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Reversible water capture by a charged metal-free porous polymer

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ABSTRACT

Climate change and industrial pollution threatens the availability of clean water. Although established protocols of water treatment exist, water capture by porous materials has emerged as a viable alternative to energy intensive processes. Here we introduce a new charged porous polymer that is capable of capturing and releasing water by simple humidity or temperature swings. The quaternary amines on the framework structure attract water molecules and further solvate by coordination. The porosity of the network structure also provides enough void where water can diffuse throughout the solid. Water uptake capacity of the porous polymer surpasses common desiccants like silica gel and molecular sieves, and has the potential to act as an organic desiccant in applications like electronics or food packaging. © 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Water scarcity, driven by a rapidly changing climate can threaten food sources of all living things [\[1\].](#page-4-0) Dry land farming, which depends on accurate timing of seeding with the rainfall, leaves soil unprotected against dust storms if a shift in precipitation spoils the plantation schedules. Water in air is in practically unlimited amounts because of the active equilibrium between vast liquid water sources and the earth's atmosphere [\[2\]](#page-5-0). In order to rapidly capture water from air, two mechanisms are the most appropriate: (i) Namibian beetle way $-$ dewdrop harvesting on hydrophilic-hydrophobic alternative surface by condensation over temperature swings between day and night (physisorption) [\[3\],](#page-5-0) (ii) Zeolites – strong chemical binding (chemisorption) $[4,5]$. The former concept involves physical condensation of water on a hydrophilic (ideally chilled) surface, which is suitable in highly humid conditions. On the other hand, chemisorption would be best for dry atmospheres in which vapor content is diluted (10,000 ppm, data from NASA) [\[6\]](#page-5-0), but there is a chance of difficulty in desorption due to the strong binding of water. It is important to note that physical adsorption of water from atmosphere happens on all hydrophilic surfaces but mostly not in economically feasible production levels.

Organic or hybrid materials could offer a middle ground by providing less strong binding to water (hence easier desorption) but more affinity than physical condensation, i.e., beetle-like

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mechanisms. Examples include a deliquescent polymer [\[7\],](#page-5-0) sponge-like cotton fabric for reversible water uptake $[8]$, porous metal-organic frameworks (MOFs) with mesoporous cages as water adsorbents in energy-efficient dehumidification [\[9\],](#page-5-0) zirconium MOFs for water adsorption $[10]$ and active carbons cuboids for atmospheric water capture $[11]$. The challenge in all these advanced materials is always the imbalance between capacity and cost.

Porous organic polymers (POPs) [\[12\]](#page-5-0) have drawn attention in recent years as due to their structural designability [\[13\]](#page-5-0) and tunability [\[14\]](#page-5-0), high porosity [\[15\]](#page-5-0), and physical and chemical properties for applications such as gas storage [\[16,17\]](#page-5-0), gas separation $[18,19]$, catalysis $[20,21]$, charge carriers $[22]$, and sensors $[23]$. It is important to note that many acronyms have been used without inferring or intending much chemical information (unlike zeolitic materials) but rather a family name for the respective class of new POPs. We have been working on a class of inexpensive POPs, indexed as Covalent Organic Polymers (COPs) for applications like gas capture [\[24\]](#page-5-0) and water treatment [\[25\]](#page-5-0). These network polymers have permanent pores and are insoluble, amorphous structures with quantifiable functional group distributions. COPs are generated via covalent linkages between cores and linkers, and in principle, they are neutral polymers. When tertiary nitrogen-containing linkers are used, however, quaternary ammonium bridges form and in turn, lead to the charged network polymers. The charged COPs can have improved solubility in polar solvents, as well as higher reactivity through improved electrostatic interactions [\[26,27\]](#page-5-0). The stronger charge-based interaction is known to achieve better and

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sometimes unexpected selectivity toward target molecules [\[25\]](#page-5-0).

Despite their potential, charged COPs are rarely reported, maybe because the charge-assisted synthesis often yields low surface area [\[28\],](#page-5-0) and requires sacrificing agents (such as silica nanoparticles) to further generate porosity [\[29\]](#page-5-0). Here, we designed and synthesized a charged porous polymer, COP-120 that features quaternary ammonium linkages. COP-120 exhibits a unique hygroscopic nature owing to its inherent charges on the superstructure. The intrinsic porosity and hydrophilic functionality of COP-120 facilitate a reversible and rapid uptake of water from atmosphere, which could be triggered by a simple variation of relative humidity. In an identical set-up, COP-120 wins over commercial desiccants such as molecular sieve and silica gel blue, in terms of moisture adsorption capacity and recyclability.

2. Experimental methods

Synthesis of COP-120. The COP-120 was synthesized by a modified triazine containing COP making procedure [\[30\]](#page-5-0) (Fig. 1). In a typical experiment, 1,4-Diazabicyclo[2.2.2]octane (12.5 g, 0.112 mol) is dissolved in 1,4-dioxane (500 mL) and kept at 288 K. Cyanuric chloride (13.75 g, 0.075 mol) dissolved in 1,4-dioxane (150 mL) was added drop-wise to the above solution with continuous stirring at 288 K. The solution was stirred at 288 K for 1 h, before being stirred at 298 K for 2 h and then at 358 K for 21 h. The white precipitate was filtered and washed with 1,4-dioxane three times. Finally, the precipitate was dried at 383 K under vacuum for 5 h, and the obtained product was stored in moisture-free condition to prevent from any unwanted degradation.

Characterization. FT-IR spectra were obtained as KBr pellet using a Perkin-Elmer FT-IR spectrometer. Elemental analysis (CHNO) was performed on a FLASH 2000 of Thermo Scientific. Ion Chromatography for chlorine detection was carried out using a Compact IC Flex of Metrohm. Thermogravimetric analysis (TGA) was conducted with a DTG-60A of Shimadzu by heating the samples to 800 $^{\circ}$ C at 10 $^{\circ}$ C min⁻¹ under desired atmosphere. Porosity of samples was analyzed with Micromeritics Triflex accelerated surface area analyzer at 77 K after all the samples were pre-degassed at 120 \degree C for at least 6 h under vacuum. The specific surface area of the samples was derived from Brunauer-Emmett- Teller (BET) model, and the pore size distribution was determined by Barrett-Joyner-Halenda (BJH) model. FE-SEM (Field Emission Scanning Electron Microscopy) was performed using a Nova 230. XRD (X-ray Diffraction) pattern of samples was acquired from 5° to 60° by

using a Rigaku D/MAX-2500 Multi-purpose High power X-ray diffractometer. For XRD measurement under vacuum condition, sample was loaded on an air-sensitive sample holder of Rigaku in air-free glove box. Hydrodynamic size of samples was measured by DLS (Dynamic Light Scattering) method using an Otsukael ELS-Z2. ¹H NMR was measured on a Bruker AVANCE 300 MHz with D_2O as a solvent.

Water uptake studies. Volumetric water isotherms were measured on a BELSORP-aqua³ of Microtrac BEL. The measurement temperature was controlled with a water circulator. Gravimetric water uptake and cyclic performance were analyzed using Dynamic Vapor Sorption (DVS) Intrinsic of Surface Measurement Systems. The DVS system is equipped with an electronic Ultrabalance™ and humidity sensor for measuring mass and humidity change, respectively. Mass resolution was \pm 0.1 µg and humidity accuracy was \pm 1% RH (Relative Humidity). The procedure involved 5% steps of RH between 0 and 90% RH following an initial drying at RH 0% under He condition. The measurement was started to be monitored when the mass equilibrium was established with no weight change of more than 1 μ g over a period of 5 min. All samples for water uptake were pre-gassed at 120 \degree C for at least 6 h under vacuum. The water uptake in weight percentage (wt %) is derived from $[(adsorbed amount of water)/(amount of absorbent) x 100].$

3. Results and discussion

Physicochemical properties of COP-120. The formation of charged COP-120 was analyzed first with FTIR ([Fig. 2\)](#page-2-0). When compared with the starting precursors (Cyanuric chloride $-$ CC, and DABCO), the tertiary amine C-N stretching vibration from DABCO at 1055 cm⁻¹ disappears after the COP formation, indicating the successful quaternization of the core triazines. Since the resulting COP-120 is highly charged it attracts atmospheric water, therefore, eOH vibrations are expected due to the adsorption of moisture during the analysis. COP-120 (powder) shows several bands around 1500 cm^{-1} region, which corresponds to the typical stretching modes of C-N heterocycles. The band at 800 cm^{-1} is from triazine moiety and a broad band at 3500 cm^{-1} is coming from $-OH$ vibration from water. COP-120 aqueous solution displays similar trend with its original spectrum but a stronger band from $-\text{OH}$ region.

Interestingly, COP-120 also exhibits ordered structure. It is not commonly observed during the irreversible formation of porous polymers, except a few studies where pi-stacking and charge

Fig. 1. Synthesis of charged COP-120.

Fig. 2. FTIR spectrum of COP-120 and its starting materials.

repulsions govern the 3D stacking [\[31\].](#page-5-0) When subjected to moisture, however, the hygroscopic nature of COP-120 also affects its crystallinity. Once the sample was measured in standard atmosphere at room temperature, it absorbed water from the atmosphere so that COP-120 exhibited very poor crystallinity (Fig. 3). When the sample was pre-evacuated and measured in vacuum condition, the XRD pattern becomes much stronger in intensity with clear crystallinity (Fig. 3). The low angle peak before 10° was found in COP-120, indicating the presence of ordered arrangement with mesoporosity. In particular, the low angle peak before 10° was not detected in the normal condition, however, it only appeared when measured in vacuum condition. In the presence of moisture,

Fig. 3. XRD patterns of COP-120 measured at (a) vacuum condition with preevacuation, (b) when exposed to humidity, and (c) after recycling.

as water molecules hinder the arrangement of polymer structure, the structure is disoriented, leading to the less crystallinity. This recyclable ordering implied the reversible water adsorption promise of COP-120.

The COP-120 was not highly porous compared to other COP structures in the literature, since there is stacking between charged pi-systems. BET specific surface area of COP-120 was about 42 m^2/g with pore volume of 0.15 cm^3/g . The N₂ adsorption-desorption isotherm exhibited type II isotherm of mesoporous structure, corresponding to the calculated pore size of 28.6 nm [\(Fig. 4](#page-3-0)a). From thermogravimetric analysis, COP-120 was turned out to be stable up to 170 °C both in air and N_2 condition ([Fig. 4b](#page-3-0)). Compared to porous materials for atmospheric water uptake such as Zr-MOF [\[10\]](#page-5-0) and carbon cuboid $[11]$, COP-120 has much lower surface area, but highly comparable water uptake capacity. Large pores and high affinity toward water molecules result in high water uptake capacity in a low pressure.

In order to verify the composition of COP-120, we carried out elemental analysis [\(Table 1\)](#page-3-0). C, H, N and O were detected through combustive methods and the amount of chlorine was analyzed by ion chromatography with aqueous COP-120 samples. COP-120 shows very similar nitrogen content in all structures. The oxygen presence is clearly due to adsorbed water and this was also reflected by the elevated hydrogen content. An important observation is the preservation of the chlorine content, even with small increase in relative quantity.

If COP-120 is mixed with liquid water, a complete dissolution is observed without a noticeable change in its viscosity. The soluble COP-120 shows a hydrodynamic size ranging over micron scale ([Fig. 5](#page-3-0)). Owing to high affinity toward water molecules, surface of COP-120 is covered with electric dipole layer of adhering water, finally generating larger size with the solvation layers. COP-120, however, was insoluble in common organic solvents owing to its network structure (Fig. S1).

Thanks to the high solubility in water, COP-120 was further characterized by ¹H NMR in D₂O. From the ¹H NMR spectrum of COP-120 (Fig. S2), three sets of signals were observed; (a) methylene protons in a disubstituted DABCO unit at 3.74 ppm, (b) protons of a monosubstituted DABCO unit at 3.95 and 3.64 ppm, and (c) protons of DABCO units in polymeric units shown in the range between 3.53 and 4.23 ppm. The NMR analysis shows that if COP-120 is fully immersed in water, it will reveal macrocycles and polymeric units, mainly due to a partial dissociation of COP-120 in water.

Reversible moisture uptake capability of COP-120. The deliquescent nature of COP-120 led us to measure its maximum water adsorption capacity and, more importantly, its cyclability. As displayed in [Fig. 6a](#page-3-0), COP-120 exhibited type III isotherm and the maximum water uptake analyzed from volumetric analysis reaches 561.65 cm³/g (44.93 wt%, at $P/P_0 = 0.9$). The adsorption isotherm has been steep in the middle ($P/P₀ = 0.7$) owing to phase transition of COP-120 as large amount of water is absorbing. Desorption was conducted via pressure-swing method, and hysteresis occurs with 111.6 cm^3/g (8.93 wt%) of remnant water. The reversible moisture uptake capability of COP-120 was investigated in a continuous flow using Dynamic Vapor Sorption (DVS) system with relative humidity programming set-ups. The moisture uptake of COP-120 was measured in relative humidity from 0 to 90%, and the mass change was monitored as the humidity changes. The maximum adsorption was achieved at RH 90%, showing significant increase in mass by taking water vapor from the atmosphere ([Fig. 6b](#page-3-0)). The total water uptake from gravimetric analysis is 72.02 wt%, which is 1.6 times higher than that of the volumetric measurement. The adsorption and desorption isotherm is highly reversible, and adsorption hysteresis is 1.94 wt%, 4.6 times lower than that of the volumetric

Fig. 4. (a) N₂ adsorption-desorption isotherm of COP-120 with the corresponding BJH pore size distribution (inset), and (b) thermogravimetric analysis plot.

Table 1

Elemental analysis of COP-120. Chlorine content was analyzed by Ion Chromatography. All the samples were pre-dried at 120 \degree C to remove remnant water as much as possible. Once saturating with water, COP-120 was freeze-dried for characterization.

Material	Element		N	н	$\mathbf{\Omega}$	
COP-120-Theo	Expected (%)	40.87	23.83	5.14	$\qquad \qquad -$	30.16
COP-120	Found $(\%)$	3915	22.58	6.40	7.95	18.53
COP-120 cycled	Found $(\%)$	36.72	21.72	6.26	11 57	20.03

Fig. 5. Hydrodynamic size in water (measure by dynamic light scattering) at 25 \degree C with 10 wt% COP-120 aqueous solution.

Fig. 7. DVS cycles using COP-120 and two control samples. The RH condition was controlled to simulate dry day time and humid night time. Day and night time shifts every 12 h. Day time humidity was to be RH 30% and night time humidity was RH 80%. Pre-dry was done at RH 0%. During all the experiments, temperature was adjusted at room temperature, 25 °C.

Fig. 6. (a) Volumetric, (b) gravimetric water vapor adsorption-desorption isotherms of COP-120 at room temperature. Fully saturated COP-120 was dried at 120 °C for 24 h under vacuum, and further tested for dynamic vapor adsorption. The cycled sample did not exhibit any loss in uptake capacity after being exposed to moisture.

Fig. 8. Photograph of (a) as-synthesized COP-120, (b) the powder exposed to humid air for overnight (25 °C, 60% RH), and (c) fully saturated COP-120 in water. SEM image of (d) the as-synthesized COP-120, (e) the cycled powder after being dried at 120 °C, and (f) COP-120 film from COP-120 aqueous solution drop-casted and dried at 120 °C.

We believe the deliquescent nature of COP-120 is originated from the interaction between quaternary ammonium sites of COP-120 and the lone pair of water molecules. As the water is attracted and covered on the surface of COP-120, the water shell further accelerates more water molecules to be adsorbed. COP-120 absorbs water until the moisture of the atmosphere is equilibrated with that in COP-120.

The moisture uptake cycles were measured by varying RH conditions. At room temperature, RH was simulated to be day and night conditions as a cycle, and the RH for day and night time was set to be 30% and 80%, respectively. Three cycles of mass change was monitored. As displayed in [Fig. 7,](#page-3-0) the cyclic water adsorptiondesorption of COP-120 was reversible for three cycles with average capacity of 36%. At the very first cycle, the capacity went up to 46%, however, the capacity from the second cycle stayed around 36%. The day time RH was 30% in which the COP-120 at RH 30% can take about 7% of moisture [\(Fig. 7\)](#page-3-0). The capacity difference of 10% is thus attributed to moisture equilibrium of COP-120 at day time atmosphere.

The moisture uptake capability of COP-120 was then compared with commercially available desiccants, molecular sieve 4A and silica gel blue. Interestingly, under the simulated cycling set-up, both desiccants showed less capacity as well as slower desorption behavior. The average capacity of three cycles for molecular sieve 4A and silica gel blue was 5.6% and 15.8%, respectively, which is 6.4 and 2.3 times lesser than that of COP-120, respectively. Compared to the COP-120, the desorption speed for the two control desiccants was also slow with gradual decrease in mass. This may be due to the smaller pore size of the desiccants which makes them suffer from the difficulty in desorbing water molecules as the RH decreases ([Fig. 7](#page-3-0)).

Lastly, we have tested the morphological evolution of COP-120 during the moisture adsorption (Fig. 8). The as synthesized COP-120 has a white color and powder morphology with randomly distributed plates at micro-scale. Upon exposing to moisture, the deliquescence turns the solid into a yellow viscous liquid, with potential for film formation ability. After humidity cycle, the plates are more smooth (Fig. 8e) but not fully continuous. Once COP-120 is fully solubilized in water and spread on a carbon tape, a flat film is achieved (Fig. 8f).

4. Conclusion and future directions

In summary, we introduced a new COP with inherent charge in the network structure. Thanks to the quaternary ammonium linkages, the COP-120 exhibited excellent moisture uptake capacity from atmosphere. The capacity and kinetics of the cycles far exceeded the common desiccants such as silica gel and molecular sieves. Future studies should focus on the characterization of its micro-structure to better understand its exact mechanism for capturing atmospheric water. The hygroscopic nature of COP-120 can also be used for moisture sensing [\[32\]](#page-5-0) and heat exchange applications [\[33\].](#page-5-0) The counter anion on COP-120 (typically, chlorine ions) can be easily exchanged into other anions, and the effect of the anions on its toxicity, moisture uptake capacity, and stability can be investigated in the subsequent studies. COP-120 containing quaternary ammonium sites can act as effective catalysts for Lewis acid catalyzed reactions such as $CO₂$ epoxidation into cyclic carbonates [\[34\]](#page-5-0).

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Appendix A. Supplementary data

Supplementary data related to this chapter can be found at [http://dx.doi.org/10.1016/j.polymer.2017.05.071.](http://dx.doi.org/10.1016/j.polymer.2017.05.071)

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The authors regret that the printed version of the above article missed the co-author name and affiliation for Dr. Bandar A. Fadhel from Saudi Aramco-KAIST CO2 Management Center, Daejeon, South Korea. The authors would like to apologise for any inconvenience caused.

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