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

DOI: 10.1039/x0xx00000x

www.rsc.org/

A hollow microshuttle-shaped capsule covalent organic framework for protein adsorption

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Covalent organic frameworks (COFs) have emerged as crystalline porous materials for various potential applications. However, the development of hollow structure COFs with defined morphology is important for their further application and rare. Herein, COF with unique hollow shuttle morporlogy was prepared by a Schiff condensation reaction between 4- (4-aldehyde phenyl) ethylene (TPE) and tetra-(4-aminophenyl) porphyrin (TAP). A detailed mechanistic investigation reveals initial self-assembly and following similar inside-out Ostwald ripening processes is responsible for the hollow capsule formation. The hollow microshuttle-shaped capsule COF is used for hemoglobin adsorption study, which shows an uptake of 550.82 mg· g⁻¹ of hemoglobin. These studies could foreshadow new avenues for development of porous materials with defined morphology for biomolecules adsorption.

1. Introduction

Published on 25 January 2019. Downloaded on 1/28/2019 1:56:37 AM

Covalent organic frameworks (COFs) are a class of crystalline porous materials with regular pore structure, high surface area, thermal stability and controlled properties ^[1], which have been successfully utilized in various fields, such as photoconductive devices, catalysis, energy storage, separation, adsorption, drug delivery, sensing and confined-space chemical reactions, etc ^[2-9]. COFs can be synthesized under relatively mild conditions through a reversible dynamic nucleation-elongation process, generally including boronic acid trimerization, boronate eater formation, the trimerization of nitriles, and Schiff base reaction ^[10-13]. The reversibility of the reaction allows the self-assembly of the structural units until they achieve long-range periodicity, which leads to the crystallization of the COFs and further forms a variety of morphologies for COFs ^[14]. However, COFs are usually synthesized into microcrystalline powders with irregular morphologies in most cases.

The morphology of the materials is crucial for its applications in many fields. Especially, hollow structural materials have received much attention in recent years because of their potential applications in drug delivery, catalysis, molecular recognition, proteins and energy storage, etc ^[15-22]. Enzyme loading is an important research field in biomedicine and pharmaceutical industry ^[23]. The immobilization process not only improves the recoverability

Herein, COF with hollow capsule morphology was prepared by a Schiff condensation reaction between 4- (4- aldehyde phenyl) ethylene (TPE) ^[45] and tetra-(4-aminophenyl) porphyrin (TAP). A detailed time-dependent study for the formation of hollow shuttle reveals that initial self-assembly and following similar inside-out Ostwald ripening processes are responsible for the formation of hollow capsule. To the best of our knowledge, this is the first example of COFs materials with shuttle-shaped hollow capsule by template-

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of expensive enzymes, but also promotes the stability of enzymes under extreme conditions. Therefore, the use of COF materials to load enzymes has great potential applications in the field of biomolecule ^[24-26]. So far, for most COFs with hollow structures mainly rely on template strategies. Zeolites, metals oxides and metals organic frameworks (MOFs) are commonly used as removable organic and inorganic templates ^[27-30]. However, removing templates to form the hollow structures will introduce other toxic components and cause the shell collapse, which restrict the scope of applications, especially in biological aspects ^[31-32]. This template-assisted method is cumbersome and time-consuming ^[33-35]. Moreover, the shape of COFs was limited into cubes, sheets, fibres, belts, spheres and platelets morphologies ^[36-41].

Self-assembly is a powerful and elegant eternal theme for fabricating various architectures. This technique has been successfully applied to the preparation of hollow COFs without the assistant of templates ^[42]. Rahul Banerjee' research group has successfully synthesized chemically stable COFs hollow spheres by Ostwald ripening procedure ^[43]. Florian Beuerle's group prepared COFs with microtubes shape via a bottom-up self-assembly process based on rolled-up crystallite sheets. Despite these advances for the preparation of COFs with defined morphology via template-free methods, the development of COFs with other defined morphologies has rarely been explored ^[44].

Fig. 1 (A) Synthesis scheme of 4- (4- aldehyde phenyl) ethylene (TPE); (B) Synthetic scheme of TPE-TAP-COF; (C) Top view and (D) side view of AA (eclipsed) stacking of TPE-TAP-COF (gray, carbon; blue, nitrogen)

free method. Moreover, the COF with shuttle-shaped hollow capsule an uptake amount of 550.82 mg·g -1 of hemoglobin, which is the highest adsorption capacity among known COFs.

2. Experimental section

2.1 Chemicals and materials

4, 4'-dimethylbenzophenone, titanium tetrachloride (TiCl4), pyridine,N-bromobutanimide (NBS), dibenzoyl peroxide (BPO) were purchased from Aladdin.Anhydrous tetrahydrofuran, silver nitrate, sodium acetate trihydrate, 1, 4-dioxane, acetic acid, hemoglobin, chloroform-*d*, 99.8 atom % D were purchased from Energy Chemical. silver nanoparticles (about 10 nm) purchased from sigma. All other reagents were analytical grade and used as received. Ultrapure water was prepared using a Milli-Q water purification system. The phosphate buffer solution was prepared by dibasic sodium phosphate with sodium dihydrogen phosphate to the required pH values.

2.2 Apparatus

The NMR spectra were recorded by AVANCEDRX400 NMR spectrometer (Bruker, Germany) operated at 400 MHz. X-ray powder diffraction patterns were taken using a D/max-TTR III X-ray diffractometer (Rigaku, Japan) with a scan speed of 0.1 s per step and a step size of 0.01°. High resolution solid-state NMR spectra were recorded at ambient pressure on a Bruker AVANCE III 400 M spectrometer using a standard CP-TOSS pulse sequence (cross polarization with total suppression of sidebands) probe with 4 mm (outside diameter) zirconia rotors. Cross-polarization with TOSS was used to acquire ¹³C data at 100.37 MHz. The ¹³C ninety-degree pulse widths were 4 μ s. The decoupling frequency corresponded to 72 kHz. The TOSS sample-spinning rate was 5 kHz. Recycle delays was 2 s. The ¹³C chemical shifts are given relative to glycine as 176.03 ppm. The morphology of TPE-TAP-COF were characterized by scanning electron microscopy (SEM) (Quanta, FEI) and a JEM 2100 high resolution transmission electron microscope (HRTEM, JEOL, Japan). The specific surface areas of TPE-TAP-COF were tested by BrunauerJournal Name

Emmett-Teller (BET) method using nitrogenicle or gas adsorption/desorption at 77 K (BET, Micromeritide ASAP 2020, USA). The Fourier transform infrared (FT-IR) spectra were obtained on a FT-IR spectrophotometer (Thermo Nicolet 365). The UV-Vis absorption was characterized by a UV/Vis/NIR spectrophotometer (Shimadzu, Japan).

2.3 Synthesis of TPE-TAP-COF

The synthesis of 4- (4- aldehyde phenyl) ethylene refers to our previous article. Synthesis of TPE-TAP-COF was carried out by the Schiff base reaction between 4- (4-aldehyde phenyl) ethylene (TPE, 50 mg) and tetra-(4-aminophenyl)porphyrin (TAP, 40 mg) in toluene-dioxane (1 mL:1 mL) solvent combination with a catalytic amount of 0.2 mL (6 M) acetic acid has been under static heating at 150 °C for 5 days and then can obtain solid. The precipitates were washed with anhydrous THF and acetone and then were dried for 24 h under high vacuum at 120 °C to provide TPE-TAP-COF as a dark purple powder in ~56 % yield.

2.4 Structural simulation and power X-ray diffraction analysis

The Pawley refinements were performed within the Material Studio Reflux module to infer the crystalline structure and the unit cell parameters. Certainly, the structures were optimized in the Dmol3 module of Materials Studio package, which can help to provide a more rational layer morphology and higher consistency with the experimental PXRD pattern. Furthermore, the simulation of two possible structures AA (eclipsed), AB (staggered) modes were also constructed by using an optimized P1 spaced group.

2.5 Loading of Hb in TPE-TAP-COF

A

C

For the loading studies, 5 mg of the TPE-TAP-COF was firstly sonicated in 4 mL of the phosphate buffer (pH=7.4) for 5 min in order to get a homogeneous dispersion. This buffer solution was treated with different concentrations ($0.1^{-1} \text{ mg} \cdot \text{ml}^{-1}$) and stirred at 4 °C for 24 h. Then the solution was centrifuged and recorded using UV – vis spectrometer, and then the isothermal adsorption curve is obtained. The adsorption dynamic curve shows the adsorption capacity of the COF to Hb of 0.8 mg • ml^1at different time.



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Fig. 3 (A) Experimental PXRD (black curve); theoretical eclipsed (red curve); stacked (blue curve); (B) top view of simulated AA stacking (C) Pawley refinement of PXRD; (D) AB stacking.

2.6 Loading of nanoparticles in TPE-TAP-COF

Au NPs synthesis method [46]: before the experiment, all the instruments were soaked in aqua regia and cleaned with ultrapure water. 100 mL HAuCl₄ • 3H₂O with a mass fraction of 0.01 % was stirred and heated to 130 $^\circ C$, and then 3.6 mL sodium citrate with a mass fraction of 1 % was added , remaining heating. It can be observed the color of solution turned from pale yellow to purple and then to bright red. Stop heating and remain stirred till it was cooled down to room temperature. For the adsorption studies, 5 mg TRE-TAP-COF was added into aqueous solution Container /ABTNP387AD stirred at room temperature for 12 h. Then the solution was centrifuged at 8000 rpm for 1 minute and the UV-vis spectra of the supernatant were recorded. The sample for TEM imaging was without centrifugal treatment. The experiment process of the adsorption of Ag NPs is the same as the experiment process of Au NPs (5 mg COF, 1 mL Ag NPs solution and 3 mL water.).

3. Results and discussion

3.1 Preparation and Characterization of TPE-TAP-COF

The TPE-TAP-COF was synthesized by solvothermal reactions (Fig. 1A, B). Fourier transform Infrared (FTIR) and ¹³C cross polarized (CP) solid-state MAS are commonly applied as proof of the detection strategy for the formation of imine bond (C=N). The structural integrity of the framework was confirmed by solid-state CP-MAS NMR, which displays the resonance signal around 156.7 ppm for the carbon of C=N bond (Fig. 2A). In the FTIR spectrum (Fig. 2B), the absorption band near 1696 cm⁻¹ for the C=N bond stretching modes indicates that the presence of the imine group forming from the tetraphenylethene and porphyrin moiety. As shown in Fig. S1, the thermogravimetric analysis (TGA) results revealed a weight loss of around 36.07 % until the temperature reach to 450 °C, suggesting the TPE-TAP-COF with high thermal stability. By measuring the capacity N₂ adsorption/desorption experiment at 77 K, the permanent porosity of the TPE-TAP-COF was determined, this result shows a type I isotherm, which is the characteristic of the intrinsic microporosity characteristics of the TPE-TAP-COF (Fig. S2). The Brunauer–Emmett–Teller surface area is \sim 218 m² g⁻¹. The sample was activated at 150 °C to remove the solvent molecule from the lattice for sorption analysis. The distribution of the pore diameter based on the theory of non-local density functional shown a single peak porosity at 1.6 nm (Fig. S3).



Fig. 4 (A) SEM and (B) TEM images of TPE-TAP-COF recorded at different intervals of time, respectively; (C) Mechanism of the formation of COF hollow microshuttle.

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Published on 25 January 2019. Downloaded on 1/28/2019 1:56:37 AM

The possible crystal structure of TPE-TAP-COF was obtained by experimental XRD measurement and theoretical structure simulation. The crystalline nature of TPE-TAP-COF was revealed that by powder X-ray diffraction (PXRD) analysis. Considering the construction type (4+4) is similar to SB-PORPy-COF [47], TPE-TAP-COF was constructed from TPE and TAP by using Materials Studio Software package (see table S2). The strong PXRD peaks at the position $2\theta = 5.4$, and 7.9° , which can be assigned to the (100) and (010) facets, respectively. The hump centered at ${\sim}22^\circ$ may be caused by zigzag π - π stacking of 2D layers. The appearance of (100) facet in the XRD pattern is a convincing evidence to validate the layer-bylayer structures arranged by the manner of typical 2D COFs. Therefore, TPE-TAP-COF is a typical 2D COFs with layer-by layer arrangement. The theoretical 2D eclipsed structure (AA) and the experimental peak position of PXRD, whereas the AB stacking model (blue, Fig. 3A) is totally different. A simulated PXRD pattern shows good agreement with the one of the XRD measurement result. The Pawley refinement yielded a PXRD that is well consistent with the experimentally surveyed pattern, as the evidence by their negligible differences and very staggered structure (AB) as shown in the Fig. 3D. The theoretical model of PXRD for TPE-TAP-COF AA stacking model (red, Fig. 3B) is almost exactly the same as the of R_{wp} =9.45 % and R_p=6.41 % (Fig. 3C, refined and difference spectra). A 3D triclinic unit cell (P1 space group) with the parameters of a =31.9982 Å, b=31.5291 Å, c = 4.28402 Å, α = 90.4039°, γ = 89.9188° and β = 92.4525° was derived from the theoretical optimization of TPE-TAP-COF. Based on these results, the diameter of TPE-TAP-COF is about 16.645 Å, which is consistent with the one of the BET result. Interestingly, scanning electron microscopy (SEM) images showed that TPE-TAP-COF remarkably assembles into well-defined microcapsule structures (Fig. 2C, Fig. S4) with 5 µm in length. As shown in Fig. 2C and Fig. 4A, some microcapsule with partly broken structures have been circled in red in the SEM image. The SEM images with larger magnification of intact and broken microcapsule were shown in Fig. S4 A and B, respectively. These results revealed the microcapsule was hollow structure. The statistic about the size distribution could be presented in Fig. S5 and the length of the TPE-TAP-COF most is 5 $\mu m.$ Transmission electron microscopy (TEM) images further confirmed that these microcapsule COF is hollow (Fig. 2D).

3.2 The behavior of self-assembly

To study the mechanism of the formation of shuttle-shaped hollow capsule, we have studied the synthesis and morphological changes of TPE-TAP-COF at different time intervals (1-, 2-, 3-, 4- and 5 days). TPE-TAP-COF synthesis was quenched by removing the reaction tubes from the oven at those specific time intervals. Furthermore, we have analyzed the TPE-TAP-COF samples isolated after 1-, 2-, 3-, 4- and 5-days reaction time using SEM, TEM, FTIR and PXRD measurements. Fig. 4A and B display SEM and TEM images of the self-assembly process at different time intervals of the TPE-TAP-COF. SEM and TEM images of the one-day sample show dense spherical agglomerates of small individual crystallites (nanosphere, NS). Starting from this spherical agglomerates with hundreds nanometers in diameter, the TPE-TAP-COF self-assemble into nanorod structure with hundreds nanometers in diameter and micrometer in length after 2 days (nanorod, NR).

Thereafter, these nanorods gradually fuse to form microcapsule morphology after 3 days (dense microcapsule, DMS). The shuttle-

shaped structure which assembled from nanorods can be observed at the third day. The anisotropy structure Pevealed 3that the final shuttle-shaped hollow capsule was original from the following growth process, rather than packaging of the hollow capsule during the drying process (Fig S8). However, the surface of the microcapsule formed at 3 days is rough. As the reaction progress, the SEM images recorded that the surface of microcapsule gradually became smooth and the TEM images revealed that inner of microcapsule is solid (hollow microcapsule, HMS). Finally, TEM images recorded for TPE-TAP-COF after a reaction time of 4 days showed the formation of hollow cavities inside the microshuttle. According to the literature reference, our COF self-assembly should belong to the template-free methods in the formation of many hollow structures, at present, there are few reports on the self-assembly of COFs. We speculate that the formation mechanism of hollow capsules structures is similar to the Ostwald ripening process in outward diffusion [48]. As the reaction proceeds, the internal microcrystals have high surface energy, and the surface energy can be reduced to the minimum by dissolving or migrating the crystals from the inner core. This speculation was supported by the shell thickness of 5 days is thinner than that of 4 days (shown as Fig. 4A, S9). Moreover, Schiff base is a reversible dynamic bond, which is benefit for recrystallize/selfassemble. As mentioned earlier, this happens as a result of inside out Ostwald ripening. Identical FTIR and PXRD patterns of the TPE-TAP-COF at different time intervals (Fig. S6, S7) indicate that the C=N bond and COF crystallite formation is complete even at shorter reaction time and the following self-assembly and Ostwald ripening processes

of these crystallites did not disturb the internal ordering in the COF. Based on these observations, we postulate that the formation of hollow shuttle of TPE-TAP-COF underwent several processes including fusing nanosphere into nanorods, nanorods selfassembling towards microshuttle and inside-out Ostwald ripping (Fig. 4C).

3.3 Loading of Hb



Fig. 5 (A) UV absorption spectra of TPE-TAP-COF before and after adsorption of Hb; (B) Images of TPE-TAP-COF before and after adsorption of Hb daily light; (C) Adsorption isotherms of Hb on TPE-TAP-COF; (D) Adsorption dynamic curves of TPE-TAP-COF.

The chemical stability of the hollow microcapsule TPE-TAP-COF in water and phosphate buffer (pH=7.4) was firstly investigated by submerging the 40 mg material in 10 mL solution for 3 days. The unchanged position and intensity of peaks in the PXRD pattern and non-alteration of FTIR peak after the solution treatment show the structural stability of this COF in phosphate buffer and water (Fig. S10, 11).

The adsorption of proteins from aqueous solutions is of practical and fundamental significance. The TPE-TAP-COF was applied to the adsorption of hemoglobin (Hb) by monitoring the UV-vis absorption spectrum. As shown in Fig. 5A, TPE-TAP-COF has an obvious adsorption of Hb, and the UV absorption spectrum shows that the absorption at 410 nm is significantly decreased after the 0.8 mg·mL⁻¹ Hb and 5 mg COF are mixed in the phosphate buffer after stirring 12 h. The solution of Hb mixed with TPE-TAP-COF after the centrifugation was turn to colorless (Fig. 5B). The adsorption dynamic curves revealed that the adsorption was finished within 8 h (Fig. 5D). The amount of Hb absorbed in TPE-TAP-COF was calculated to be 550.82 mg \cdot g⁻¹ from the adsorption isotherms (Fig. 5C). To the best of our knowledge, this value is the highest adsorption capacity for Hb among known COFs.

Moreover, the adsorption behavior of different shapes of TPE-TAP-COF were investigated. As shown in the Fig. 5C, D and Table S1, these results indicated that the morphology of TPE-TAP-COF had much affection on the maximum adsorption capacity and adsorption equilibrium time. The maximum adsorption capacity was increased from 52.25 to 166.12, 488.16, 550.82 mg \cdot g⁻¹ when the morphology changes from nanosphere, nanorod, dense microcapsule to hollow microcapsule. Simultaneously, the adsorption equilibrium time was decreased from 16 to 14, 10 and 8 h, respectively. These results indicated that the high adsorption capacity and fast adsorption equilibrium were benefited from the unique hollow microcapsule structure of TPE-TAP-COF.

In order to investigate the interaction of Hb with TPE-TAP-COF, we have recorded the PXRD, FTIR and BET of the Hb-loaded COF samples. It was found that the PXRD peak remained constant even the maximum adsorption capacity was reached, indicating that the adsorption of Hb did not destroy the crystal structure of TPE-TAP-COF (Fig. S13). Some peaks ascribed to Hb were observed in the FTIR spectrum after the loading in COF, indicating the presence of Hb in COF. The absorption peak intensity of C=N decreased significantly, suggesting hydrogen bonding interaction between Hb and COF (Fig. S14). N₂ adsorption measurement of Hb-loaded TPE-TAP-COF sample shows a decrease in the BET surface area value (from 218 to 43 m²g⁻¹) (Fig. S15).

We chose two nanoparticles for further adsorption studies: gold nanoparticles and silver nanoparticles for the adsorption studies, As shown in Fig. S16, TPE-TAP-COF has an obvious adsorption of Au NPs, and the UV absorption spectrum shows that the absorption at 520 nm is significantly decreased after stirring Au NPs with TPE-TAP-COF for 12 h. The color of Au NPs solution mixed with TPE-TAP-COF changed from purple to colorless after the centrifugation (Fig. S18). TEM image shows that gold nanoparticles are almost adsorbed on the surface of COF (Fig. S20). The reduction of UV absorption at 400 nm reveals that COF partially adsorbs silver nanoparticles (Fig. S17). After centrifugation, the color of the Ag NPs solution mixed with TPE-TAP-COF turned from yellow to light yellow (Fig. S19). TEM image can further prove that silver nanoparticles are adsorbed on the surface of COF (Fig. S21). These results indicated that gold han oparticles and silver nanoparticles can be adsorbed onto the surface of TPE-TAP-COF, and the size of these particles is much larger than the pore size of the COF. Therefore, they are very difficult to enter COF through the pore. Therefore, the previous adsorption mechanism is problematic. Moreover, Zeta potentials of Au NPs, Ag NPs, Hb and the TPE-TAP-COF were measured. As shown in Fig. S23, the zeta potential of the TPE-TAP-COF was positively charged, while the Hb, Au NPs and Ag NPs were negatively charged, indicating that the absorption process of TPE-TAP-COF with Hb, Au NPs and Ag NPs could occur through electrostatic attraction. In addition, as shown in Fig. S22, the TEM image of TPE-TAP-COF after adsorption Hb clearly shows that the COF surface is covered with film-like complex. Therefore, the previous diffusion transfer into the COF mechanism is wrong, and surface adsorption by electrostatic attraction should be apprved.

4. Conclusions

In summary, for the first time, a microshuttle-shaped capsule structure COF was developed and underwent initial self-assembly and following similar inside-out Ostwald ripening processes. The hollow microcapsule TPE-TAP-COF was applied to the adsorption of the Hb, which displayed the highest adsorption capacity among all COFs. This work will inspire more insight into the development of porous materials with defined morphology for biomolecules adsorption.

5. Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC, 21765024) and program for changjiang scholars and innovative research team in university (IRT __17R94)

6. Notes and references

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