Conductive Polymers

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Electrochemical Synthesis of a Microporous Conductive Polymer Based on a Metal–Organic Framework Thin Film**

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Abstract: *A new approach to preparing 3D microporous conductive polymer has been demonstrated in the electrochemical synthesis of a porous polyaniline network with the utilization of a MOF thin film supported on a conducting substrate. The prepared porous polyaniline with well-defined uniform micropores of 0.84 nm exhibits a high BET surface area of 986 $m^2 g^{-1}$ and a high electric conductivity of 0.125 $S cm^{-1}$ when doped with I_2, which is superior to existing porous conducting materials of porous MOFs, CMPs, and COFs.*

The construction of highly porous organic-based conducting porous materials with defined structures has recently spurred intense interest owing to their great potential for applications in photovoltaics,[1] super capacitors,[2] batteries,[3] microelectronics,[4] and sensors.[5] Conventional conducting polymers, such as polyaniline,[6] polyphenylene,[7] and poly(thiophenes)[8] have been well-developed, but they are one-dimensional (1D) linear-backbone polymers with extremely low surface areas. Recently, two-dimensional (2D) conducting porous polymers based upon conjugated organic ligands have been explored, as exemplified by electroactive organic frameworks (EOFs),[9] conjugated microporous polymers (CMPs),[10] and lamella covalent organic frameworks (COFs).[11] These materials exhibit interesting redox-, doping-, or photoinduced electrical properties, but their electrical conductivities are very low, which is presumably due to the inefficient stacking of the π-systems or low charge density. The bridging of linear-backbone conducting polymers into a three-dimensional (3D) architecture is a tempting approach to afford both high porosity and high conductivity; however, this kind of porous conducting polymer network with well-defined 3D structure has not yet been achieved.

Among the large family of conductive polymers, polyaniline has been most studied owing to its interesting electronic, magnetic, and optical properties.[12] Polyaniline can be prepared by homogeneous or heterogeneous polymerization using different reagents through either chemical or electrochemical synthesis.[13] "Hard templates" (for example, MCM-41,[14] porous alumina,[15] track-etched polymeric thin films[16]) and "soft templates" (for example, liquid crystal,[16] micelles,[17] and reverse microemulsion[18]) have been employed for the preparation of polyaniline nanofibers and nanowires, which however exhibit virtually very low porosities. The construction of 3D highly porous polyaniline architecture remains a challenge and necessitates the exploration of new types of templates with interconnecting 3D channels.

Metal–organic frameworks (MOFs),[19] which are built from multidentate organic ligands and metal ions or in situ generated metal ion clusters (also known as secondary building units (SBUs)) through coordination bonds, are a new type of porous materials featuring tunable pore sizes, structural diversity, and designable functionality.[20] MOFs have been extensively explored as a new class of functional materials for applications in gas storage,[21] gas separation,[22] carbon capture,[23] catalysis,[24] and sensing.[25] The employment of MOFs as templates for the syntheses of nanosized polymers has recently been demonstrated.[26] Nevertheless, the poor chemical stability of most MOFs precludes their utilization as templates for the polymerization of aniline under harsh redox chemical reaction conditions. Instead of using direct chemical synthesis, herein we report the approach of employing electrochemical synthesis to prepare microporous polyaniline with the utilization of a MOF thin film supported on conducting substrate.

Our approach mainly includes the following steps (Figure 1): a layer of conducting polyaniline is first casted on the electrode followed by the growth of MOF thin film; the polyaniline layer plays the role of tightening the combination with MOF layer through the imino groups and mediating electrons to the MOF, which can template the formation of 3D porous architecture of polyaniline under electrochemical conditions. Employing this approach, we have successfully prepared microporous polyaniline that exhibits a high surface area of 986 $m^2 g^{-1}$ and a high electric conductivity of 0.125 $S cm^{-1}$ when doped with I_2, which is superior to existing porous conducting materials of porous MOFs, CMPs, and COFs, thereby advancing it as a new route for the preparation of high porous 3D conductive polymer networks.

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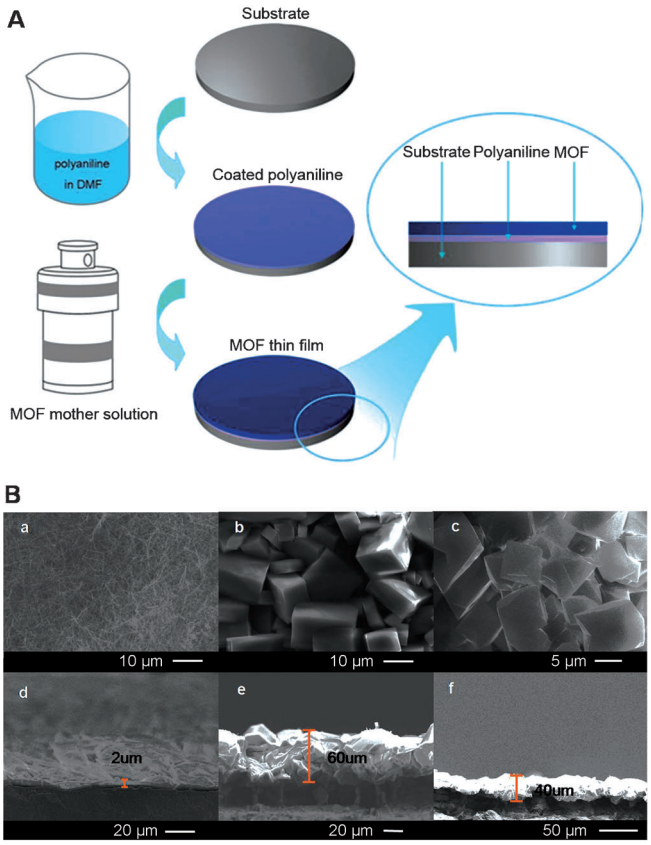

Figure 1. A) Preparative procedures for different MOF thin films (HKUST-1, $Zn_2(BDC)_2DABCO$, MIL-68 (In)); B) SEMs of MIL-68 thin film (a, d) on polyaniline/Pt, $Zn_2(BDC)_2DABCO$ thin film (b, e) on the polyaniline/Pt, and HKUST-1 thin film on the polyaniline/Pt (c, f) (a, b, c is the top view, d, e, f is the cross-sectional view).

To prepare a 3D porous architecture of polyaniline, we developed the conducting polyaniline-supported MOF thin film method to modify the Pt electrode, as illustrated in Figure 1 A. In a typical procedure, for example, in the context of preparing HKUST-1[27] thin films/Pt electrode, polyaniline was first dissolved in DMF and then coated onto the Pt electrode. After dried at 60 °C, the polyaniline/Pt was introduced into the solution of reactants of HKUST-1 in the teflon-lined autoclave to allow heterogeneous nucleation and crystal intergrowth at 120 °C for 3 days. Subsequently, the HKUST-1/polyaniline/Pt were washed for several times with ethanol and dried at room temperature. Using this method, we have also successfully grown $Zn_2(BDC)_2DABCO$[28] and MIL-68 (In)[29] MOF thin films onto the surface of stainless steel slice or copper slice to demonstrate the general applicability of this method. The SEM of the three polyaniline supported MOF thin films on Pt are shown in Figure 1 B a–f. It is clear that no obvious defects or cracks between MOF thin film and supporting polyaniline layer were observed on the top view of the MOF thin films (Figure 1 B a–c). The tight combination between the MOF thin film and the polyaniline layer as shown from the cross-section of MOF thin film and polyaniline indicates that the imino groups of polyaniline main chain have been effectively consumed for the hydrogen binding with carboxylic group of MOF framework, thus affording abundant heterogeneous nucleation. The thickness of MOF thin films grown by this method is about 2–100 μm and their crystalline phases of corresponding MOFs were verified by powder X-ray diffraction (PXRD) analysis (Supporting Information, Figure S1), which are consistent with previous results and confirm that these MOF thin films take the homogeneous pure phase.[27–29] This also highlights the polyaniline support method as an effective and general method for MOF thin film preparation on a solid surface.

To demonstrate the application of MOF thin film supported by conductive polyaniline on electrode surface for targeted electrochemical synthesis, we chose HKUST-1/polyaniline/Pt for the preparation of porous polyaniline under electrochemical conditions. As illustrated in Scheme 1 A, a polyaniline-modified Pt electrode covered by $1 \times 2\ cm^2$ HKUST-1 thin film with the thickness about 40–50 μm first was immersed in a 3 M potassium chloride solution containing 0.1 M aniline to load aniline monomer into the micropores of HKUST-1; subsequently, potentiodynamic synthesis of polyaniline was performed in a new batch of 3 M KCl solutions containing 0.1 M aniline, by the cycling of potential (for 10–20 cycles) of the substrate between −0.2 and 1.0 V versus Ag/AgCl at a $10\ mV\ s^{-1}$ scan rate at 25 °C (Supporting Information, Figure S2);[30] finally, the MOF thin film was digested in HCl solution (pH 3) at room temperature to afford nanoporous polyaniline, hereafter denoted as nano-polyaniline. It is worth noting that after the removal of the MOF thin film, the supporting polyaniline layer remains adhered to the surface of Pt electrode (Scheme 1). The nano-polyaniline was then collected by filtration and washed with ethanol and water several times to give a black powder. The purity was confirmed by the energy dispersive spectrometer (EDS), which revealed the existence of only C and N and the absence of Cu (Supporting Information, Figure S3). The chemical structure of nano-polyaniline was determined by ^{13}C cross-polarization magic-angle spinning nuclear magnetic resonance (CP/MAS NMR) analysis. As shown in the Supporting Information, Figure S4, five pronounced signals were resolved at $\delta = 158$, 142, 136, 123, and 114 ppm, characteristic of polyaniline.[31] The intense signals at $\delta = 158$, 142, and 123 ppm are unambiguously assigned to C_1 the quinoid ring and C_3, C_5 in the benzene ring respectively, and the two relatively weaker signals at $\delta = 136$, 114 ppm correspond to C_2 and C_4, respectively. IR spectra show that the absorption band at $3240\ cm^{-1}$ correspond to the N–H stretching bonded to carbonyl and the peak at $3055\ cm^{-1}$ is assigned to C–H stretching of the aromatic ring. The peaks at 1354, 1300, 1232, 1180, and 1101 are attributed to N–H bending and C–N and C–C stretching. The characteristic peaks at 1446 and $1500\ cm^{-1}$ are assigned to the C=C stretching modes of the benzenoid ring and the quinoid ring, respectively, thereby indicating that the state of the nano-polyaniline is emeraldine rather than solely the leucoemeraldine or pernigraniline form.[32] The Raman spectroscopy was employed to confirm the presence of "phenazine-like" segments with characteristic absorption band at about 574, 1375, and $1642\ cm^{-1}$ (Supporting Information, Figure S5),[33] indicating the cross-linking nature between main chains in the nano-polyaniline. The 3D cross-linked architecture of nano-polyaniline should be

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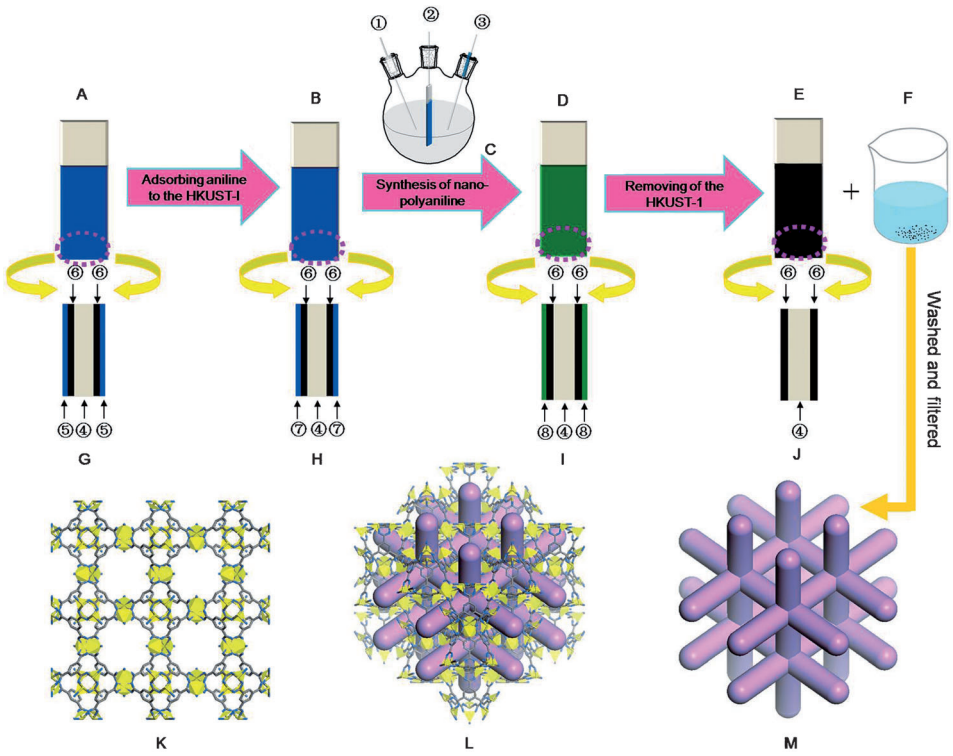

Scheme 1. The preparation of nano-polyaniline with HKUST-1 thin film. (A: HKUST-1/polyaniline/Pt electrode; B: HKUST-1/polyaniline/Pt electrode which is loaded with aniline; C: the electrochemical reaction equipment; D: HKUST-1/polyaniline/Pt electrode containing nano-polyaniline after the electrochemical reaction; E: polyaniline/Pt electrode; F: HCl solution (pH 3) which is used to digest the MOF thin film; G: the section of A; H: s the section of B; I: the section of D; J: the section of E; K: the structure of ⑤; L: the simulated structure of ⑧ (purple is on behalf of nano-polyaniline); M: the 3D cross-linked nano-polyaniline; ① is the Pt wire (pair electrode); ② is B (working electrode); ③ is the Ag/AgCl electrode (reference electrode); ④ is the Pt slice; ⑤ is HKUST-1 thin film; ⑥ is the polyaniline layer; ⑦ is HKUST-1 thin film loaded with aniline; ⑧ is HKUST-1 thin film containing nano-polyaniline after the electrochemical reaction.)

templated by the 3D interconnecting porous structure of HKUST-1. PXRD studies indicated the amorphous structure of nano-polyaniline, which coincides with the worm-like pore structure as revealed by high-resolution TEM analysis (Supporting Information, Figure S6).

To further verify the 3D porous structure of nano-polyaniline, N_2 sorption isotherms were collected at 77 K. As shown in Figure 2 A, nano-polyaniline exhibits a type I sorption isotherm and a sharp uptake in a relative pressure range from 10^{-5} to 10^{-2}, which is a characteristic of microporous materials. Derived from the N_2 adsorption data, the Brunauer–Emmett–Teller (BET) surface area of nano-polyaniline is 986 $m^2 g^{-1}$. Pore-size distribution analysis based upon the density functional theory (DFT) model indicates the pore size of nano-polyaniline is predominantly distributed around 0.84 nm, in good agreement with the size of Cu paddlewheel cluster in HKUST-1. These results further highlight the template function of the MOF thin film. Thermogravimetric analysis reveals a circa 5% weight loss was observed between 50 °C and 389 °C, which is followed by the decomposition of the network (Supporting Information, Figure S7).

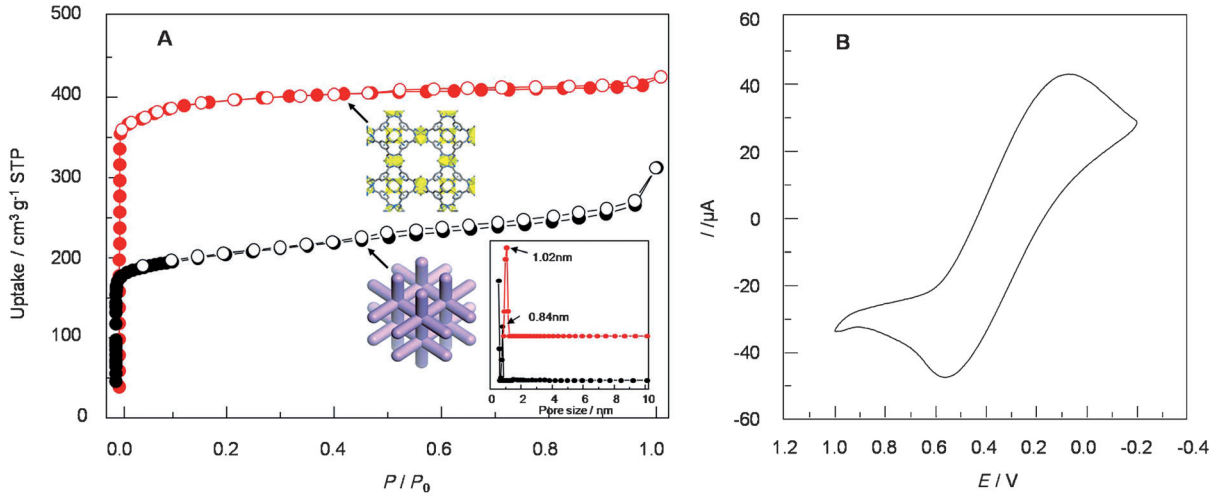

Figure 2. A) N_2 sorption isotherms and pore size distribution of HKUST-1 (red) and nano-polyaniline powder (black) (BET surface area (red): 1525 $m^2 g^{-1}$, pore size: 1.02 nm; BET surface area (black): 986 $m^2 g^{-1}$, pore size: 0.84 nm); B) Cyclic voltammograms of the nano-polyaniline film on Pt microelectrode in 3 M KCl solution between −0.2 and 1 V, Pt as an auxiliary electrode, and Ag/AgCl as the reference electrode at a scan rate 10 $mV s^{-1}$ at 25 °C.

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The nano-polyaniline also exhibits interesting conductive and electroactive properties along the 3D microporous framework. Measured by four-probe method, the I_2-doped nano-polyaniline demonstrates a high electrical conductivity of $0.125\,S\,cm^{-1}$ (Supporting Information, Table S1), which outperforms that of conductive porous MOFs,[34] I_2- doped MOFs,[35] TCNQ-doped MOF,[36] CMPs,[10] and COFs.[11a–e] Compared with normal I_2-doped polyaninline,[37] the conductivity is higher owing to higher efficency doping in the porous material. The attempt to assess the porosity of I_2-doped nano-polyaniline unfortunately could not generate reliable results because I_2 was readily to sublime under vacuum during the gas sorption measurement. Furthermore, it also exhibit reversible and stable electrochemical redox behaviors in electrolytes such as KCl or NaCl. Figure 2B shows the cyclic voltammogram (CV) of the nano-polyaniline at a scan rate of $10\,mV\,s^{-1}$ in dried and degassed 3 M KCl solution. The nano-polyaniline displays only one couple of reversible redox peaks ($E_{Pa} = +0.1$ V, $E_{Pc} = +0.58$ V) within the potential range applied, which are due to the emeraldine–pernigraniline transformation.[38] This result is consistent with the electroactive properties of normal polyaniline which was electrochemical synthesized at neutral solution.[26]

In summary, we have discovered a method of modifying the electrode with MOF thin film and employed the MOF thin film modified electrode for electrochemical synthesis of 3D porous conducting polymer architecture for the first time, as exemplified by the preparation of microporous polyaniline network. The prepared porous polyaniline exhibits a high BET surface area of $986\,m^2\,g^{-1}$ with well-defined uniform micropores of 0.84 nm; the I_2 doped porous polyaniline exhibits high electric conductivity of $0.125\,S\,cm^{-1}$, which is superior to existing porous conducting materials of porous MOFs, CMPs, and COFs. Our work presented herein not only provide an effective and general method for MOF thin film preparation on a solid surface, but also advance electrochemical synthesis on the basis of MOF thin film modified electrode as a new route for the preparation of highly porous 3D conductive polymer networks.

Experimental Section

Pt was chosen as the working electrode and HKUST-1 thin film was selected as the host reactor. A Pt electrode covered by $1 \times 2\,cm^2$ HKUST-1 thin film with the thickness about 40–50 μm was first prepared, and then the prepared Pt/HKUST-1 was used to synthesize conducting polymer by electrochemical synthesis method. In a typical procedure, the Pt/HKUST-1 was immersed in a 3 M potassium chloride solution containing 0.1 M aniline to adsorb aniline monomer into the micropore of the HKUST-1. Subsequently, potentiodynamically synthesis of polyaniline was performed in a new batch of 3 M KCl solutions containing 0.1 M aniline, by the cycling of the potential (for 10–20 cycles) of the substrate between −0.2 and 1.0 V versus Ag/AgCl at a $10\,mV\,s^{-1}$ scan rate at 25 °C. Finally, the synthesized polyaniline inside the pores of HKUST-1 was recovered by simply digesting the MOF thin film in HCl solution (pH 3) at room temperature. We denoted the synthesized polyaniline as nano-polyaniline. It should be noted that after removal of the MOF layer, the original polyaniline layer for growing MOF thin film was still adhered on the surface of Pt electrode. The nano-polyaniline was collected by filtration and washed by ethanol and water for several times to give a black powder.

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