

# Facile synthesis of nitrogen-enriched microporous carbons derived from imine and benzimidazole-linked polymeric framework for efficient CO<sub>2</sub> adsorption



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## ABSTRACT

Microporous organic polymers containing heteroatoms are considered as promising substrates for CO<sub>2</sub> capture and separation with a tangible effect on the atmosphere and clean energy applications. In the present work, we have reported a cost-effective strategy for designing a series of carbonized products by high-temperature treatment of an imine and benzimidazole linked polymer (IBLP). The resulting materials exhibit a high surface area with narrow micropores. CO<sub>2</sub> adsorption measurements reveal a notable uptake capacity up to 130.4, 98.4, and 87.5 mg/g at 273, 298, and 308 K, respectively, along with the high isosteric heats of adsorption (30.4–32.2 kJ/mol). Presence of micropores and heteroatom in the solid adsorbents with the high thermal stability accompanied with excellent CO<sub>2</sub>/N<sub>2</sub> selectivity proclaimed the nitrogen-enriched carbon as promising candidates for CO<sub>2</sub> scrubbing technology.

## 1. Introduction

The recent progress in material design has triggered the fabrication of porous materials comprising of organic [1] and organic-inorganic hybrids [2] as potential contenders for gas adsorption [3], sensing [4] energy storage [5], drug delivery [6], electronic devices [7], and catalysis [8]. One of the emerging class of porous materials is the organic polymers, tailored by covalently bonded monomer units to achieve high porosity, low skeletal density and excellent chemical and thermal stability. These covalently bonded polymers were synthesized previously by various chemical reactions, including Schiff base reactions [9], nitrile trimerization [10], boronate ester formation [11], Yamamoto coupling [12], alkyne trimerization [13], and Sonogashira coupling reactions [14]. Different classes of functionalized microporous polymers such as imine-linked poly(Schiff bases) [15], polybenzimidazoles [16], polycarbazoles [17], polyamides [18], and polyphenylene [19] have been recently explored as CO<sub>2</sub> adsorbents by generating Lewis acid-base interactions among the basic active sites of heteroatoms and electron-deficient CO<sub>2</sub>.

With the full swing of industrial revolution in the last century, fossil fuels are being burnt extensively in power generation plants, automobiles, airplanes, etc. Burning fossil fuels discharges large amounts of CO<sub>2</sub> into the atmosphere, thus presenting serious environmental problems at the global level [20]. Additionally, CO<sub>2</sub> is one of the major

contaminant in natural gas (10%), and responsible for the corrosion of pipelines owing to its acidic nature. For a sustainable environment, the level of atmospheric CO<sub>2</sub> needs to be maintained within permissible limits while meeting the growing demands for fossil-based fuels [21]. To address this alarming issue, effective measures for CO<sub>2</sub> capture and storage are being proposed. Previously, amine solutions were frequently used as scrubbers, but regeneration of the sorbent was economically unfavorable [22]. With the advanced technologies, use of porous solid sorbents is deemed to be an effective method to capture CO<sub>2</sub> through weak Van der Waals forces by physisorption for facile regeneration of the porous sorbents [23–25]. To date, numerous microporous adsorbents have been explored as alternatives for CO<sub>2</sub> capture, such as amine-functionalized mesoporous materials [26,27], zeolites [28], silica [29], metal organic frameworks (MOFs) [30], inorganic capillary membranes [31], porous organic molecules (POMs) [32,33], microporous organic polymers (MOPs) [34,35], and microporous carbons [36]. Among them, covalent organic polymers (COPs) is an emerging class of polymers with moderately high surface area and thermal stability. Moreover, the performance of COPs can be enhanced by pyrolysis of the polymer chains to design microporous carbons. Microporous carbons presents a new class of adsorbents with high surface area, light weight, diverse availability, robust physicochemical stability, and facile synthesis [37,38]. Few examples from literature presents the outstanding performance of microporous polymers and

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carbon materials; a series of POPs exhibited 73.9–99.0 mg/g CO<sub>2</sub> uptake (273 K/1 bar) with CO<sub>2</sub>/N<sub>2</sub> selectivity in the range 31.1–38.6 [39]. Wang et al. reported microporous polyimides with the adsorption capacity of 104–135 mg/g CO<sub>2</sub> at 273 K/1 bar [40]. Porous aromatic frameworks (PAF-1) and carbonized PAF-1 showed 89.2–193.8 mg/g of adsorbed CO<sub>2</sub> at 273 K/1 bar [41], while 180.1 mg/g by the extra carbon loaded PAF-1/C-900 at 295 K/1 bar. Kaskel et al. reported the porous polyimine and nitrogen-doped porous carbons (NPCs) outperforming most of the adsorbents with the storage capacity of 86.7–231.4 mg/g at 273 K/1 bar and CO<sub>2</sub>/N<sub>2</sub> selectivity up to 23.4 [42]. Moreover, it is suggested that the introduction of nitrogen-containing functional groups into porous materials can ameliorate the adsorption capacity for gas storage applications [43]. For instance, N-TC-EMC; the nitrogen-doped template carbon, fabricated from zeolite EMC-2 showed an excellent CO<sub>2</sub> capture performance of 4.00 mmol/g (298 K and 1 bar) [44]. Similarly carbonized product of porous polyimine, NPC-650 have an improved adsorption potential with 5.26 mmol/g of adsorbed CO<sub>2</sub> at 1 bar and 273 K [42]. In addition, NC900 a nitrogen-decorated nanoporous carbon prepared from nitrogen-rich ZIF-8 shows the adsorption capacity of 5.1 mmol/g at 1 bar and 273 K [45], and the nitrogen-enriched porous carbon spheres synthesized by the sol-gel method adsorbed 6.2 mmol/g CO<sub>2</sub> at 1 bar and 273 K [46]. It is noteworthy that the carbonized materials derived from organic precursors exhibited better performance under ambient conditions.

Herein, motivated by the above mentioned literature, we designed a series of carbonized products (IBLP-T) by high-temperature treatment of an imine and benzimidazole linked polymer (IBLP). As a result of carbonization, the CO<sub>2</sub> adsorption capacity increased in two possible ways: 1) by an increase in the surface area; 2) via the incorporation of nitrogen moieties that enhances the binding affinity due to Lewis acid-base interactions between the adsorbent and CO<sub>2</sub> molecules.

## 2. Experimental

### 2.1. Materials

Terephthalaldehyde (98%), 3,3'-diaminobenzidine (99%), acetone (99%), acetic acid (99%), methanol (98%), tetrahydrofuran (97%) and DMF (98%) were procured from Sigma Aldrich and used as received.

### 2.2. Synthesis of imine and benzimidazole linked polymer

According to Scheme 1, the Schiff-base condensation was performed under inert atmospheric conditions. In a prebaked round bottom flask,

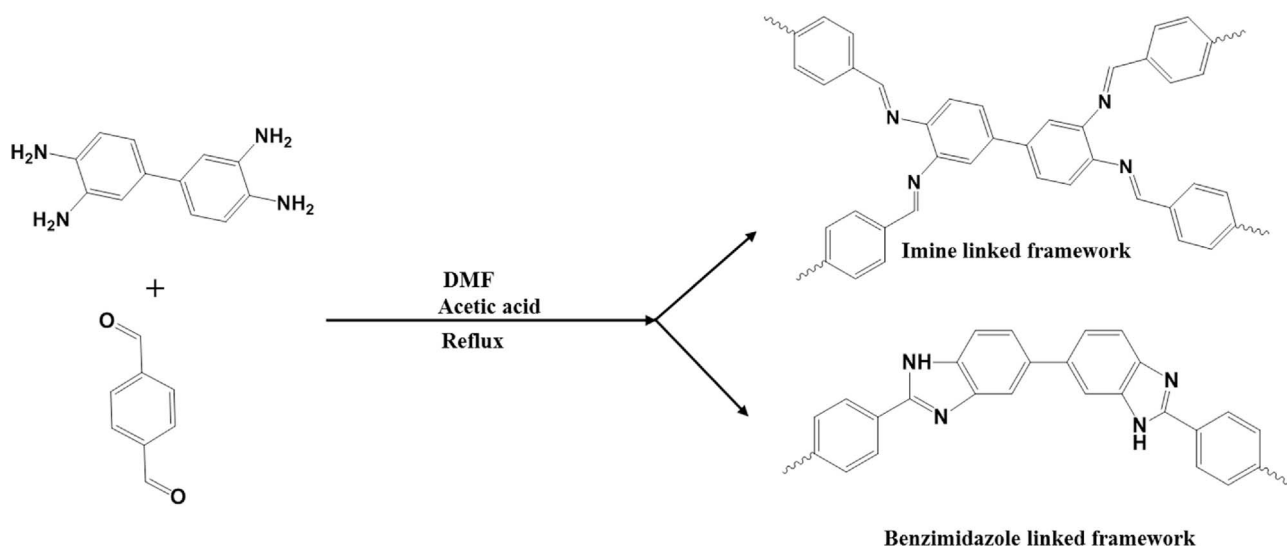
1 mmol of terephthalaldehyde was dissolved in 10 mL of DMF. To this solution, 15 mL–0.5 mmol 3,3'-diaminobenzidine in DMF was added dropwise with continuous stirring. In the reaction mixture, few drops of acetic acid (3 M) were added with vigorous stirring and continued to reflux at 150 °C for 1 h until orange-red precipitates appeared. The polymer precipitates were collected by filtration and washed sequentially with methanol, acetone, and tetrahydrofuran. Finally, the procured polymer was allowed to dry under vacuum at 80 °C for 12 h and labeled as IBLP.

### 2.3. Preparation of carbon materials through carbonization

A series of carbon materials was prepared through carbonization of the precursor IBLP at three different temperatures. Samples were prepared by heating in a tube furnace for 1 h at desired temperature and a heating rate of 3 °C min<sup>-1</sup>, under the flow of nitrogen gas. After cooling to the ambient temperature, the black carbonized samples were collected and labeled as IBLP-T, where T represents the corresponding treatment temperature.

### 2.4. Characterization

The physicochemical characteristics of fabricated sorbents were explored by different characterization techniques. Fourier transform infrared (FTIR) spectra were attained over the range 4000–400 cm<sup>-1</sup> using a VERTEX 80 V fourier transform-infrared vacuum spectrometer VERTEX 80 V. X-ray diffraction (XRD) patterns of the samples were recorded by D2 PHASER, BRUKER instrument over the 2θ range 2°–80°. High-resolution scanning electron microscopy (HRSEM, Model SU8010, Hitachi Co., Ltd.) was used to explore the surface morphology of prepared samples. Elemental analysis was performed using an EA1112 element analyzer. X-ray photoelectron spectroscopy (XPS, VG Scientific Co., ESCA LAB MK-II) was performed for surface analysis. The thermal stability of IBLP was determined using a thermal gravimetric analyzer TGA TG209F3; for these measurements, 2–5 mg of the sample was heated up to 800 °C at the heating rate of 10 °C/min under a nitrogen and air atmospheres. The textural characteristics of the samples were evaluated from N<sub>2</sub> adsorption-desorption isotherms obtained from the Model Belsorp Max instrument (BEL Japan, Inc.). CO<sub>2</sub> adsorption-desorption isotherms were obtained at 273, 298, and 308 K using a Model Belsorp Max instrument (BEL Japan, Inc.). To determine the CO<sub>2</sub>/N<sub>2</sub> selectivity, the adsorption isotherms for both gases were obtained at 273 and 298 K by Model Belsorp Max instrument (BEL Japan, Inc.). The samples were heated at 120 °C for 6 h under vacuum to evaporate all



Scheme 1. Synthesis of IBLP with imine and benzimidazole linked frameworks coexisting.

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