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Ultrahigh volatile iodine uptake by hollow microspheres formed from a heteropore covalent organic framework

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We herein report the construction of a new heteropore COF which consists of two different kinds of micropores with unprecedented shapes. It exists as hollow microspheres and exhibits an extremely high volatile iodine uptake (up to 481 wt %) by encapsulating iodine in the inner cavities and porous shells of the microspheres.

Global environmental problems resulted from combustion of fossil fuels have become more and more serious over the past decade. Compared with fossil fuels, nuclear power holds ultrahigh energy density as well as emits fewer greenhouse gases, and thus is gradually growing into one of the pillars of energy sources around the world. However, disposal of the inevitable nuclear waste generated from nuclear fission of uranium still faces great challenges. In this regard, radionuclide iodine-129 is one of the most dangerous waste products of nuclear power plants because of its long radioactive half-life $(1.57 \times 10^7 \text{ years})$, high volatility, and adverse effects on human metabolic processes and environment.¹ In this context, great efforts have long been focused on effective capture and storage of radioactive iodine for safe utilization of nuclear energy. The early adsorbents developed for iodine capture are inorganic adsorbents, including silver-based zeolites and aerogels.² However, those inorganic adsorbents usually exhibited low uptake capacities. In recent years, inorganicorganic hybrid porous materials such as metal-organic frameworks (MOFs) have also been exploited as iodine capturing materials and moderate uptake capacities have been achieved.³ More recently, porous organic polymers (POPs) have been found to exhibit great potential for iodine capture and storage, and among them a maximum iodine uptake up to

336 wt% was reported.⁴ Given their features of facile syntheses, low densities, structural diversities, and chemical/thermal stability, POPs are very promising candidates for practical applications in capturing radioactive iodine from exhaust fumes of nuclear power plants. To reach this goal, improving performance of POPs on iodine capture is highly desired.

Among POPs, covalent organic frameworks (COFs) distinguish themselves from the others by their highly ordered internal structures which endow them with crystallinities.⁵ Compared to amorphous POPs, the pore shapes and sizes of COFs can be precisely controlled through elaborate design of building blocks, which makes them highly efficient for selective storage,⁶ separation,⁷ sensing,⁸ or transportation of guest molecules.⁹ However, to our surprise, while COFs have been extensively used for gas storage, so far the capacity of COFs on iodine capture have not been examined yet. Very recently we¹⁰ and others¹¹ have developed a new class of COFs, that is, heteropore COFs, which bear different kinds of pores in one framework and thus endow them with hierarchical porosities. Since hierarchical porous materials have been reported to be favorable for transportation of guest molecules,¹² heteropore COFs, which combine the features of highly ordered internal structures and hierarchical porosities, might be conducive to iodine capture. We herein report a hollow spherical heteropore COF (SIOC-COF-7) which greatly facilitates the adsorption of volatile iodine. An iodine uptake of 481 wt % was obtained. To the best of our knowledge, it is the first COF-base iodine adsorbent and the highest iodine uptake value reported to date.

SIOC-COF-7 was synthesized as an orange powder by condensation of 4,4"-bis(bis(4-formylphenyl)amino)-[1,1':4',1"-terphenyl]-2',5'-dicarbaldehyde (BFATD) and 1,4diaminobenzene in а mixed solvent of dioxane/mesitylene/acetic acid (aq., 6 M) (5:5:1 by volume) in a sealed glass ampoule at 120 °C for 72 h (Scheme 1). The asprepared powder, which is insoluble in common organic solvents and water, exhibits a high thermal stability. As revealed by thermogravimetric analysis (TGA), less than 10%

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⁺ Electronic Supplementary Information (ESI) available: Procedures for the preparation of the monomer and COF, FTIR spectra, TGA profiles, additional TEM images, photographs for iodine capture in solution, summary of iodine uptakes of porous materials, and BET plot. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis and structure of the heteropore COF SIOC-COF-7

weight loss was observed for the COF when the temperature increased from 25 to 500 °C (Fig. S1, ESI). TEM investigation indicated that the COF existed as hollow microspheres with diameters around one to two micrometers and shell thicknesses being several hundred nanometers. Their hollow nature was strongly evidenced by the clear contrast between the shells and the inner parts of the spheres (Fig. 4a, vide infra).

The as-prepared COF was firstly characterized by FTIR spectroscopy. While nearly complete disappearance of the peaks corresponding to C=O and -NH₂ indicates a high degree of polymerization by consuming almost all the aldehydes and amine groups of the monomers, a band assignable to the vibration of C=N was observed at 1619.8 cm⁻¹, giving direct evidence for the formation of imine linkages (Fig. S2, ESI). The crystal structure of SIOC-COF-7 was elucidated by comparing the experimental powder X-ray diffraction (PXRD) with the simulated PXRD patterns which were generated by Accelrys Materials Studio 7.0 software package. As illustrated in the experimental PXRD profile (Fig. 1a), diffraction peaks at 2θ = 3.24°, 5.94°, 10.03° and 23.16°, are observed, which are assignable to the (100), (2-10), (1-20) and (001) facets, respectively. In order to determine the packing manner of the 2D layers, two stacking models, eclipsed AA stacking (Fig. 1c) and staggered AB stacking (Fig. 1d), were constructed and their theoretical PXRD patterns were simulated. It was found that the simulated PXRD pattern of the AA stacking model coincided with experimental PXRD data, strongly suggesting that the as-prepared powder holds the dual-pore COF structure as illustrated in Scheme 1 and the 2D layers adopt eclipsed packing. The disappearance of (1-10) and (3-10) peaks in the experimental PXRD pattern might be resulted from a preferential orientation of the microcrystals. Pawley refinement yielded unit cell parameters of a = 32.22 Å, b = 18.41 Å, c = 3.91 Å, α = β = 90°, and γ = 122.78°, with factors of Rwp = 3.65% and Rp = 2.84%. As revealed by the difference



Fig. 1 Left: (a) Experimental (black) and refined (red) PXRD patterns of SIOC-COF-7. (b) Difference plot between the experimental and refined PXRD patterns. And simulated PXRD patterns for (c) eclipsed AA model and (d) staggered AB model. Right: Illustrations of AA and AB stackings.



Fig. 2 (a) N_2 adsorption-desorption isotherm curve of $\mbox{SIOC-COF-7}$ at 77 K and (b) its pore size distribution profile.

plot (Fig. 1b), the experimental PXRD pattern is well reproduced by the refined PXRD pattern.

To further confirm the as-prepared crystalline polymer possessing the dual-pore COF structure as elucidated by PXRD analysis above, N₂ adsorption-desorption measurements were carried out. The N₂ adsorption curve of SIOC-COF-7 matched the classical type I sorption model characterized by a steep nitrogen uptake in the low-pressure range ($P/P_0 = 0-0.01$), which is indicative of permanent microporosity (Fig. 2).¹³ Its Brunauer-Emmett-Teller (BET) surface area was estimated from the isotherm data in the range of $P/P_0 = 0.01-0.3$, which afforded a value of 618 m^2/g (Fig. S3, ESI). The total pore volume was calculated to be 0.41 cm³/g at P/P₀ = 0.99. Its pore size distribution was reflected by using non-local density functional theory (NLDFT). It reveals that SIOC-COF-7 exhibits two main pore size distributions at 5.0 and 11.8 Å, respectively (Fig. 2b), which are almost same as the theoretical values of 5.0 and 11.9 Å estimated by PM3 calculations. This result corroborates again that SIOC-COF-7 possesses two different kinds of micropores, with the one centered around 11.8 Å being attributed to the deformed hexagonal pores and the smaller one assignable to the parallelogram pores (Fig. S4, ESI).

After the structure of **SIOC-COF-7** has been established, its iodine capture capacity was then examined. The experiment was carried out by exposing a certain amount of **SIOC-COF-7** to excess iodine vapor at 75 °C and ambient pressure, which is close to the typical nuclear fuel reprocessing conditions. Upon standing, the COF darkened gradually, indicating that iodine diffused into the COF (Fig. 3a, inset). The performance for iodine capture was investigated by gravimetric method (see

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Fig. 3 (a) Gravimetric uptake of iodine as a function of time at 75 °C. (b) Cartoon illustration for iodine capture in the spherical COF. Note: Some of iodine molecules encapsulated in the shell were removed for clarity.

ESI for the procedure). On the basis of the data obtained, an iodine loading curve of SIOC-COF-7 was plotted as a function of time. As can be seen in Figure 3a, within the initial 15 hours the amount of iodine uptake increases quickly and an uptake of 391 wt % is observed after 15 hours. Along with the extending of time, the rate of adsorption slows down and an iodine uptake of 481 wt % (4.81 g iodine per 1.00 g SIOC-COF-7) is obtained after 48 hours. No obvious change in the iodine loading amount is observed between 48 and 60 (486 wt %) hours, implying that a saturated adsorption is achieved after 48 hours. This value of iodine uptake is considerably higher than those of all the previously reported solid porous adsorbents including metal-based porous zeolitic materials, MOFs and amorphous POPs (see detailed comparisons in Table S1), and the capturing rate of SIOC-COF-7 is comparable to them, suggesting that SIOC-COF-7 is an excellent iodine adsorbent. TGA analysis was also performed for the iodineloaded COF under a nitrogen atmosphere. The TGA curve revealed a significant weight loss of the iodine-loaded COF in the range of 90 to 350 °C. Since the pristine COF is stable under this condition, the mass loss should be mainly attributed to the release of iodine from the iodine-loaded COF upon being heated. The mass loss of iodine was thus estimated to be 493 wt % relative to the mass of SIOC-COF-7 (Fig. S5, ESI). The iodine uptake capacity derived from TGA analysis is fully in consistence with that obtained by gravimetric method above.

This record value promoted us to investigate why **SIOC-COF-7** has such high iodine uptake capacity. Since **SIOC-COF-7** has a total pore volume of 0.41 cm³/g, a theoretical maximum iodine uptake of 202 wt % would be calculated from the product of density of solid iodine and the total volume of the COF by assuming all the pores were filled with iodine molecules. This value is still far lower than the experimental result 481 wt %, not to mention in the case of the pores just being partially filled. Therefore, there should be extra space accounting for the extraordinarily high iodine uptake of **SIOC-COF-7**. Since **SIOC-COF-7** exists as hollow microspheres, we envisioned that the inner cavities of the COF microspheres as well as their porous spherical shells should be responsible for the iodine



Fig. 4 TEM images of **SIOC-COF-7** (a) before and (b) after the COF being exposed to iodine vapor and EDX profiles of the COF (c) before and (d) after being exposed to iodine vapour, and (e) EDX element mapping image of an iodine-loaded microsphere, and (f) TEM image of a sample fabricated by heating the iodine-loaded COF at 160 °C for 6 hours. Note: the copper peaks in EDX profiles were generated from the copper support grids

1 µm

capture by providing a large amount of storage space for iodine molecules. It is reasonable because the eclipsed stacking of the layers of SIOC-COF-7 and its dual-pore feature leads to the formation of two kinds of channels (dimeters ca. 5 and 12 Å, respectively) across the shells of the COF spheres, which not only can accommodate iodine molecules but also facilitate diffusion of iodine molecules into the inner cavities of the microspheres due to the hierarchical porosity which can improve mass transport and decrease diffusion barriers (Fig. 3b). This assumption was proved by TEM investigations. As can be seen in Figure 4a and 4b (also Fig. S6 in the ESI for magnified TEM images), the hollow spheres exhibit clear contrast between the shells and inner parts. However, the contrast completely disappears after exposing the COF to iodine vapor for 48 hours, which suggests that the inner cavities of the hollow microspheres are filled with iodine.

The spherical COF before and after being exposed to iodine vapor was also investigated by energy-dispersive X-ray (EDX) spectroscopy (Fig. 4c and 4d). For the pristine microspheres, strong peaks corresponding to carbon and nitrogen appear (a weak peak corresponding to oxygen was also observed and it could be attributed to the residual C=O groups at the peripheral of the COF). In the case of iodine-loaded microspheres, in addition to the peaks of carbon and nitrogen, strong peaks corresponding to iodine are also observed. The

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iodine encapsulated in the microspheres was also visually illustrated by EDX element mapping, from which uniform dispersion of iodine in the whole microsphere could be observed (Fig. 4e). The iodine encapsulated in the COF microspheres can be released by heating the iodine-loaded COF under vacuum. It is evidenced by the TEM image of a sample fabricated by heating the iodine-loaded COF at 160 °C for 6 hours at 0.01 MPa, for which clear contrast between the shells and the inner parts was observed again (Fig. 4f). The regenerated hollow COF spheres were further reused to capture iodine by exposing it to iodine vapor again. It was found that the iodine uptake still maintained at 96% of its initial capacity after the COF was used five times (Fig. S7, ESI), suggesting excellent recyclability and stability of **SIOC-COF-7**.

Iodine capture by SIOC-COF-7 in solution phase was also examined. When SIOC-COF-7 was immersed in a hexane solution of iodine (10.0 mmol L⁻¹) in a small sealed vial at ambient temperature, the purple solution was found to fade slowly and became colorless 9 hours later, accompanied with the color of SIOC-COF-7 getting darker and darker (Fig. S8, ESI). This result suggested that the iodine was encapsulated in the COF. Its iodine capture capability in hexane was estimated to be 127 wt % (Fig. S8, ESI). The lower iodine uptake in solution than that of solid state could be attributed to the coencapsulation of solvent molecules. For the inner cavities of the COF microspheres, in particular they should be filled with iodine solution, instead of pure iodine, which significantly decreases its iodine capture capacity. The captured iodine could be readily released from the COF by immersing the iodine-loaded material in ethanol at room temperature. The color of the ethanol solution deepened from colorless to dark brown as time went on, which clearly indicates that the iodine guests were dissociating from the spherical COF (Fig. S10, ESI).

In summary, a novel heteropore 2D COF has been synthesized. It exists as hollow microspheres and exhibits an extremely high volatile iodine capture capacity. An iodine uptake of 481 wt % has been obtained, which is the highest value reported to date. While the abundant aromatic rings, high nitrogen content and well-ordered network of the hetero COF should be favorable for iodine enrichment, the inner cavities of the hollow microspheres and the highly ordered channels in the shells also make significant contributions to the extraordinarily high iodine capture capacity. This research not only is an auspicious beginning to utilize COF for efficient iodine capture and storage, which has exploited a new application of COFs, but also suggests that COF-based hollow micro/nanospheres^{10d,14} have high potential for application in substances capture and storage. Moreover, since micro/nanospheres constitute a large number nanomaterials, the finding in this work may provide guidance to the design of functional materials for effective capture of harmful volatile substances.

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