Hollow Microporous Organic Capsules

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Fabrication of hollow microporous organic capsules (HMOCs) could be very useful because of their hollow and porous morphology, which combines the advantages of both microporous organic polymers and non-porous nanocapsules. They can be used as storage materials or reaction chambers while supplying the necessary path for the design of controlled uptake/release systems. Herein, the synthesis of HMOCs with high surface area through facile emulsion polymerization and hypercrosslinking reactions, is described. Due to their tailored porous structure, these capsules possessed high drug loading efficiency, zero-order drug release kinetics and are also demonstrated to be used as nanoscale reactors for the preparation of nanoparticles (NPs) without any external stabilizer. Moreover, owing to their intrinsic biocompatibility and fluorescence, these capsules exhibit promising prospect for biomedical applications.

Porous materials have attracted considerable research interest for several years because of their widespread technological applications in gas storage1–5, separation6,7 and heterogeneous catalysis8–10. Recently microporous organic polymers (MOPs)11 have emerged as an important class of materials due to their high thermal and hydrothermal stabilities, which stem from the stronger covalent bonds, compared to extensively studied systems like metal-organic frameworks (MOFs). In this regard, several kinds of MOPs, such as covalent organic frameworks (COFs)12,13, amorphous hyper-crosslinked polymers (HCPs)14–17, polymers of intrinsic microporosity (PIMs)18 and conjugated microporous polymers (CMPs)19,20, have been investigated to control their pore size and the surface area. MOPs are usually formed by C-C coupling reactions, e.g., Sonogashira, Suzuki- or Yamamoto-coupling21, trimerization of ethynyl22 or nitrile groups23, by amide, imide or imine formation24–26, via 'Click' chemistry27,28 and oxidative polymerization29,30. Despite all these efforts, a little attention has been paid to control micro-morphology of MOPs and their subsequent applications. There are only a few reports of MOPs with nanoparticulate4,31 or a tubular morphology32. The HCPs nanoparticles accelerate the hydrogen adsorption rate and enhance the hydrogen storage capacity compared to their macro-analogues. It is also possible to synthesize fluorescent CMP particles which may find their application in bio-imaging and sensing33. These findings demonstrate that the properties of MOPs are highly dependent on their morphology. Among diverse particle geometries, hollow capsules have recently received more attention. This interest is primarily fueled up due to their ability to confine the chemicals within their hollow cavities and their controlled release34,35, to serve as highly active nanoreactors36 and to keep metal nanoparticle catalysts isolated and avoid their ripening37 or poisoning38. In this regard, fabrication of hollow microporous organic capsules (HMOCs) could be very useful to broaden the scope of MOPs. Similarly nanocapsules of MOPs may also offer additional advantages due to their hollow and porous morphology. They may have their use as storage materials or reaction chambers while supplying the necessary path for the design of controlled uptake/release systems. Compared to other inorganic capsules, HMOCs have better tolerance to acid/alkali and are more compatible with the organic molecules39–41. Recently, Wu et al.42 have reported the preparation of the nanostructured porous network of MOPs. They used surface-initiated atom-transfer radical polymerization (SI-ATRP) on the silica nanoparticles, followed by intra/inter-particle carbonyl crosslinking of polystyrene. However, their method is associated with some disadvantages especially being complicated, inter-particle cross-linking, and uncontrollable porous structure.

In this work, a facile traditional emulsion polymerization method was used to prepare SiO2@PS-DVB core-shell precursors, which were then hypercrosslinked followed by chemical etching of the sacrificial SiO2 cores to obtain HMOCs (Fig. 1). The hollow cavity and the shell thickness of these novel HMOCs can easily be controlled by varying the size of sacrificial SiO2 core and the dose of monomers used to form the polymer shell. The tunable microporous shell of HMOCs added an additional dimension to them and could be useful for various interesting applications.
Results

SiO$_2$@PS-DVB precursor nanoparticles. Silica nanoparticles (SiO$_2$ NPs) were synthesized through traditional Stöber method. The vinyl group of 3-(trimethoxysilyl)propyl methacrylate (MPS) grafted on the SiO$_2$ NPs can react with monomers (styrene and DVB) to form macromolecular chains anchored on their surface, thus forming SiO$_2$@PS-DVB core-shell structures$^{43}$. Previously, we have demonstrated that the pore structure can be controlled from macro to microscale by changing the DVB contents$^{44}$. Hence, to vary the porous structure of HMOCs, a series of precursor NPs (SiO$_2$@PS-DVB) were prepared with different DVB contents (0.5, 1, 2.5, 5, 10 and 15 wt.% of styrene). It was observed that co-monomer (DVB) has a significant effect on the core-shell morphology of SiO$_2$@PS-DVB NPs (Fig. 2). The SiO$_2$@PS-DVB NPs with 0.5, 1 and 2.5% DVB exhibited eccentric SiO$_2$ cores, while the SiO$_2$ cores in SiO$_2$@PS-DVB NPs with 5, 10 and 15% DVB were centric. By increasing the DVB contents, the SiO$_2$@PS-DVB tended to have concentric core–shell morphology. By decreasing the DVB contents were low, the PS chains were weakly crosslinked by DVB and the rigidity of the shell could not be balanced with the gravity of SiO$_2$ core. Increasing the DVB content enhanced the rigidity of the shell, therefore the SiO$_2$ spheres tended to be located in the center$^{44}$.

Hypercrosslinking reactions and hollow microporous organic capsules. After hypercrosslinking, sacrificial SiO$_2$ cores were etched by hydrofluoric acid (HF). From TEM and SEM images of precursor (SiO$_2$@PS-DVB) NPs (Fig. 2 and Fig. S1–S6) and hollow HMOCs (Fig. 3a to 3f and Fig. S7–S12) after hypercrosslinking and etching, it is obvious that HMOCs retained their original morphology after the removal of SiO$_2$ cores. Low DVB contents (0.5 wt.%) led to the formation of HMOCs with rough surface. This might be due to the low degree of crosslinking resulting in the twisting of some macromolecular chains leading to the rough surface. Shell's surface became smooth when the DVB content was up to 1 wt.% or higher. These observations are in consistence with the previous reports$^{44}$. The HMOCs with varying size of hollow cavities and different

![Figure 1](https://www.nature.com/scientificreports/srep02128/figure1.png)  
**Figure 1** | Schematic synthetic route of hollow microporous organic capsules (HMOCs).

![Figure 2](https://www.nature.com/scientificreports/srep02128/figure2.png)  
**Figure 2** | TEM images of SiO$_2$@PS core-shell precursors with different DVB contents. (a) SiO$_2$@PS-0.5% DVB, (b) SiO$_2$@PS-1% DVB, (c) SiO$_2$@PS-2.5% DVB, (d) SiO$_2$@PS-5% DVB, (e) SiO$_2$@PS-10% DVB, (f) SiO$_2$@PS-15% DVB. Styrene is 10 ml. The SiO$_2$ nanoparticles core is 130 nm. The mass of SiO$_2$ nanoparticles is 1.2 g. The scale is 200 nm.

![Figure 3](https://www.nature.com/scientificreports/srep02128/figure3.png)  
**Figure 3** | TEM images of HMOCs obtained after hypercrosslinking of SiO$_2$@PS core-shell precursors with different DVB content and etching SiO$_2$ core. (a) 0.5% - HMOCs, (b) 1% - HMOCs, (c) 2.5% - HMOCs, (d) 5% - HMOCs, (e) 10% - HMOCs, (f) 15% - HMOCs. Styrene is 10 ml with 130 nm hollow cavities. TEM images of HMOCs with different thickness of the shell by varying the dose of styrene in SiO$_2$@PS core-shell precursors, (g) 10% - HMOCs - 2.5 ml, (h) 10% - HMOCs - 5 ml, (i) 10% - HMOCs - 10 ml, (j) 10% - HMOCs - 15 ml with 130 nm hollow cavities. TEM image of HMOCs with 200 nm hollow cavities. (k) 10% - HMOCs - 5 ml–200 nm, (l) 10% - HMOCs - 10 ml–200 nm. The mass of SiO$_2$ nanoparticles is 1.2 g. The scale is 200 nm.
The mass of SiO$_2$ nanoparticles is 1.2 g. In order to obtain the HMOCs with different shell thickness, the dose of styrene was varied from 2.5 to 15 ml for the synthesis of SiO$_2$@PS-DVB nanoparticles with ~130 nm SiO$_2$ cores (S15–S18). The TEM images of HMOCs after hypercrosslinking and etching are shown in Fig. 3g to 3j. It was observed that the resulting particle size (including core and shell) and shell thickness (excluding core) increased with a decrease in initial emulsifier to monomer ratio which was consistent with the dominant micellar nucleation mechanism proposed by Harkins$^{45}$. According to this mechanism, a decrease in the initial emulsifier to monomer ratio decreases the relative amount of micelles which in turn decreases the number of polymer particle nuclei formed early in the reaction per unit time resulting in formation of polymer particles with smaller in numbers but larger in size$^5$. It was also possible to change the size of hollow cavities of HMOCs (Fig. 3k and 3l) by using SiO$_2$ cores with different sizes (e.g. 200 nm, Fig. S19 and S20). The mass of SiO$_2$ nanoparticles is 1.2 g.

**Surface areas and porous structures.** It is clearly evident from the TEM images that the size of hollow cavity of HMOCs and their shell thickness can easily be tuned. However, the microporous structure of their shell cannot be observed by these imaging techniques. Nitrogen gas adsorption and desorption experiment were, therefore, employed to confirm their microporous structure. The BET surface area, Langmuir surface area, and pore volume are summarized in Table 1 and Table S1. It is clearly evident that by increasing the DVB contents, the surface area of HMOCs decreases, which can be attributed to the decrease in the hypercrosslinking of styrene. The nitrogen adsorption and desorption isotherms were obtained as expected. In order to obtain the HMOCs after hypercrosslinking and etching are shown in Fig. 3g to 3j. It was observed that the resulting particle size (including core and shell) and shell thickness (excluding core) increased with a decrease in initial emulsifier to monomer ratio which was consistent with the dominant micellar nucleation mechanism proposed by Harkins$^{45}$. According to this mechanism, a decrease in the initial emulsifier to monomer ratio decreases the relative amount of micelles which in turn decreases the number of polymer particle nuclei formed early in the reaction per unit time resulting in formation of polymer particles with smaller in numbers but larger in size$^5$. It was also possible to change the size of hollow cavities of HMOCs (Fig. 3k and 3l) by using SiO$_2$ cores with different sizes (e.g. 200 nm, Fig. S19 and S20). The mass of SiO$_2$ nanoparticles is 1.2 g.

![Figure 4](https://example.com/figure4.png)

**Figure 4** | (a) Nitrogen sorption isotherms at 77.3 K and (b) pore distribution of pore size calculated using DFT methods (slit pore models, differential pore volumes) of HMOCs with 130 nm hollow cavity.

**Discussion**

HMOCs were also evaluated for their possible potential biomedical applications. Prior to that, the toxicity of HMOCs was investigated through an MTT assay, and cell viability of HepG2 cells was determined in the presence of HMOCs (Fig. S21). HMOCs showed almost no cytotoxicity over the range of concentrations studied (0, 15.6, 62.5, 125, 250 and 500 $\mu$g/mL). As HMOCs are around 250 nm in diameter, usually they will be sequestered by phagocytic cells of the spleen and eliminated from the body eventually$^{47}$. Interestingly, these HMOCs were also found to be fluorescent, which may be useful for their applications in bio-imaging and bio-labeling. The origin of fluorescence in these HMOCs is not clear yet but it may be due the stacking of benzene rings and nanoscale size effect. The optical images of HMOCs under UV light in simulated body fluid (PBS, pH = 7.4, buffer solution) are shown in Fig. S22. The emission

**Table 1** | Surface area and porosity of HMOCs

| Samples    | DVB (%) | $S_{BET}$[a] m$^2$/g | $S_I$[b] m$^2$/g | $M.A.$[c] m$^2$/g | PV$^d$ cm$^3$/g | M.P.V.$^e$ cm$^3$/g | M.A.$^f$ [%] |
|------------|---------|----------------------|-----------------|-------------------|----------------|-------------------|-------------|
| 0.5% - HMOCs | 0.5     | 1129                 | 1549            | 361               | 0.98           | 0.15              | 32.0        |
| 1% - HMOCs  | 1       | 815                  | 1098            | 496               | 0.61           | 0.22              | 60.8        |
| 2.5% - HMOCs | 2.5     | 697                  | 932             | 431               | 0.59           | 0.20              | 61.8        |
| 5% - HMOCs  | 5       | 589                  | 788             | 407               | 0.42           | 0.19              | 69.1        |
| 10% - HMOCs | 10      | 516                  | 691             | 351               | 0.35           | 0.16              | 68.0        |
| 15% - HMOCs | 15      | 478                  | 640             | 296               | 0.35           | 0.14              | 61.9        |
| 10% - Solid HCPs | 10    | 616                  | 829             | -                 | 0.83           | -                 | -           |

[a] Surface area calculated from nitrogen adsorption isotherms at 77.3 K using BET equation.
[b] Surface area calculated from nitrogen adsorption isotherms at 77.3 K using Langmuir equation.
[c] $M.A.$: Mole adsorption.
[d] Pore volume calculated from nitrogen isotherm at $P/P_0 = 0.995$, 77.3 K.
[e] M.P.V.: Mole pore volume.
[f] % Pore volume calculated from nitrogen isotherm at $P/P_0 = 0.995$, 77.3 K.

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**Note:** The table provides a summary of the surface area and porosity of HMOCs under different DVB contents, with emphasis on the changes in surface area and pore volume as the DVB content increases. The table includes measurements for BET surface area ($S_{BET}$), Langmuir surface area ($S_I$), and pore volume ($PV$) obtained from nitrogen adsorption isotherms at 77.3 K, using both BET and Langmuir equations. The pore volume ($M.P.V.$) is calculated using the DFT method with slit pore models. The data highlight the significant reduction in surface area and pore volume as the DVB content increases, while the micropore area remains relatively constant. This indicates a transition from mesoporous to microporous structures as the DVB content increases, which may have implications for the use of HMOCs in biomedical applications.
higher surface area (616 m²/g) than that (516 m²/g) of 10% -silica core achieved for solid HCP nanoparticles prepared in the absence of profen/g, which is much higher than that (0.80 g of ibuprofen/g) summarized in Table S2, HMOCs can uptake 1.68 to 2.04 g of ibuprofen of HMOCs itself. But prior to that, the weight loss observed in the weight loss at and above 450°C corresponds to the decomposition of HMOCs itself. However the shells of 10% -HMOCs were maintained, which indicates the entrapment of drug inside the hollow cavity of HMOCs. The surface area of 10% - HMOCs was found to be lower than that of 10% - solid HCPs, which may be due to an extra internal surface of 10% - HMOCs for being hollow. Moreover, the benzene rings present on the external and internal surfaces of precursor shell cannot be hypercrosslinked as effectively as those present inside the precursor shell. The drug release profile (Fig. 5) indicates that the porous structure of shell also affects the drug release kinetics. The shell of 0.5% - HMOCs to 5% - HMOCs possess meso- and microporous structure and their drug release kinetics fit for the first order model. This model indicates that the release mechanism of ibuprofen is mainly controlled by the simple diffusion. HMOCs release the drug at a rate which is proportional to the amount of drug remaining in its interior. However the shells of 10 and 15% - HMOCs are almost pure microporous and their drug release kinetics fit well for zero order model. As shown in Fig. S40, the molecular size of ibuprofen is up to 10.285 Å which is smaller than the pore size of 10 and 15% - HMOCs.

The micropores are more confined in comparison to mesopores and thus they restrict the free diffusion of drug molecules resulting in a constant drug release rate for 10% - HMOCs and 15% - HMOCs with shear microporous structure. The constant release rate makes the drug amount in blood stable which is an ideal situation for clinical therapy. Compared to the MOFs such as MIL-53\(^{49}\) and MIL-101\(^{50}\), which have been studied as drug carriers, HMOCs exhibit a higher release rate. But the release behavior of HMOCs is close to that of another microporous organic polymer PAF-6\(^{51}\) which is the first microporous organic material reported for drug delivery. Although the literature for microporous organic materials for drug delivery is very limited, drug release data of HMOCs still describes their promising prospect as an alternative choice for drug delivery through adjustable micropore size.

The HMOCs have uniform hollow cores, which can be used as nanoscale reactors to change the composition within the hollow core. For example, herein we have demonstrated it through the synthesis of 5 nm Fe\(_3\)O\(_4\) magnetic NPs via 10% - HMOCs - 2.5 ml as shown in Fig. 6a. Fe\(_3\)O\(_4\) NPs were formed through co-precipitation of iron precursors (FeCl\(_2\) and FeCl\(_3\)), absorbed within the restricted space of hollow cores, using ammonia as precipitator and without using any other external stabilizer. The superparamagnetic properties of 10% - HMOCs - 2.5 ml - Fe\(_3\)O\(_4\) NPs, as shown in the Fig. 6b, also prove the existence of Fe\(_3\)O\(_4\) nanoparticles inside the HMOCs. After soaking in PBS for 2 days, the magnetic properties of Fe\(_3\)O\(_4\) nanoparticles loaded HMOCs were maintained, which indicates the confinement of Fe\(_3\)O\(_4\) nanoparticles within HMOCs cavities. It also implies that the HMOCs- Fe\(_3\)O\(_4\) NPs can retain magnetic properties in body fluid. Interestingly, 10% - HMOCs - 2.5 ml -Fe\(_3\)O\(_4\) NPs also showed high drug uptake (2.04 of ibuprofen/g) and zero order kinetic model for drug release (Fig. S41), similar to 10% - HMOCs - 2.5 ml (2.06 of ibuprofen/g, Fig. S42). The super-paramagnetic properties of 10% - HMOCs -2.5 ml-Fe\(_3\)O\(_4\) NPs were also maintained after drug loading, promising their potential application in the development of magnetically controlled drug delivery systems.

In summary, we have demonstrated the synthesis of a family of hollow microporous organic capsules (HMOCs). Successful efforts

![Figure 5](image)

Figure 5 | Drug release profile of (a) 0.5% - HMOCs, (b) 1% - HMOCs, (c) 2.5% - HMOCs, (d) 5% - HMOCs, (e) 10% - HMOCs, (f) 15% - HMOCs. Red line is fitting line.

![Figure 6](image)

Figure 6 | (a) TEM image of 10% - HMOCs - 2.5 ml - Fe\(_3\)O\(_4\) NPs.(b) 300 K magnetization isotherms of 10% - HMOCs - 2.5 ml - Fe\(_3\)O\(_4\) NPs, (red line) 10% - HMOCs - 2.5 ml - Fe\(_3\)O\(_4\) NPs after soaked in PBS for 48 h (blue line) and 10% - HMOCs - 2.5 ml - Fe\(_3\)O\(_4\) NPs loaded with drug (green line).
were made to precisely control the size of hollow cavities, shell thickness as well as the porous shell structure of these HMOCs. The importance of microporous structure in a new dimension has been demonstrated. Moreover, the multifunctional HMOCs possessing zero order drug release kinetics, fluorescence and super-paramagnetic properties, indicate their attractive applications in medical field. The development of synthetic routes to nanostructured MOPs may receive more scientific attention due to their attractive applications in heterogeneous catalysis and separation technologies.

**Methods**

**Preparation of hollow microporous hollow capsules (HMOCs).** The HMOCs were dispersed in 0.4 M FeCl₃ and 0.2 M FeCl₂ aqueous solution. These HMOCs were separated by centrifugation and dispersed in toluene and then mixed with ammonia water, to obtain nanoscale magnetic particles inside the hollow cavity.

**Drug loading and release.** A typical procedure for the loading of ibuprofen in HMOCs is as follows: 150 mg of HMOCs were suspended in 5 ml of 90 mg/ml ibuprofen solution in hexane under stirring for 96 h in a closed container to avoid the evaporation of hexane. The drug-loaded sample was then separated from the solution by vacuum filtration, washed with hexane, and dried at room temperature. The drug-loaded samples (200 mg) were then transferred to semi-permeable bag, and the drug release test was determined by analyzing the drug-loaded samples in 100 ml of simulated body fluid (PBS, pH = 7.4, buffer solution, 37 °C) at pre-determined time intervals, 3 ml samples were withdrawn periodically for analysis and the remaining suspension replenished with an equal volume i.e., 3 ml of PBS immediately. Samples were analyzed for ibuprofen content at 265 nm using UV-Vis spectrophotometer.

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Author contributions
B.L. and X.Y. synthesized and characterized the HMOCs. X.L. performed the drug release experiments. B.T., B. L. and M. I. M. discussed the results and prepared the manuscript. B.T. conceived the project.

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