Construction of hierarchically porous monoliths from covalent organic frameworks (COFs) and their application for bisphenol A removal

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GRAPHICAL ABSTRACT

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ABSTRACT

Subject to synthetic conditions, covalent organic frameworks (COFs) are usually in powder form. Herein, taking an azine-linked COF as an example, detailed characterizations indicated that accessible aldehyde groups and hydrazine groups (−C=N−NH\textsubscript{2}, 88 μmol g\textsuperscript{−1}) concurrently existed on its surface. Intrigued by such feature, we have developed an approach based on ring-opening polymerization to shape COF powder into monoliths. The crystallinity and micropore of COF in monoliths were well remained, meanwhile, the ring-opening polymerization remarkably generated macropores ranging from 0.43 to 3.51 μm, indicating a hierarchically porous structure. The BET surface area of resultant monoliths with different COF mass fractions of 16%, 28% and 43% ranged from 105 to 281 m\textsuperscript{2} g\textsuperscript{−1}. Due to the π−π interaction and hydrogen bond interaction, COF-based monoliths exhibited strong retention and rapid adsorption for bisphenol A (BPA) in aqueous medium. When 29 mL BPA solution (22.8 mg L\textsuperscript{−1}) passed through COF-based monolith (28%), the adsorption capacity was up to 61.3 mg g\textsuperscript{−1}. Furthermore, the COF-based monolith demonstrated excellent cycle use for catalyzing Suzuki-Miyaura coupling reaction after being coordinated with palladium acetate.

1. Introduction

Hierarchically porous monoliths generally exhibited multilevel pores with at least two kinds of sizes (micropore, < 2 nm; mesopore, 2–50 nm; macropore, > 50 nm) in a single architecture \cite{1}. The combination of more than two-scale pore sizes facilitates the high surface area and enhanced mass diffusion for monoliths. Up to now, various hierarchically porous monoliths constructed from silica gel \cite{1,2}, metal
oxides [3], organic polymers [4–6], zeolite [7,8], carbon [9–14], and metal-organic frameworks (MOFs) [15–17] have been widely applied in gas adsorption, energy storage, separation, catalysis, etc. In particular, the starting materials like zeolite and MOFs are commonly powders in form and show satisfactory nanoporous structure. Freeze-drying is a very popular processing strategy to shape these powders into monoliths with desired geometries [8,15,18,19]. The resulting monoliths not only maintained the intrinsic porosity of starting materials, but also generated macropores during freeze-drying process. Shaping these starting materials into monoliths made them very promising for industrial applications, avoiding the packing steps, such as for particles.

Covalent organic frameworks (COFs) are a new class of porous organic polymers with an ordered structure and high crystallinity, in which the organic building blocks are linked by strong covalent bonds [20–27]. COFs that generally offer high surface area have attracted much attention in the field of gas adsorption. However, subject to synthetic conditions, COFs are usually in powder form, and show poor processability due to their insolubility in common solvents (Fig. S1). Thus, shaping COF powder into other forms is something of a challenge. For instance, to fabricate COFs into the membrane form, a layer of aldehyde groups was firstly modified on surface of porous α-Al₂O₃ substrate, and then a COF membrane with thickness of ∼4 μm was in situ prepared on such substrate and evaluated by gas permeation experiments [28]. To obtain ultrathin and homogenous COF membranes, a ∼100-nm-thin membrane was fabricated via the assembly of exfoliated COF nanosheets on porous ceramic support [29]. Besides, to achieve self-standing COF membrane, the exfoliated COF nanosheets could be also blended with polymers, such as poly(ether imide) and polybenzimidazole, to form mixed matrix membranes (MMMs) via slow vaporization of solvents [30–32]. The crystallinity and nanopores of COFs were well remained in these MMMs that demonstrated great potential for application in gas separation. Recently, Smith et al. reported homogeneous polymerization conditions for the formation of colloidal suspensions of COF nanoparticles rather than microcrystalline powders [33]. Then the colloidal COF was used to fabricate freestanding COF film by solution casting, demonstrating a novel strategy to process COFs into desired geometries for device applications.

It should be noted that, to meet the requirements for gas separation, there are not any macropores in such COF membranes that would show bad mass transfer process if being used as adsorbents or catalyst supports in liquid medium [34–36]. To the best of our knowledge, there is no report on shaping of COF powder into hierarchically porous monoliths. Among the building blocks in COFs, the typical reversible covalent reaction of amine groups and aldehyde groups has been widely exploited to synthesize COFs that showed good chemical stability in organic solvents, water, and even aqueous HCl and NaOH solutions [37,38]. Herein, taking an azine-linked COF synthesized by 1,3,5-triformylbenzene and hydrazine hydrate as an example, it was found that accessible aldehyde groups and hydrazine groups (–C≡N–NH₂) coexisted on its surface. Inspired by such feature, we adopted ring-opening polymerization of amine groups with epoxy groups, to construct COF-based monolith by introducing azine-linked COF powder into fresh prepolymerization solution (FPS) as shown in Scheme 1. The FPS was comprised of poly(ethyleneimine) (PEI, Mₐ = 1200), octacyclidimethylsilyl POSS (POSS-epoxy, Fig. S2), poly(ethylene glycol) (PEG, Mₐ = 10 000), 1-propanol and 1,4-butanediol. The crystallinity of COF in monoliths was confirmed by powder X-ray diffraction (PXRD). The morphology and porosity for COF-based monoliths were characterized by scanning electron microscopy (SEM), adsorption-desorption measurements and mercury intrusion porosimetry (MIP). Finally, the COF-based monoliths were used as adsorbent for the removal of bisphenol A in aqueous medium, as well as the catalyst support for coordinating palladium acetate to catalyze the Suzuki-Miyaura coupling reaction.

2. Experimental section

2.1. Chemicals and materials

Hydrazine hydrate (98%) and 4-nitrobenzophenone were purchased from J&K Scientific Ltd. (Beijing, China). POSS-epoxy (98%), PEI (50 wt% in H₂O), 1,3,5-triformylbenzene, PEG 10 000, bisphenol A (BPA, 99%), 1,4-diaminobenzene (99%), (3-Aminopropyl)triethoxysilane (APTES, 99%), palladium acetate (98%), phenylboronic acid (95%), p-nitrobromobenzene (99%), human IgG, sodium periodate (NaIO₄), formic acid, acetic acid and 2,5-dihydroxybenzoic acid (DHB, 98%) were obtained from Sigma-Aldrich (St Louis, Mo, USA). Other reagents including potassium carbonate (K₂CO₃), 1-propanol, 1,4-butanediol, xylene, 1,4-dioxane, 4-nitrobenzaldehyde, etc. were gotten from Tianjin Kemiou Chemical Reagent Co. Ltd. (Tianjin, China). CA membrane filter (0.2 μm) was purchased from Aladdin (Shanghai, China). Azine-linked COF and COF-LZU1 were synthesized according to the reported methods (Supporting information) [34,39].

2.2. Preparation of COF-based monoliths

Firstly, the FPS was prepared by mixing POSS-epoxy (50 mg), PEI solution (54 mg), PEG10,000 (25 mg), 1-propanol (280 μL) and 1,4-butanediol (40 μL) in a 2 mL centrifuge tube. Then, the COF powder (0%, 5%, 9% and 16%, mass fraction of COF with respect to total mass of COF and monomers, the same to the below 28% and 43%) was added to form a suspension of COF, and then reacted in water bath at 50 °C for 12 h. The resulting monoliths were washed with ethanol, water and ethanol in sequence to remove residuals, and then dried at 90 °C under vacuum for 24 h. The monoliths were denoted as M0, M5, M9 and M16, respectively.

To prepare the monoliths with relatively high COF content, the COF powder (28% or 43%) was immersed into anhydrous toluene in centrifuge tube. After shaking with 1000 rpm at 25 °C for 1 h, the toluene-saturated COF powder was collected by centrifugation at 23,000g, to which the FPS was added subsequently. The suspension reacted in water bath at 50 °C for 12 h. The resulting monoliths were washed with ethanol, water and ethanol in sequence, to remove residuals, and then dried at 90 °C under vacuum for 24 h. These two monoliths were denoted as M28 and M43, respectively.
2.3. Preparation of monolith (M0-16) inside capillary

Prior to use, the inner wall of fused-silica capillary (150 μm i.d.) was modified with a layer of amino groups for anchoring monolith by APTES (50 v% in methanol) at 50 °C. The mixture of FPS and COF was introduced into the pre-treated capillary with a syringe. After sealing both ends with rubbers, the capillary was immersed in a water bath at 50 °C for 12 h, and then flushed with ethanol and water to remove residuals.

2.4. Instruments and measurements

FT-IR characterization was carried out on Thermo Nicolet 380 spectrometer using KBr pellets (Nicolet, Wisconsin, USA). The images of pore structure and energy-dispersive X-ray (EDX) mapping of monoliths were obtained on SEM (Gemini SEM 300, Zeiss, Germany). Transmission electron microscopy (TEM) images were obtained by JEM-2000 EX (JEOL, Tokyo, Japan). PXRD data were collected on an X’Pert Pro X-ray diffractometer with Cu Kα radiation (PANalytical B.V., Holland). X-ray photoelectron spectroscopy (XPS) data were acquired using an ESCALAB 250Xi XPS spectrometer with an Al Kα X-ray source (Thermo Scientific, USA). Compressive modulus was measured on an Instron 4505 machine. Thermogravimetric (TG) analysis was carried out on a simultaneous thermal analyzer (STA449F3, Netzsch, Germany). The macropore size distribution was determined by MIP (Poremaster 60, Quantachrome, USA). Nitrogen adsorption-desorption measurements were carried out on an Autosorb iQ2 (Quantachrome, USA). The samples were outgassed under vacuum for 7 h at 120 °C before measurements. The surface area was calculated via the Brunauer-Emmett-Teller (BET) method. The pore size distribution was determined from adsorption isotherm by the NLDFT model. The total pore volume was determined at P/Pθ = 0.99. UV–vis spectra were obtained on a V550 spectrophotometer with the wavelength from 200 to 600 nm (JASCO, Japan). High-performance liquid chromatography (HPLC) for monitoring reaction was performed on Hitachi Chromaster (Japan).

2.5. Application of monoliths for adsorption of BPA

2.5.1. Removal efficiency and adsorption kinetics

To better study the adsorption performance, the monolith (14 mg) was ground into amorphous particles and dispersed in water (7 mL) to form a suspension under stirring. Then the stock aqueous solution of BPA (7 mL, 45.6 mg L⁻¹) was added. The final mixture was continually stirred, and 1 mL aliquot of the suspension was taken at given intervals via syringe and filtered immediately by a CA membrane filter (0.2 μm). The residual concentration of BPA was determined by UV–vis spectroscopy (λ = 276 nm).

The efficiency of pollutant removal (%) is determined by the following equation:

\[
\text{Removal efficiency} = \frac{(C_0 - C_1)}{C_0} \times 100
\]  

(1)

where \(C_0\) (mmol L⁻¹) and \(C_1\) (mmol L⁻¹) are the initial and residual concentration of BPA in the stock solution and filtrate, respectively.

The amount of pollutant adsorbed onto the materials is determined by the following equation:

\[
Q_e = \frac{(C_0 - C_1)VM_0}{m}
\]  

(2)

where \(Q_e\) (mg g⁻¹) is amount of pollutant adsorbed per g of material at time of \(t\) (min); \(V\) (L) is the total volume of solution; \(m\) (g) is the mass of material; \(M_0\) (g mol⁻¹) is the molar mass of BPA.

Pseudo-second-order adsorption kinetics is described by using the following equations:

\[
\frac{t}{Q_t} = \frac{1}{Q_e} + \frac{1}{KQ_e^2}t
\]  

(3)

where \(Q_t\) (mg g⁻¹) and \(Q_e\) (mg g⁻¹) are the adsorbate uptakes at time \(t\) (min) and at equilibrium, respectively, and \(K\) (g mg⁻¹ min⁻¹) is second-order rate constant.

2.5.2. Flow adsorption for BPA

The M0 or M28 (1 mg) was packed into a syringe (inner diameter, 5 mm) that equipped with sieve plates. One milliliter BPA solution (22.8 mg L⁻¹) each time flowed through the packed material at a flow rate of about 3 mL min⁻¹. The filtrate was collected, in which the residual BPA content was determined by UV–vis spectra. The removal efficiency was calculated according to the Eq. (1). When the materials showed very low removal efficiency, methanol (2 × 1 mL) and water (2 × 1 mL) flowed through, successively, to regenerate.

2.6. Preparation of Pd@M28 for the Suzuki-Miyaura coupling reaction

The Pd@M28 was prepared according to the reported method by Wang et al. [34]. Briefly, the M28 (∼ 200 mg) was immersed into the palladium acetate solution (3 mL, 0.02 mol L⁻¹ in dichloromethane), and then gently oscillated. The reaction solution was replaced with fresh palladium acetate solution every 6 h for four times. Finally, the Pd@M28 was washed with dichloromethane for several times, and dried at 80 °C under vacuum for 12 h.

Prior to catalyzing the Suzuki-Miyaura coupling reaction, Pd@M28 was cut into millimeter-scale amorphous particles. Then Pd@M28 (20 mg) was added into the mixture of phenylboronic acid (92 mg, 0.75 mmol), p-nitro bromobenzene (101 mg, 0.50 mmol) and K₂CO₃ (138 mg, 1.00 mmol) in xylene (4 mL). The reaction was carried out under stirring at 150 °C for 3 h. After cooling to temperature, the Pd@M28 was separated and washed with acetonitrile (ACN) by centrifugation. All the supernatants were merged and diluted with acetonitrile to 50 mL. The concentration of 4-nitrophenylbenzyl in diluted solution was determined by reversed-phase liquid chromatography with three runs (C18-packed column, ACN/H₂O = 50/50, v/v, detection wavelength, 214 nm). To investigate the recyclability, the separated Pd@M28 was washed with xylene for three times and directly used for catalyzing the Suzuki-Miyaura coupling reaction.

3. Results and discussion

3.1. Surface compositions of azine-linked COF

As for the extended framework in two-dimensional COFs, we are interested in the surface compositions. Residual functional groups arising from starting monomers might exist and remain active to some target molecules, leading to covalent interaction and irreversible adsorption. Like COF-LZU1 reported by Wang and co-workers, the chemical shift at 191 ppm in ¹³C CP/MAS NMR spectrum was assigned to the unreacted aldehyde group [34]. Herein, taking an azine-linked COF as an example [39], we have studied its surface composition by XPS. As shown in Fig. 1a, the high-resolution Cls spectrum was fitted using three components with binding energies of 284.1, 284.8 and 287.7 eV corresponding to C=N, C=C and C=O, respectively. The atomic ratio of [C=N]:[C=C]:[C=O] was about 1:1.6:0.1, and the percentage of C=O was calculated to be 3.7%, possibly indicating the existence of aldehyde group. In high-resolution N1s spectrum (Fig. 1b), the major peak at 399.3 eV was assigned to the binding energy of C=N, suggesting the formation of Schiff base from condensation reaction of 1,3,5-triformylbenzene with hydrazine hydrate. It should be noted that a minor peak concurrently appeared at 403.0 eV, likely resulting from the protonated amine nitrogen (C=N–NH₃⁺) [40], because the protonated amine nitrogen is more difficult to lose electron, leading to a high binding energy.
It is reasonable that the signal peaks of C=O and C=N−NH3⁺ were very weak in XPS spectra for COF due to high conversion of starting monomers. If there were accessible hydrazine groups (−C=N−NH₂), the azine-linked COF would have irreversible adsorption for aldehyde-containing molecules. Generally, glycopeptides in tryptic digest show relative low abundance, and are needed to be enriched prior to analysis. Among enrichment protocols, the hydrazide chemistry method is based on the formation of Schiff base between oxidized glycopeptides and hydrazine groups on the material surface [41]. Similarly, the azine-linked COF was blended to the IgG digest oxidized by NaIO₄ (Fig. S3). As expected, deglycosylated peptides were successfully identified according to the m/z of 1158.7064 and 1190.7050 in MALDI-TOF MS (Fig. 1c). The result strongly indicated the existence of accessible hydrazine groups on surface of azine-linked COF. Then the density of hydrazine group in pristine azine-linked COF was quantified by the reaction of hydrazine group with 4-nitrobenzaldehyde, with a value of 88 μmol g⁻¹ (Fig. 1d). Note that the hydrazine density increased to 245 μmol g⁻¹ when the azine-linked COF was further treated with hydrazine hydrate, demonstrating the existence of accessible aldehyde groups in pristine COF.

3.2. Preparation, morphology, and porosity of monoliths

Based on the surface composition of azine-linked COF, epoxy-amine ring-opening polymerization was adopted to transform COF powder into monolith format. Ideally, the monomers POSS-epoxy and PEI not only polymerized to form crosslinked polymer network, but also were employed to link COF powders together through the accessible aldehyde groups and hydrazine groups. In our original strategy, the azine-linked COF powder with different content was directly added into the FPS to form suspension solution, which then reacted at 50 °C in water bath to yield monoliths within the confines of molds. However, FPS was almost adsorbed by COF when the content of COF was higher than 16%. To address this limitation, the COF powder was firstly immersed into toluene. After centrifugation, the toluene-saturated COF powder was mixed with FPS. As expected, monoliths with high content of COF were

Fig. 1. (a) C1s and (b) N1s XPS spectra, (c) MALDI-TOF MS spectra of deglycosylated peptides captured by azine-linked COF, and (d) hydrazine density of azine-linked COF.

Fig. 2. (a) FT-IR spectra and (b) PXRD patterns of azine-linked COF and monoliths.
also successfully fabricated, which were denoted as M28 and M43, respectively.

In FT-IR spectra (Fig. 2a), the peak at 1623 cm\(^{-1}\) for azine-linked COF powder was assigned to C\(=\)N stretching vibration, while the peaks at 680 and 960 cm\(^{-1}\) were arisen from benzene ring. For all monoliths, the absorption band at 1085 cm\(^{-1}\) was ascribed to stretching vibration of Si\(=\)O\(\cdots\)Si, resulting from POSS units. Compared to the pristine POSS-epoxy/PEI monolith (M0), the M16, M28 and M43 began to generate new absorption peaks at 680, 960 and 1623 cm\(^{-1}\), which were represented for the benzene ring and C\(=\)N group, respectively. Note that signals became stronger with the increase of COF mass fraction in monoliths. These results indicated that the azine-linked COF was stable in FPS, and successfully introduced into resultant monoliths.

It is well known that one of the important features for COFs is the crystalline structure. Crystallinities of both COF powder and monolith were confirmed by PXRD patterns. As shown in Fig. 2b, the pristine monolith M0 was amorphous without any diffraction peaks. As for M16, M28 and M43, peak positions were in accord with those for pristine azine-linked COF powder [39]. Additionally, the peak intensity decreased with the decrease of COF content in monolith. Even for M16, peaks at \(\theta = 7.01^\circ, 12.12^\circ\) and \(26.93^\circ\) were still detected, suggesting that the crystallinity of COF was well remained in the resulting monoliths.

The morphology of monoliths was characterized by SEM. Low content of COF had few effects on the morphology of M5 and M9 (Fig. S4). Their network structure was very similar to that in M0 with uniform macroporous structure. For M16, COF fragments were clearly seen, and inlaid in the three-dimensional network (Fig. 3a). With relatively high content of COF (Fig. 3b and c), the M28 and M43 showed distinct morphology comparing to other monoliths. Not all faces of the nubby COF were surrounded and coated with polymers generated from ring-opening polymerization of POSS-epoxy with PEI. In fact, the volume fraction of FPS was very small in synthetic conditions for M28 and M43. Note that other additives including PEG 10,000, 1-propanol and 1,4-butanediol also played important roles to induce phase separation in the formation of three-dimensional through-pore. Monoliths could not be obtained if only monomers were mixed with COF powder. Furthermore, EDX mapping images showed the silicon was homogeneously distributed in monoliths (Fig. S5), suggesting the FPS was well diffused into the space between COF powders. These results indicated our approach was able to shape the azine-linked COF powder into macroporous monoliths. With such mild synthetic conditions, it was possible that the monoliths could be shaped into many desired geometries. It was worth noting that our approach was also suitable for another COF-LZU1 linked by imine bonds (Fig. S6).

The mechanical stabilities were determined by uniaxial compression.
The BET surface area increased from 154 to 281 m$^2$ g$^{-1}$ to 0.15 cm$^3$ g$^{-1}$ when COF mass fraction was 43% (M43). Similarly, the total pore volume decreased to 105 m$^2$ g$^{-1}$ than those of COF powder. The pristine monolith M0 showed negligible stabilities of COF powder and monoliths were analyzed by TG-DSC curves (Fig. 4). For COF powder, the first weight loss continued to 140 °C resulted from the loss of physically adsorbed guest molecules, and the second weight loss starting at 360 °C was assigned to pyrolysis of skeleton. The thermal decomposition of pristine monolith (M0) began at 210 °C. It was interested that COF-based monoliths (M16, M28 and M43) showed combinational weight loss behaviors, sequentially including loss of adsorbed guest molecules, decomposition of polymer generated via ring-opening polymerization, and pyrolysis of COF skeleton. We thus could conclude that the COF-based monoliths were stable for application at temperature lower than 210 °C under air atmosphere.

The porosities of COF powder and monoliths were measured by nitrogen adsorption-desorption analysis. The BET surface area of COF powder was calculated to be 1354 m$^2$ g$^{-1}$ (Table 1, Figs. 5a and S7). The BET surface area increased from 154 to 281 m$^2$ g$^{-1}$ for M16 and M28, however, which then decreased to 105 m$^2$ g$^{-1}$ when COF mass fraction was 43% (M43). Similarly, the total pore volume firstly increased from 0.17 to 0.31 cm$^3$ g$^{-1}$ (M16 and M28), and then decreased to 0.15 cm$^3$ g$^{-1}$ (M43). It was acceptable that BET surface area and total pore volume of COF-based monoliths were apparently smaller than those of COF powder. The pristine monolith M0 showed negligible BET surface area (6 m$^2$ g$^{-1}$) and total pore volume (0.02 cm$^3$ g$^{-1}$), indicating that there were not any micropores and mesopores in the network generated by polymerization of POSS-epoxy with PEI. We then analyzed the pore size distribution obtained from nitrogen adsorption curve via NLDFT model (Fig. 5b). The pore size of ~0.70 nm was observed in both COF powder, M16 and M28, suggesting that the porous structure of COF was remained in M16 and M28. Comparing to COF powder, there were also pores with size of 1.27 and 3.78 nm in M16, as well as of 1.38 nm in M28. Such kinds of pores may be related to aggregation of COF powder and polymers. However, there were not any micropores in M43. As described above, more toluene was required to saturate COF powder to fabricate M43. It was found that toluene showed good compatibility with FPS, possibly resulting in that FPS diffused into COF and blocked the intrinsic pore of COF. Such a phenomenon resulted in low surface area.

To study the macroporosity, we then adopted MIP to characterize monoliths (Table 1, Fig. 5c). M16 had macropore size of 0.43 μm, which was the same with pristine monolith M0 (0.43 μm). Note that the macropore size increased to 3.15 and 3.51 μm for M28 and M43, respectively. In fact, M0 would remarkably shrink during dry process, leading to a smaller macropore size comparing to the solvent-saturated monolith. These results indicated the introduction of COF impeded shrinkage and helped to remain larger pore size in dried monoliths.

3.3. Application of monoliths for adsorption of BPA

Besides bulk monoliths, the mixtures of FPS and COF for preparation of M0-16 were also introduced into capillary with an inner diameter of 150 μm, while the mixtures for M28 and M43 seriously blocked the inlet of capillary. As shown in Fig. 6a, the prepolymerization mixture for M0 inside capillary was transparent under optical microscope. As for M5, M9 and M16, the mixture became darker with an increase of COF content. The resultant M16-based capillary column was studied by liquid chromatography. It was found that the BPA, which is one kind of relatively hydrophilic pollutants and has prompted researchers to exploit adsorbent with highly removal efficiency [42,43], could be firmly retained on the M16-based capillary column when mobile phase was 100% water. Note that the signal of BPA was apparently observed since mobile phase was switched in 100% methanol at 40 min, indicating that BPA could be eluted with methanol (Fig. 6b).

Inspired by this phenomenon, we studied adsorption kinetics for...

Table 1: Compositions and porosities of azine-linked COF and COF-based monoliths.

<table>
<thead>
<tr>
<th>Sample</th>
<th>COF /wt%</th>
<th>$S_{\text{BET}}$ /m$^2$ g$^{-1}$</th>
<th>$V_{\text{total}}$ /cm$^3$ g$^{-1}$</th>
<th>$D_{\text{BET}}$ /nm</th>
<th>$D_{\text{MIP}}$ /μm</th>
<th>Porosity /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>0</td>
<td>6</td>
<td>0.02</td>
<td>–</td>
<td>0.43</td>
<td>–</td>
</tr>
<tr>
<td>M16</td>
<td>16</td>
<td>154</td>
<td>0.17</td>
<td>0.70; 1.27; 3.78</td>
<td>0.43</td>
<td>54.5</td>
</tr>
<tr>
<td>M28</td>
<td>28</td>
<td>281</td>
<td>0.31</td>
<td>0.70; 1.38</td>
<td>3.15</td>
<td>53.8</td>
</tr>
<tr>
<td>M43</td>
<td>43</td>
<td>105</td>
<td>0.15</td>
<td>3.17</td>
<td>3.51</td>
<td>16.4</td>
</tr>
<tr>
<td>COF powder</td>
<td>100</td>
<td>1354</td>
<td>1.08</td>
<td>0.70</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* MX, X% represents fraction of COF with respect to total mass of COF and monomers.
* Surface area obtained via multi-point BET method.
* Determined at $P/P_0 = 0.99$.
* Pore diameter obtained via NLDFT model; macropore diameter and porosity determined by MIP.
both COF powder and monoliths in the aqueous solution of BPA (22.8 mg L\(^{-1}\)). As shown in Fig. 7, the absorbance in UV–vis spectra for BPA solution significantly decreased after adsorbed by COF powder and monoliths. For M0, the removal efficiency reached \(\sim 93.8\%\) of its equilibrium adsorption in 5 min. It should be attributable to the PEI structure in its skeleton, which is likely to show strong interaction with hydroxyl groups in BPA. By comparison, COF powder required 0.5 min to reach equilibrium, however, with only 77.4% removal efficiency. In fact, the strong \(\pi-\pi\) interaction and hydrogen bond interaction between COF surface and BPA facilitated rapid uptake, while slow diffusion of BPA into nanopores of COF should be responsible for relative low removal efficiency. For M16, M28 and M43, it took \(\sim 3\) min to reach equilibrium. The pseudo-second-order rate constant \((K_2)\) was calculated to be 0.82, 0.58, 0.65, 0.63 and 0.90 g mg\(^{-1}\) min\(^{-1}\) for M0, M16, M28, M43 and COF powder, respectively (Table 2, Fig. S8), which were higher than those obtained by some reported materials, such as non-porous \(\beta\)-CD-based polymers and granular activated carbon [42].

In addition, the M0 or M28 (1 mg) was packed into syringe that was equipped with sieve plate, and BPA solution (22.8 mg L\(^{-1}\)) passed through at a flow rate of \(\sim 3\) mL min\(^{-1}\). The BPA removal efficiency

![Fig. 6. (a) Optical images of prepolymerization mixtures inside capillary prior to the formation of monoliths, (b) retention behavior of BPA on M16-based capillary column.](image)

![Fig. 7. UV–vis spectra measured at different adsorption time for (a) M0, (b) M16, (c) M28, (d) M43 and (e) COF powder, and (f) time-dependent removal efficiency of aqueous BPA by COF powder and monoliths.](image)

![Fig. 8. Removal efficiency of BPA upon flowing volume of solution through syringe packed with M0 or M28. The regenerations were carried out by washing with methanol.](image)

**Table 2**

Pseudo-second-order rate constant \((K_2)\) and \(Q_e\) obtained by Eq. (3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(K_2) (g mg(^{-1}) min(^{-1}))</th>
<th>(Q_e) (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>0.82</td>
<td>21.7</td>
</tr>
<tr>
<td>M16</td>
<td>0.58</td>
<td>21.9</td>
</tr>
<tr>
<td>M28</td>
<td>0.65</td>
<td>18.5</td>
</tr>
<tr>
<td>M43</td>
<td>0.63</td>
<td>20.4</td>
</tr>
<tr>
<td>COF powder</td>
<td>0.90</td>
<td>18.1</td>
</tr>
</tbody>
</table>
was successfully regenerated by 11% for M28. Furthermore, it was worth noting that both M0 and M28 BPA solution reached 18 mL. However, removal e-
was higher than 97% for M28 even though the cumulative volume of (c) before and (d) after Fig. 9.

3.4. Pd@M28 for the Suzuki-Miyaura coupling reaction

Besides adsorption for organic molecules, Schiff base ligands, which are prevalent to coordinate and stabilize many kinds of metals [44,45], also make it possible to prepare Pd-containing COF (Pd/COF-LZU1) as reported by Wang and co-workers [34]. The Pd/COF-LZU1 catalyst exhibited excellent performance for the Suzuki-Miyaura coupling reaction, and was easily recycled. Taking advantage of azine-linked COF moieties in monolith, we adopted M28 to immobilize palladium acetate (Pd@M28) that was then used to catalyze the Suzuki-Miyaura coupling reaction. In original strategy, monolithic Pd@M28 was directly used to catalyze the reaction of phenylboronic acid with p-nitro bromobenzene in xylene (Fig. 9a). Unfortunately, the conversion was lower than 90%. It was possibly related to the bad mass diffusion for Pd@M28 (Fig. S9) in such large solution volume (> 4 mL). The ideal catalysis performance may be achieved by using Pd@M28 as fixed-bed catalytic reactor. However, it is difficult in our laboratory to perform. Therefore, Pd@M28 was cut into millimeter-scale amorphous particles to examine the feasibility of monolith as catalyst support in present work.

As shown in Fig. 9b, the yield of 4-nitro biphenyl was greater than 98.2% for four cycles, and even 93.5% in the fifth cycle. TEM images indicated that the catalyst still showed good dispersity after five cycles uses (Fig. 9c and d). Combined with hierarchically porous structure, such Pd-containing monolith would be very promising for practical application.

4. Conclusion

In summary, a facile and efficient approach based on ring-opening polymerization has been developed to shape azine-linked COF powder into monoliths. Besides the remained porosity for COF moieties, macropores were also generated in COF-based monoliths, suggesting a hierarchically porous feature that made such monolith very promising for application as adsorbents and catalyst supports. To date, many kinds of COFs have been designed and synthesized, but generally produced and used in powder form. We hope our mild fabrication approach would facilitate COF materials in practical applications by shaping them into the desired forms like rod, film, sponge, etc.

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Appendix A. Supplementary data

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References


