Grafting of sulfonated monomer onto an amino-silane functionalized 2-aminoterephthalate metal – organic framework via surface-initiated redox polymerization: proton-conducting solid electrolytes

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Abstract

A post-polymerization method for metal–organic frameworks (MOFs) has been developed to produce super-acidic solid nanoparticles. Thus, the NH$_2$MIL-53(Al) MOF was functionalized with (3-aminopropyl)triethoxysilane (APTES) from amine groups to yield active site anchored MOF nanoparticles. Then, sulfonated polymer/MOF hybrid nanoparticles were prepared by redox polymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid (MOF-g-PAMPS), initiated onto the surfaces of aminopropyl-functionalized NH$_2$MIL-53(Al) nanoparticles. The synthesis and modification of NH$_2$MIL-53(Al) nanoparticles were characterized by Fourier transform infrared (FTIR) spectroscopy and TGA. FTIR and TGA results indicated that APTES modifier agent and AMPS monomer were successfully grafted onto the MOF nanoparticles. The grafting efficiency of PAMPS polymer onto the MOF nanoparticles was estimated from TGA thermograms to be 33%. Also, sulfonated polymer/MOF hybrid nanoparticles showed a proton conductivity as high as $4.9 \times 10^{-5}$ Scm$^{-1}$. Nitrogen adsorption of modified NH$_2$MIL-53(Al) showed also a decrease in pore volume. The morphology and crystalline structure of MOF nanoparticles before and after the modification processes were studied by SEM and XRD, respectively.

INTRODUCTION

Nowadays, metal–organic frameworks (MOFs) have attracted considerable attention because of their versatile structures and higher surface areas compared to conventional fillers that allow almost unlimited ways to extend their functionality and improve their properties.$^{1,2}$ Due to their diverse porous structures and high surface areas, MOFs are used for a variety of important applications such as size-selective molecular catalysis,$^{3,4}$ gas adsorption/storage,$^{5,6}$ adsorption of organic molecules,$^{7-11}$ as carriers for proton exchanger material$^{12-16}$ etc. Recently, a few reports have demonstrated that the ion conductivity in MOFs could approach the specifications required for battery electrolytes and proton exchange membrane fuel cells (PEMFCs).$^{17,18}$ In the PEMFC, the most important part for cell efficiency and durability is the proton exchanger. The proton exchanger performance of a PEMFC is related to the presence and amount of acidic groups such as carboxylic, sulfonic or phosphonic groups in the polymer electrolyte membrane.

Different strategies have been followed to introduce new super-acidic MOFs using self-assembly of the corresponding functionalized ligands (or direct synthesis)$^{19-28}$ traditional sulfonation methods$^{29,30}$ post-synthetic modification$^{31,32}$ and the host – guest method.$^{13,16}$ The main limitations of a direct synthesis strategy are the choice of a cation and anion with weak coulombic interaction and the necessity of a new functional ligand. In fact, the synthesis of functional MOF materials has been a challenge because ligand functionality may directly coordinate to the metal ions. For this reason, the introduction of efficient functionalization methods without using functional ligands is the main issue in the synthesis of functional MOF materials. On the other hand, the sulfonation method uses as a post-synthetic treatment method; however, this method has not found wide use because of its harsh functionalization conditions and the limited chemical stability of MOF structures in acidic aqueous solutions.$^{29,30}$ Subsequently, the post-synthetic modification of

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MOFs with some reagents such as sulfonic acid functionalities. An alternative new approach is to absorb the pores of MOF particles with non-volatile proton conductive molecules in order to induce continuous proton transport pathways for efficient proton transport. The inclusion of various type of guest molecules such as weakly acidic triazole, imidazole and histamine in porous metal–organic structures could provide new proton conducting solids and efficient proton exchangers, but only at temperatures above 100 °C. Therefore, introducing a new approach to achieve super-acidic MOFs is one of the research priorities of material scientists.

There is an increasing use of the post-polymerization modification, and it seems that this approach can also be promising for introducing organic/inorganic hybrid MOFs as new super-acidic solid (nano)materials for PEMFC application. Polymerization of sulfonated monomers such as 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and styrene sulfonic acid can be a good route to prepare intact MOF nanoparticles with higher sulfonic acid functionality. Three major methods to modify inorganic and organic substrates have been investigated: ’grafting from’, ‘grafting through’ and ’grafting to’. Grafting methods using various kinds of polymerization are good routes to achieve higher surface modification efficiency and grafting density. To our knowledge, there is no report on using post-polymerization modification onto the surface of functionalized MOF. It is expected that the surface-initiated polymerization of sulfonated monomers can create a flexible grafting sulfonated polymer shell that provides strong interfacial interaction with the polymer matrix and also enhances the proton conductivity properties of MOF nanoparticles at low temperature.

The present work describes the development of a new method to prepare sulfonic acid functionalized frameworks as proton-conducting solid electrolytes to create hybrid MOFs with new properties. In this study, we utilized amino-terminal silanes to introduce a new amino functionalized MOF as a precursor for surface-initiated redox polymerization modification. It is expected that amino-silane shell protects the MOF nanoparticles in various functionalization conditions and makes MOF nanoparticles with higher amino functionality, thereby facilitating high grafting efficiency. Subsequently, we take advantage of post-polymerization modification to attain intact MOF nanoparticles containing pendant sulfonic acid groups.

**EXPERIMENTAL**

**Materials**

Silica nanoparticles (Sigma, Iran, Tehran), AMPS (99% from Aldrich, Iran, Tehran), 2-amino-terephthalic acid (2-ATA) (99% from Aldrich, Iran, Tehran), aluminium nitrate hexahydrate (Al(NO3)3·9H2O) (99.997% from Sigma-Aldrich, Iran, Tehran), (3-aminopropyl)triethoxysilane (APTES) (97% from Aldrich, Iran, Tehran), N,N-dimethylformamide (DMF) (99.9% from Merck, Iran, Tehran) and ammonium cerium sulfate (ACS) (>94% from Sigma-Aldrich, Iran, Tehran) were received.

**Synthesis of amino-functionalized MOF [NH2-MIL-53(Al)]**

NH2-MIL-53(Al) nanoparticles were synthesized as previously reported. A solution of Al(NO3)3·9H2O (0.75 g, 2 mmol) and 2-ATA (0.58 g, 3.2 mmol) in DMF (27 mL) was kept at 130 °C for 72 h in a Teflon-lined autoclave bomb. Then the obtained solids were suspended in DMF and separated from the solution by centrifugation. The NH2-MIL-53(Al) nanoparticles were washed with DMF under sonication for 20 min. After centrifuging, the obtained functionalized MOF was washed several times with acetone. Washing with excess hot acetone (60 °C) was also done to remove any unreacted reagent. The MOF nanoparticles were dried under vacuum at 80 °C (yield 37%).

**Synthesis of amino-silane modified NH2-MIL-53(Al) (MOF/Si)**

NH2-MIL-53(Al) nanoparticles (0.2 g) were suspended in ethanol (60 mL) through sonication. APTES (5 mL) and distilled water (2 mL) were added to the solution for a mild sol–gel reaction of silica on MOF nanoparticle surfaces and stirred for 48 h at room temperature. After centrifuging, the modified MOF obtained was suspended in ethanol and stirred for 48 h at room temperature. The amino-silane modified MOF nanoparticles were then dried under reduced pressure at 60 °C (yield 5.4%).

**Graft polymerization of AMPS from amino-silane modified NH2-MIL-53(Al) (MOF-g-PAMPS)**

The redox graft polymerization was performed in a 100 mL laboratory reactor which was placed in an oil bath thermostatted at the desired temperature. MOF/Si (0.2 g) was suspended in AMPS salt solution (3 g, 0.014 mol, dissolved in 10 mL methanol/deionized water mixture, pH 5), and then the reactor was degassed and backfilled with nitrogen gas three times and left under N2. The bath experiment was run by adding ACS (80 mg, 0.13 mmol, dissolved in 10 mL deionized water) and then increasing the reaction temperature to 40 °C; the mixture was stirred at this temperature for 12 h. After polymerization, the suspension obtained was precipitated by adding an excess of acetone. The MOF-g-PAMPS was protonated by dispersing in a 0.1 mol L⁻¹ HCl solution for 1 h. The product was washed with an acetone/water mixture three times and dried under reduced pressure at 60 °C (yield 33%).

**Characterization**

Fourier transform infrared (FTIR) spectroscopy was carried out on a Bomem FTIR instrument by averaging 32 scans with a wavenumber resolution of 4 cm⁻¹. XRD patterns were collected on an X-ray diffraction instrument (Siemens D5000) with a Cu target (λ = 0.1540 nm) at room temperature. The system consisted of a rotating anode generator which operated at 35 kV and 20 mA. The samples were scanned from 2θ = 0°−50° in the step scan mode; the diffraction pattern was recorded using a scintillation counter detector. TGA measurements were done on a PL thermogravimetric analyzer (Polymer Laboratories, TGA 1000, UK). Samples of about 10 mg were analyzed from ambient temperature to 800 °C at a heating rate of 10 °C min⁻¹. All TGA analyses were done under a nitrogen atmosphere. SEM (Zeiss SUPRA 35VP) was used to examine the morphology of the MOF nanoparticles. The MOF surface area was measured at 70 K using a BELSORP-minil. An Autolab PGSTAT302N Potentiostat-Galvanostat Impedance Analyzer (Ecochemie) was used to obtain the proton conductivity of the pellets in the frequency range from 0.1 to 10⁹ Hz. The proton conductivity was calculated using

\[ \sigma = \frac{L}{RA} \]  

where \( \sigma \), \( A \) and \( L \) are the conductivity (S cm⁻¹), pellet thickness (cm) and electrode area (cm²), and \( R \) is the bulk resistance of the pellets (Ω).
RESULTS AND DISCUSSION
Characterization of the organic/inorganic hybrid MOFs demonstrates that it is possible to synthesize sulfate-stable MOF structures using the post-polymerization method. It should be noted that use of the post-polymerization method is not limited to MOFs with a high chemical stability and can be applied to a wide variety of MOF structures ranging from high to low chemical stability. The synthesis of an amino-silane modified NH2MIL-53(Al) and surface-initiated redox polymerization of AMPS monomer from MOF nanoparticles are shown in Scheme 1. A capping layer of silica forms on MOF nanoparticle surfaces when the alkoxyl groups of APTES hydrolyze and react with amine groups on the surface of the MOF. The amino-silane compound is one of the most commonly used capping agents and it can be used for post-modification of the nanoparticles. In fact, amino-silane compound is used to improve the chemical stability of MOF nanoparticles in acidic conditions by providing a silane layer around them. In addition, modification of MOF surfaces with APTES modifier agent makes it easy to attach polymer chains to the surface. The methylene group bonded with an amine group is activated at redox polymerization conditions and generates radical active sites for further modification of the NH2MIL-53(Al). The successful preparation of NH2MIL-53(Al), MOF/Si and MOF-g-PAMPS was confirmed by FTIR and TGA analysis.

The FTIR spectra of NH2MIL-53(Al), MOF/Si and MOF-g-PAMPS are shown in Fig. 1. According to the results, some characteristic peaks which can be attributed to \(-\text{COO}^-\) asymmetric stretching vibration at 1608 and 1505 cm\(^{-1}\) as well as to the \(-\text{COO}^-\) symmetric stretching vibration at 1422 cm\(^{-1}\) are present in all MOF samples. The absorption peak at 1690–1670 cm\(^{-1}\) is attributed to free aminoterephthalic acid molecules in both NH2MIL-53(Al) and MOF/Si, encapsulated within their pores in the protonated form (\(-\text{COOH}\)). The bands at 3400–3500 cm\(^{-1}\) are due to the \(\text{NH}_2\) group as well as the aminoterephthalic acid in the pores. Additionally, the characteristic peaks at 3400–3500 cm\(^{-1}\) are due to the NH\(_2\) group as well as the aminoterephthalic acid in the pores. The bands at 3400–3500 cm\(^{-1}\) are due to the NH\(_2\) group as well as the aminoterephthalic acid in the pores. Additionally, the characteristic peaks at 1100 and 600 cm\(^{-1}\) relate to the stretching vibration of Si – O – Si and Si – O bonds and indicate that APTES is successfully coated onto the MOF. In the case of the MOF-g-PAMPS samples
The first T NH2MIL-53(Al) mainly because of the presence of silane compounds in the pores of the structure. The second decomposition temperature (highest temperature peak) is related to the decomposition of the polymer-grafted MOF occurs in more than one step. For the MOF/Si nanoparticles, the residual weight loss at 800 °C is higher than that of unmodified NH2-MIL-53(Al), in which unreacted amino-silane modified MOF is distinctly lower and broader than NH2MIL-53(Al) nanoparticles. This disappearance and broadening of XRD peaks is attributed to the formation of low crystallinity and a partially amorphous morphology.

The structural stability and changes in the crystallinity before and after amino-silanization were monitored using XRD patterns. The diffraction patterns of the synthesized NH2-MIL-53(Al) (Fig. 3) showed high crystallinity with reflections in the range 5°–30°. XRD patterns of as-synthesized NH2-MIL-53(Al) matched well with the previously reported diffraction.10,43 The appearance of the main peak at 9.7° indicated that the pattern corresponded to the as-synthesized NH2-MIL-53(Al), in which unreacted amino-terephthalic acid was trapped in the pores. From the XRD patterns it is concluded that the height of the diffraction lines of as-synthesized NH2-MIL-53(Al) is distinctly lower and broader than for NH2-MIL-53(Al) nanoparticles. This disappearance and broadening of XRD peaks is attributed to the formation of low crystallinity and a partially amorphous morphology.48,49 In fact, this
Figure 3. XRD patterns of NH₂MIL-53(Al) and amino-silane modified NH₂MIL-53(Al).

Figure 4. N₂ adsorption–desorption isotherms of NH₂MIL-53(Al) and amino-silane modified NH₂MIL-53(Al) at 70 K.

means that the NH₂MIL-53(Al) nanoparticles are completely covered by the APTES layer. A variation in the XRD patterns of amino-silane modified NH₂MIL-53(Al) further confirms that APTES is attached on the surface of the MOF nanoparticles through amino-silanization. The successful synthesis and modification of NH₂MIL-53(Al) were further confirmed by Brunauer–Emmett–Teller (BET) analyses. In Fig. 4, a comparison of the N₂ adsorption at 77 K of the NH₂MIL-53(Al) and amino-silane functionalized NH₂MIL-53(Al) is depicted. According to the BET results, the measured surface area of NH₂MIL-53(Al) is 782 m² g⁻¹ which is in agreement with the surface area values reported in the literature. Additionally, nitrogen adsorption reveals a decrease in the specific surface area of NH₂MIL-53(Al) nanoparticles after the amino-silanization process (138 m² g⁻¹). The observed large decrease in the pore volume of the NH₂MIL-53(Al) is due to the functionalization of the outer and inner surfaces of MOF nanoparticles with APTES modifier agent and the formation of a silica shell on the MOF nanoparticle surfaces, as shown in the TGA analyses (Fig. 2). Additionally, this decrease may also be a result of pore blocking on the crystal surface during the silanization modification which is also confirmed by the attachment of APTES modifier agent on the surface of NH₂MIL-53(Al) nanoparticles.

SEM was used to detect the morphology and particle size of NH₂MIL-53(Al), MOF/Si and MOF-g-PAMPS. SEM micrographs of the synthesized NH₂MIL-53(Al) crystals before and after amino-silanization are shown in Fig. 5. The SEM images (Fig. 5(A)) showed rod-shaped nanoparticles approximately 100 nm in length and with a diameter less than 50 nm for the NH₂MIL-53(Al), and the size distribution of NH₂MIL-53(Al) nanoparticles is quite uniform. SEM images of amino-silane functionalized MOF showed no change in the nanoparticle morphology after amino-silanization; however, the average nano-rod length increased from 100 to 400 nm while the diameter stayed relatively constant (40–50 nm). The increase in length resulted in an increase in aspect ratio (rod length divided by diameter) of amino-silane functionalized MOF nano-rods. The ability to synthesize high aspect ratio nanoparticles is an important objective in nanocrystal synthesis, as this parameter can influence various properties. Using a high aspect ratio nanofiller is also a key factor to obtain high performance nanocomposites because interfacial adhesion between nanofiller and polymer matrix is controlled by the aspect ratio of the nanofillers. A large interfacial area of polymer/nanofiller in combination with their surface interactions by both physical and chemical means can improve the nanocomposite properties. The successful amino-silane modification of NH₂MIL-53(Al) nanoparticles observed in SEM images was expected based on the grafting efficiency which is in agreement with the observed low weight loss and high char content of amino-silane modified MOF nanoparticles, as shown in the TGA analyses (Fig. 2).

Additionally, imaging of the MOF-g-PAMPS using SEM revealed distinct grafted polymer on the surfaces of the MOF nano-rods. A relatively homogeneous distribution of grafted polymer throughout the nanoparticles was also observed. From SEM images (Figs. 5C1–5C3), the graft polymerization onto the surface of the MOF did not seem to change the morphology of the NH₂MIL-53(Al) frameworks. Strong adhesion between the MOF nanoparticles is a result of the polymer shell which can be comprehended by comparison of SEM images. Furthermore, SEM shows that MOF nanoparticles closely associated with each other as a result of post-polymerization. Limited agglomeration of the MOF nanoparticles may be expected from the relatively large particle size of amino-silane modified NH₂MIL-53(Al) as evident by SEM images (Fig. 5B) because the amount of PAMPS grafted onto the MOF’s surface is relatively low (33%). The large surface area of the MOF nanoparticles and their rod shape allow easy stacking to form agglomerates. Therefore, the aggregation remains to some degree during post-polymerization of the MOF nanoparticles. Thus, a hybrid particle with larger size than unmodified MOF cannot be formed from only one original MOF nanoparticle covered by a polymer shell. It is suggested that several MOF nanoparticles may form a core with a PAMPS shell
existing around the MOF nanoparticles. The functional groups on the surface of amine-functionalized MOF can provide a starting platform for polymer grafting; the high grafting density makes a polymer shell that improves the strong interfacial interaction between the polymer matrix and the MOF. It is expected that post-polymerization provides good compatibility and a good dispersion of nanoparticles in proton exchange nanocomposite membranes and enhances the superior performance of the membranes. In addition, alternating-current impedance measurements of MOF-g-PAMPS were also carried out to study the proton conductivity value. The proton conductivities of MOF-g-PAMPS at room temperature and in the dried state were calculated using Eqn (1). The result obtained shows that the post-polymerization modification of MOF nanoparticles by AMPS as a sulfonated hydrophilic monomer provides an anhydrous proton conductivity of \(4.9 \times 10^{-5} \text{ S cm}^{-1}\) at room temperature (Fig. 6). The desirable proton conductivity value of MOF-g-PAMPS strongly supports the idea of our work that polymerization of sulfonated monomers is a good route to obtain intact MOF nanoparticles with higher sulfonic acid functionality. It is expected that sulfonic acid functionalized MOF nanoparticles as a proton exchanger can induce continuous ion transport channels in the polymer matrix and improve the proton conductivity of proton exchange membranes in fuel cells.

**CONCLUSION**

We have developed a new and straightforward procedure to prepare super-acidic MOFs with a high aspect ratio. Super-acidic MOF nanoparticles were prepared by graft polymerization initiated from the surface of amino-silane functionalized MOF nanoparticles. FTIR analysis was carried out of the amino-silane modification and grafted PAMPS polymer identification. Also, successful amino-silanization and grafting of sulfonated hydrophilic AMPS monomer onto the surface of amino-functionalized MOF nanoparticles.
nanoparticles was confirmed by TGA results. The grafted amounts of sulfonated polymers were calculated from TGA thermograms to be 33% for MOF nanoparticles. SEM results showed rod-shaped nanoparticles approximately 100 nm in length with a diameter less than 50 nm for the synthesized NH₂MIL-53(Al) nanoparticles. Also, sulfonated polymer/MOF hybrid nanoparticles showed a proton conductivity as high as 4.9 × 10⁻⁵ S cm⁻¹. They showed a uniform particle size distribution and any change in morphology of NH₂MIL-53(Al) nanoparticles was proved by XRD and SEM images. The SEM images showed a rod-shaped morphology of NH₂MIL-53(Al) nanoparticles. After two-step modification, it is expected that sulfonic acid functionalized nanoparticles can be used as a proton exchanger for improvement of the proton conductivity and the mechanical and thermal properties of proton exchange membranes in fuel cells.

REFERENCES