Au@PMPNP, showing their periodic mesoporous shell characteristic. (c) TEM image and (d) SEM image of Au@PMPNP.

The newly proposed reactive interface-guided co-assembly protocol opens many opportunities for introducing diverse functional components into the core-shell structured matrix. This is exemplified by the preparation of functionalized Au@SiO_2-CHO core-shell nanoparticles as core templates to construct yolk-shell structured Au@hollow periodic mesoporous polymer composites (Fig. 1b and S12). The resulting Au@SiO_2@polymer core-shell-shell nanoparticles possessed uniform spherical structure (Fig. S13). The periodic mesoporous characteristic of Au@SiO_2@PMPNP was clearly evident in TEM image (Fig. 4a) and low-angle XRD pattern (Fig. 4b). After selective etching of the intermediate silica layer, a uniform yolk-shell nanostructure with a unique periodic mesoporous shell was observed (Fig. 4b~4d). The as-prepared Au@PMPNP had a relatively monodisperse size distribution of *ca*.250 nm. The typical gold size, hollow core diameter and shell thickness of the yolk-shell nanoparticle structure were measured to be 20, 100 and 75 nm, respectively (Fig. 4c).

To the best of our knowledge, these are the first examples of preparation of monodisperse hollow and yolk-shell structured periodic mesoporous polymer nanoparticles. The adsorption performances of HPMPNP toward methanol vapor and vitamin B12 (VB12) were evaluated in order to demonstrate the advantages of their periodic mesoporous shell structure in improving performance. We made a comparison of the adsorption behaviors between the HPMPNP and a conventional hollow disordered microporous polymer nanoparticle (HDMPNP) with a similar BET surface area (Fig. S14).[10] It was found that the maximum adsorption rate of the HPMPNP (0.24 mg g^{-1} s^{-1}) was higher than that of HDMPNP (0.14 mg g^{-1} s^{-1}) for methanol vapor (Fig. 5). The colour of the filtered solution of VB12 with large molecular dimensions after exposure to the HDMPNP was almost constant (Fig. S15 and S16). It implied poor adsorption of VB12 into HDMPNP, mainly because of its small-sized disorder pore in the shell. In sharp

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contrast, for the HPMPNP, the filtered solution turned from pink to colorless in 3 h. These results clearly showed that HPMPNP had rapid adsorption rate and high adsorption efficiency, since its periodic mesoporous shell provided good accessibility for the adsorbates molecules.
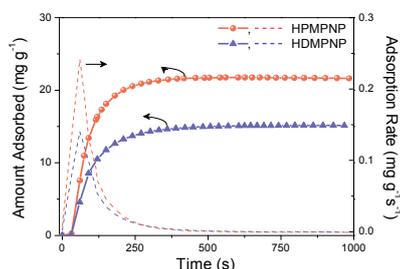
Fig. 5 Adsorption rate performance of HPMPNP and HDMPNP for 5 mb methanol vapor.

Furthermore, the catalytic ability of Au@PMPNP was evaluated. It was found that Au@PMPNP presented good performance for the catalytic reduction of nitrobenzene and 4-nitrophenol (Fig. S17). In addition, the rate constant for the reduction of nitrobenzene ($k_{app} = 1.1 \times 10^{-2}$ min^{-1}) was higher than that of 4-nitrophenol ($k_{app} = 2.4 \times 10^{-3}$ min^{-1}). This indicated that the Au@PMPNP sample was a selective catalyst (Fig. S18), probably because the hydrophobic polymeric shell favoured the diffusion of more hydrophobic nitrobenzene to contact the functional Au yolk.[11]

In conclusion, the development of an efficient reactive interface-guided co-assembly conceptual approach resulted in the pioneering design and fabrication of novel hollow and yolk-shell structured periodic mesoporous polymer nanoparticles. The important role of a reactive core template containing aldehyde groups in evolution of such a hierarchical nanoobject with a unique periodic mesoporous shell structure was carefully experimentally confirmed. The coordinated hollow periodic mesoporous polymer nanoparticles demonstrated excellent adsorption performance. We hope that these findings will lead to the development of advanced hierarchical materials with periodic porous architectures and targeted multi-functional chemical compositions, and thus provide new opportunities for designed functional materials in diverse applications including adsorption, separation, medicine, catalysis and energy.

References

1. (a)R. J. White, K. Tauer, M. Antonietti and M.M. Titirici, *J. Am. Chem. Soc.*, 2010, **132**, 17360; (b)G.H. Wang, J. Hilgert, F. H. Richter, F. Wang, H.J. Bongard, B. Spliethoff, C. Weidenthaler and F. Schüth, *Nat. Mater.*, 2014, **13**, 293; (c)Y. Fang, G. Zheng, J. Yang, H. Tang, Y. Zhang, B. Kong, Y. Lv, C. Xu, A. M. Asiri, J. Zi, F. Zhang and D. Zhao, *Angew. Chem. Int. Ed.*, 2014, **53**, 5366; (d)S. Yang, X. Feng, L. Zhi, Q. Cao, J. Maier and K. Muellen, *Adv. Mater.*, 2010, **22**, 838; (e)J. Liu, S. Z. Qiao, J. S. Chen, X. W. Lou, X. R. Xing and G. Q. Lu, *Chem. Commun.*, 2011, **47**, 12578; (f)J. Sun, J. Zhang, M. Zhang, M. Antonietti, X. Fu and X. Wang, *Nat. Commun.*, 2012, 1139.

2. (a)G. Cui, Y.S. Hu, L. Zhi, D. Wu, I. Lieberwirth, J. Maier and K. Muellen, *Small*, 2007, **3**, 2066; (b)J. Liu, S. Z. Qiao, S. B. Hartono and G. Q. Lu, *Angew. Chem. Int. Ed.*, 2010, **49**, 4981; (c)S. Hyuk Im, U. Jeong and Y. Xia, *Nat. Mater.*, 2005, **4**, 671; (d)G. L. Li, H. Mohwald and D. G. Shchukin, *Chem. Soc. Rev.*, 2013, **42**, 3628; (e)G. D. Li and Z. Y. Tang, *Nanoscale*, 2014, **6**, 3995; (f)R. Liu, F. Qu, Y. Guo, N. Yao and R. D. Priestley, *Chem. Commun.*, 2014, **50**, 478.

3. (a)C. X. Lin, W. Zhu, H. W. Yang, Q. An, C. A. Tao, W. N. Li, J. C. Cui, Z. L. Li and G. T. Li, *Angew. Chem. Int. Ed.*, 2011, **50**, 4947; (b)A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch and D. A. Weitz, *Science*, 2002, **298**, 1006; (c)C. S. Peyratout and L. Dähne, *Angew. Chem. Int. Ed.*, 2004, **43**, 3762; (d)X.H. Li, X. Wang and M. Antonietti, *Chem. Sci.*, 2012, **3**, 2170.

4. (a)S. A. Johnson, P. J. Ollivier and T. E. Mallouk, *Science*, 1999, **283**, 963; (b)A. S. Zalusky, R. Olayo-Valles, J. H. Wolf and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2002, **124**, 12761; (c)D. Wu, F. Xu, B. Sun, R. Fu, H. He and K. Matyjaszewski, *Chem. Rev.*, 2012, **112**, 3959; (d)Y. Wan, Y. Shi and D. Zhao, *Chem. Mater.*, 2008, **20**, 932; (e)Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu and D. Zhao, *Angew. Chem. Int. Ed.*, 2005, **44**, 7053; (f)Y. Liang, Z. Li, R. Fu and D. Wu, *J. Mater. Chem. A*, 2013, **1**, 3768; (g)Y. Liang, Z. Li, X. Yang, R. Fu and D. Wu, *Chem. Commun.*, 2013, **49**, 9998.

5. Y. Fang, D. Gu, Y. Zou, Z. Wu, F. Li, R. Che, Y. Deng, B. Tu and D. Zhao, *Angew. Chem. Int. Ed.*, 2010, **49**, 7987.

6. Y. Jiang, W. Huang, J. Wang, Q. Wu, H. Wang, L. Pan and X. Liu, *J. Mater. Chem. A*, 2014, **2**, 8201.

7. (a)Y. Fang, Y. Lv, J. Tang, H. Wu, D. Jia, D. Feng, B. Kong, Y. Wang, A. A. Elzatahry, D. Al-Dahyan, Q. Zhang, G. Zheng and D. Zhao, *Angew. Chem. Int. Ed.*, 2015, **127**, 8545; (b)B. You, L. Shi, N. Wen, X. Liu, L. Wu and J. Zi, *Macromolecules*, 2008, **41**, 6624; (c)A. Zhang, H. Bai and L. Li, *Chem. Rev.*, 2015, **115**, 9801; (d)C. Tang, A. Tracz, M. Kruk, R. Zhang, D.M. Smilgies, K. Matyjaszewski and T. Kowalewski, *J. Am. Chem. Soc.*, 2005, **127**, 6918.

8. (a)P. Jiang, K. S. Hwang, D. M. Mittleman, J. F. Bertone and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 11630; (b)B. Liu, C. H. Kuo, J. J. Chen, Z. Luo, S. Thanneeru, W. K. Li, W. Q. Song, S. Biswas, S. L. Suib and J. He, *Angew. Chem. Int. Ed.*, 2015, **54**, 9061.

9. (a)Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein and D. Zhao, *Chem. Mater.*, 2006, **18**, 4447; (b)Y. R. Liang, R. W. Fu and D. C. Wu, *ACS Nano*, 2013, **7**, 1748.

10. X. Kang, Y. Liang, L. Chen, W. Mai, Z. Lin, R. Fu and D. Wu, *RSC Advances*, 2014, **4**, 26166.

11. (a)J. Lee, J. C. Park and H. Song, *Adv. Mater.*, 2008, **20**, 1523; (b)B. Guan, X. Wang, Y. Xiao, Y. Liu and Q. Huo, *Nanoscale*, 2013, **5**, 2469.