Robust synthesis of free-standing and thickness controllable conjugated microporous polymer nanofilms†

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A new polymerization strategy based on Sonogashira–Hagihara reaction and Schiff-base reaction at oil–water interfaces is developed to synthesize free-standing and thickness controllable conjugated microporous polymer (CMP) nanofilms.

Conjugated microporous polymers (CMPs) have drawn particular interest in recent years,† because their extended π-conjugated system with inherent nanopores endows them with a great variety of properties and potential applications in gas adsorption,² photosensitizers,³ photocatalysts,⁴ organic electronics,⁵ electrocatalysts,⁶ energy storage,⁷ etc. In particular, CMP nanofilms can fully display the inherent π-conjugated nanopore structures for significantly enhanced properties and highly efficient applications. However, CMPs synthesized by metal-catalyzed cross-coupling reactions, such as the Sonogashira–Hagihara reaction,⁸ Suzuki cross-coupling reaction,⁹ oxidation reaction¹⁰ and Yamamoto reaction,¹¹ are usually powders which are neither soluble in any solvents nor molten at any elevated temperatures, making them hard to process into films for practical applications.⁵,⁹ In fact, processability and device integration have been widely considered as the most challenging topic in the field of CMPs.¹⁰

To work out this issue, two ways are usually used: one is spin-coating soluble CMP powders such as hyperbranched conjugated microporous polymers,¹⁰a or linear conjugated polymers of intrinsic microporosity,¹⁰b into films. Obviously, this spin-coating method is suitable only for very limited soluble π-conjugated frameworks. Another is through crosslinking polymerization with the help of specific substrate surfaces,¹¹ especially preparing CMP films on conductive substrate surfaces such as ITO-coated glass based on electropolymerization.⁵,⁹,¹⁰c,¹² Nevertheless, this strategy is restricted to these few monomers which can be electrochemically oxidized, and has to be conducted on specific surfaces such as ITO-coated glass. Thus, it is highly desirable to develop facile methods to synthesize CMP films.

Recently, an interfacial polymerization strategy based on the Schotten–Baumann reaction, in which a compound containing acid chlorides reacts with another compound containing active hydrogen atoms (–OH, –NH, –SH), has been widely used in preparing nanofiltration and reverse osmosis membranes such as polyamide membranes because of its easy operation and controllability.¹³ Here, we develop a radically new interfacial polymerization strategy to synthesize free-standing CMP nanofilms. Different from the reactions used in traditional interfacial polymerization, in this method, the Sonogashira–Hagihara and Schiff-base reactions are used in oil–water interfacial polymerization for the first time to directly synthesize a series of free-standing CMP nanofilms. What’s more, the thickness of the films can be controlled from 30 to around 200 nm, and because these nanofilms are formed at the oil–water interface,¹⁴ they are really free-standing without using any sacrificial substrates and can be freely transferred onto any desired substrates, which is highly meaningful for integration of various devices and practical applications.¹⁵ We believe that the method we present here is really versatile and can readily be extended to synthesize a series of CMP nanofilms with various compositions and properties, which are hardly achieved through the existing strategies.

Our interfacial polymerization is briefly described in Scheme 1a and b. An aqueous phase containing a catalyst is charged into a three-necked round-bottom flask, which is then charged with an organic phase consisting of conjugated monomers and even

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Scheme 1 (a and b) Schematic diagrams for the syntheses of CMP nanofilms by Sonogashira–Hagihara reaction at the oil–water interface: (a) cross-coupling reaction at the oil–water interface, and (b) the resulting CMP nanofilm at the phase boundary.
another catalyst (for the Sonogashira–Hagihara reaction) to form an oil–water interface. This system is heated to a certain temperature, and is held still at that temperature for 24 h or 72 h for the Sonogashira–Hagihara and Schiff-base reactions, respectively, to directly produce CMP nanofilms. These nanofilms formed at the oil–water interface are then transferred to an ethyl acetate reservoir to rinse the unreacted monomers from the surfaces.

When 1,3,5-triethynylbenzene (TEB) reacted with various monomers, e.g., 1,4-diiodobenzene (DIB), 4,4′-diiodobiphenyl, tris(4-iodophenyl)amine (TIPA) and tetra(p-iodophenyl)ethylene (TPE), via Sonogashira–Hagihara reaction, or 1,3,5-triformylbenzene (TFB) reacted with 1,4-diaminobenzene (DAB) via Schiff-base reaction, CMP 1–4 nanofilms and an imine-nanofilm were obtained, as shown in Fig. S1a–e (ESI†).

Based on previous reports,14,16 the mechanism for synthesizing CMP-1–4 nanofilms by the Sonogashira–Hagihara reaction can be illuminated as follows: at the phase boundary of an immiscible biphasic system created by the combination of an organic phase (containing conjugated monomers and one catalyst) and an aqueous phase (containing Et3N and the other catalyst), because the conjugated monomers and catalyst in the organic phase are insoluble in water, once this organic phase contacts with the immiscible aqueous phase, these monomers and catalyst tend to precipitate at the oil–water interface through solubility differences,13a,16a wherein the monomers react with each other through cross-coupling reactions with the help of catalysts (in the aqueous phase and the organic phase) to form a thin film at the phase boundary.16b Because this forming film is not soluble in either the organic or aqueous phase, more and more monomers and catalysts are prohibited from the organic and aqueous phases, respectively. Accordingly, fewer monomers and less catalyst can work together as the film becomes thicker and thicker. Thus the overgrowth of CMPs can be effectively suppressed, directly generating CMP nanofilms instead of three-dimensional or bulk products. The imine–CMP-nanofilm formed by Schiff-base reaction has a similar reaction mechanism to the CMP 1–4 nanofilms.

These CMP nanofilms are totally insoluble in all organic solvents tested, which indirectly validates high cross-linking in polymer structures. All the CMP 1–4 nanofilms show a FT-IR peak at around 2200 cm⁻¹ corresponding to the internal alkyne group (R₁–C≡C–R₂), as shown in Fig. 1a, confirming the successful coupling of acetylenic bonds.17 To further confirm the CMP nanofilms, the corresponding CMP powders were also synthesized by the same monomers according to the literature,8,18 and verified by solid-state ¹³C CP/MAS NMR spectra (Fig. S2–S4, ESI†),11b and showed the same FT-IR spectra as the CMP nanofilms (Fig. S5–S8, ESI†). All these results have proved that the films presented here are indeed CMP films. The FT-IR spectrum of the imine–CMP-nanofilm displays a peak at 1623 cm⁻¹ assigned to the imine group (R₁–C=N–R₂), which also demonstrates the formation of the desired products compared with the peak at around 1690 cm⁻¹ corresponding to the terminal aldehyde of TFB (Fig. S9, ESI†).18

The UV-Vis absorption spectra of the CMP nanofilms show a red-shift of maximum absorbance from 330 nm to 365 nm (Fig. 1b), which further substantiates the coupling of acetylenic bonds compared with the maximum absorbance of TEB at 300 nm. The powder X-ray diffraction (PXRD) patterns of the CMP 1–4 nanofilms reveal the amorphous character (Fig. 1c), which is consistent with previous results.8 However, the PXRD pattern of the imine–CMP-nanofilm also shows amorphous character, which may be due to the low reaction temperature (90 °C) used in this method for Schiff-base reaction.18

The elemental analysis of the CMP nanofilms was performed using energy dispersive X-ray spectroscopy (EDS), which demonstrates that the nanofilms are mainly composed of carbon element, and the contents of the remaining catalyst traces in the CMP-1–4 nanofilms are very low, and there are no large, aggregated Pd and Cu species in the nanofilms (Fig. S10 and S11, ESI†).

The porosity of the nanofilms was investigated by Kr sorption isotherm measurements at 77 K and 87 K. The nanofilms with a thickness of 180 nm were used for Kr sorption measurements. The specific surface areas were evaluated using the krypton isotherms at 77 K (Fig. 2a),19 and the pore-size distribution profiles were calculated based on the results of the Kr sorption isotherm measurements at 87 K (Fig. 2b).19,20 The Kr sorption isotherm of the imine–CMP nanofilm and the N₂ sorption isotherm of the CMP bulk powders can be seen in Fig. S12–S17 (ESI†). The pore-size distribution profiles based on the nonlocal density functional theory method reveal that the pore size of the CMP nanofilms is around 0.5–1.9 nm (Fig. S18, ESI†); however, slight fluctuations can be observed in the mesoporous regions. The Brunauer–Emmett–Teller (BET) surface areas and pore diameters of the CMP bulk powders and CMP nanofilms are listed in Table S1 (ESI†). The S\text{BET} values

![Fig. 1](https://example.com/fig1.png) (a and b) FT-IR spectra and UV-Vis spectra of TEB and CMP nanofilms. (c) PXRD patterns of the CMP nanofilms.

![Fig. 2](https://example.com/fig2.png) (a and b) Kr sorption isotherms for CMP-1–4 nanofilms measured at 77 K and 87 K (filled patterning: adsorption, open patterning: desorption).
of the CMP nanofilms are much higher than those of the CMP powders, probably because the nanoparticles of the CMP powders closely aggregate together so that some micropores of the nanoparticles are blocked (Fig. S19, ESI†).

The morphologies of the CMP nanofilms were further characterized by field-emission scanning electron microscopy (FE-SEM). As shown in Fig. 3a–d and Fig. S20 (ESI†), most of the surfaces are homogeneous. The inset cross-sectional images reveal that the nanofilms are around 100 nm thick.

The film thickness can be controlled by varying the monomer concentrations. For example, the thickness of the CMP-1-nanofilm linearly increases from 30 to 186 nm measured using atomic force microscopy (AFM) images as shown in Fig. 4a–d, with the increasing concentrations of TEB and DIB from 0.0875 to 0.35 mM and 0.125 to 0.5 mM, respectively, at an equal mole ratio of TEB to DIB (1 : 1.43) (Fig. 4e). However, too low TEB and DIB, e.g. 0.0875 mM and 0.125 mM, respectively, would considerably decrease the film compactness (Fig. S21, ESI†). While for too high TEB and DIB, e.g. greater than 0.35 mM and 0.5 mM for TEB and DIB, respectively, the thickness of the film didn’t increase anymore. The reason why the thickness of the film is linearly dependent on the monomer concentration within a certain range is probably explained as follows: in our oil–water interfacial polymerization, monomers crosslinking and rigid structural networks of this forming CMP, there are very small amounts of catalyst molecules from the water phase embedded in the CMP nanofilm. Thus, although the film is formed, the reaction will continue with the help of these residual catalyst molecules in the CMP nanofilms and the catalyst molecules from the organic phase. However, when the film is becoming thicker and thicker with increasing monomer concentration, fewer and fewer residual catalyst molecules embedded in the CMP nanofilms can touch monomers, which block further reaction. Therefore, the optical images of the CMP-1-nanofilm and the CMP-1 bulk powder can be seen in Fig. 4f, while the photo images of the free-standing CMP-1-nanofilm in the dried state can be seen in Fig. S22 (ESI†). The typical free-standing CMP nanofilm synthesized by this method can be freely transferred onto different substrates and can be further bent or processed, which is highly meaningful for integration of various devices and practical applications in the future (as shown in Fig. S23, ESI†).

To further characterize the properties of the CMP nanofilms, the surface wettability of the nanofilms was illustrated using the water contact angle (WCA) (Fig. S24, ESI†). As can be seen, the CMP-1–4 nanofilms show good hydrophobic properties; in particular, the WCA of the CMP-3-nanofilm is as high as 118°, while the WCA of the imine–CMP-nanofilm is only 56.6°, displaying a hydrophilic property. This can be accounted for by the residual terminal hydrophilic groups (aldehyde and amino groups) in the structure of the monomers. The UV-visible spectra of the CMP-1–4 nanofilms showed a high transmittance which is comparable with a bare glass plate (Fig. S25, ESI†).

Since these CMP nanofilms combine the π-conjugation with permanent microporosity, which benefits not only the diffusion of analytes in the nanofilms but also the formation of π-stacking complexes to quench luminescence, they are known as excellent candidates for sensing nitroaromatics.21 However, because the fluorescence intensity of CMP-1–3 and Imine–CMP nanofilms is too low, we further used a 180 nm thick CMP-4-nanofilm, which contains aggregation-induced emission (AIE) units to show stronger fluorescence intensity (Fig. S26, ESI†), as a chemosensor prototype for picric acid (PA), which is one kind of typical explosive. This nanofilm was adhered to a quartz plate and immersed in acetonitrile. As the acetonitrile solution of PA is gradually added, the fluorescence intensity of the film decreases linearly (Fig. 5a). According to the linear part of the Stern–Volmer plot (0.1–0.5 mM), the quenching constant $K_{sv}$ can be calculated to be $1.9 \times 10^{3}$ M$^{-1}$ (Fig. 5b), which is comparable to other porous organic polymers (Table S2, ESI†). This quenching of fluorescence can be visually seen in Fig. 5c. When this film quenched by PA was washed with acetone for 5 min, its fluorescence was restored. This procedure can be repeated, as shown in Fig. 5d, revealing that the CMP nanofilm-based chemosensor exhibits good reusability. The sensing behaviors of the CMP-4-nanofilm for other nitroaromatics such as

![Fig. 3](a–d) Surface SEM images of CMP-1–4 nanofilms, insets: cross sections of the nanofilms.

![Fig. 4](a–d) Tapping-mode AFM images of CMP-1-nanofilms synthesized using different monomer concentrations (a, TEB: 0.0875 mM, DIB: 0.125 mM; b, TEB: 0.175 mM, DIB: 0.25 mM; c, TEB: 0.263 mM, DIB: 0.375 mM; d, TEB: 0.35 mM, DIB: 0.5 mM), and their height. (e) Plot of the CMP-nanofilm thickness versus the TEB concentrations. (f) Photo image of the CMP-1-nanofilm (in the ethyl acetate phase), inset: CMP-1 bulk powder.
2,4-dinitrotoluene (DNT), 1-chloro-3-nitrobenzene (1-Cl-3-NB) and p-nitrotoluene (p-NT) and the sensing behaviors of a thinner CMP-4-nanofilm (thickness is around 100 nm) for PA were also further studied (Fig. S27, ESI†). As shown in Fig. S28 (ESI†), the CMP-4-nanofilm shows a higher quenching efficiency for PA than the other nitroaromatics, with the quenching efficiency of the order 1-Cl-3-NB < DNT < p-NT < PA, and the thinner having a higher quenching efficiency.

In summary, we have demonstrated a novel and robust polymerization method for synthesis of free-standing CMP nanofilms. The thickness of the CMP nanofilms can be controlled from 30 to around 200 nm by varying the concentrations of the monomers. The free-standing nanofilms can be easily transferred to various substrates, which have enormous practical value in device integration. Furthermore, a light-emitting CMP nanofilm consisting of aggregation-induced emission units was synthesized by this method to demonstrate a convenient, sensitive and reversible chemosensor for the sensing of explosives [picric acid] in acetonitrile. Of particular interest is that not only the Sonogashira–Hagihara reaction but also the Schiff-base reaction is suitable for this oil–water interfacial polymerization, which means that a lot of conjugated monomers can be used by this method to directly synthesize a series of novel CMP nanofilms with various compositions and properties. Thus, we believe that the method we presented here may arouse an emerging and fascinating field in synthesizing CMP nanofilms and other porous organic polymer nanofilms, which can greatly promote the practical applications of CMPs in organic electronics, optoelectronics, energy storage, etc.

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Notes and references


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