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A Zn-salen based covalent triazine framework as a promising candidate for CO_2 capture

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ABSTRACT

A Zn-salen based covalent triazine framework (**Zn@CTF**) was prepared through $ZnCl_2$ promoted one-pot procedure under ionothermal conditions using salen type precursor *N*,*N*′-Bis(5-cyano-salicylidene)-1,2-benzendiamine derived from imine condensation reaction of 3-formyl-4-hydroxybenzonitrile and 1,2-diaminebenzene. The chemical structure of the obtained polymer was characterized by solid-state ^{13}C nuclear magnetic resonance (NMR), fourier transform infrared (FT-IR), energy dispersive spectrometer (EDS) and element analysis. Powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) showed that the prepared polymer possessed amorphous structure and good thermal stability. The porous property of the polymer material was also characterized by N_2 adsorption/desorption isotherm and the **Zn@CTF** material exhibited excellent porosity with a Brunauer-Emmett-Teller (BET) surface area of up to 598.2 $m^2\ g^{-1}$. The surface microstructure property was evaculated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The CO_2 adsorption performance of the **Zn@CTF** was further investigated and it was found that the CO_2 uptake capacity was 43.9 $cm^3\ g^{-1}$ at 273 K.

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1. Introduction

Over the past decade, covalent triazine frameworks (CTFs) emerging as a new class of porous materials have attracted growing attention due to their potential applications in gas adsorption and storage, catalysis, and energy storage [1]. To date, there are a limited number of synthetic strategies for preparing CTFs, such as the condensation reaction of aldehydes and amidines [2], $AlCl_3$ mediated Friedel–Crafts reaction [3], and the trimerization reaction of carbonitriles under ionothermal conditions ($ZnCl_2$) or strong Bronsted acid conditions (CF_3SO_3H) [4,5]. Among them, the most common approach for the synthesis of CTFs is the ionothermal trimerization reaction of aromatic nitriles in the presence of a large amount of $ZnCl_2$ serving as both catalyst and reaction medium. Recently, the acid-catalyzed method has been introduced as alternative synthetic routes to construct crystalline CTFs [6]. Thus, triazine-based porous materials with high surface areas and high physico-chemical stability have been developed, and exhibited similar performance to zeolites, metal-organic frameworks (MOFs), or the covalent organic frameworks (COFs) [7].

Our research interests have focused on designing and constructing of functional porous materials including COPs, CMPs and COFs, and developing their potential applications such as gas adsorption, heterogeneous catalysis, and energy conversion [8,9]. In continuous efforts for the synthesis and application of new CTF materials, a Zn-salen based covalent triazine framework was prepared by $ZnCl_2$ promoted one-pot procedure under ionothermal conditions including trimerization of bicyano monomer *N*,*N*′-Bis(5-cyano-salicylidene)-1,2-benzendiamine and in-situ metalation of the salen ligand with $ZnCl_2$. The resulting CTF material possessed high surface area and thermal stability, unique microporous nature, and rational tunability of Zn-salen unit in such framework. The CO_2 adsorption performance of the **Zn@CTF** was further explored, and it was demonstrated that the **Zn@CTF** exhibited excellent CO_2 uptake capacity with high adsorption heat.

2. Experimental

The synthetic route of **Zn@CTF** was shown in Fig. 1, and the detailed synthetic procedures are given as below. The detailed synthetic procedures for monomer *N*,*N*′-Bis(5-cyano-salicylidene)-1,2-benzendiamine **3** were shown in the supporting information. Monomer **3** (200 mg, 0.55 mmol) and anhydrous $ZnCl_2$ (446.4 mg, 3.28 mmol) with a molar ratio of 1/6 were transferred into a

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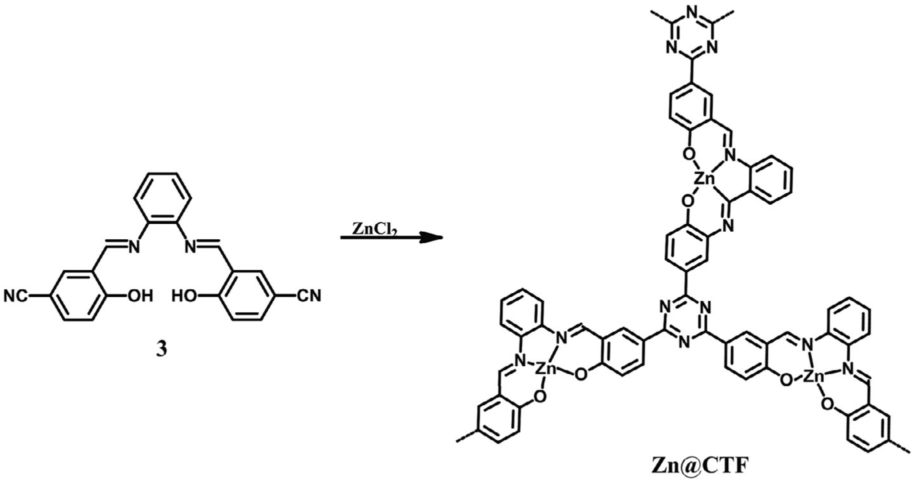

Fig. 1. Synthesized route of **Zn@CTF**.

2 mL ampoule. The ampoule was evacuated, sealed and heated to 400 °C for 48 h. The ampoule was then cooled down to room temperature and opened carefully. The reaction mixture was stirred in water for 3 h, filtrated, and followed by successive washing with water, acetone, 1 M HCl aqueous solution, water, tetrahydrofuran, and acetone. The resulting materials were activated at 120 °C under vacuum to constant weight to give **Zn@CTF** as a black powder (188.1 mg, 68.5%). For comparison, the other CTFs were synthesized by a similar procedure. The instruments used for the polymer characterization are shown in the supporting information.

The N_2 and CO_2 adsorption isotherms at different temperatures were measured with a Micromeritics ASAP 2020. Before the experiment, all samples were degassed in vacuum at 383 K for 12 h. The sample loading was about 150 mg. The heats of adsorption were calculated with a built-in heats of adsorption function in Micromeritics ASAP 2020 analyzer, which is based on the Clausius–Clapeyron equation.

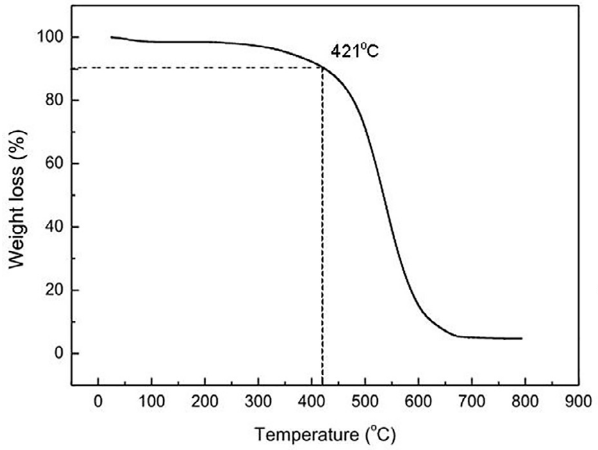

Fig. 2. TGA curve for **Zn@CTF** (N_2, 20 °C/min).

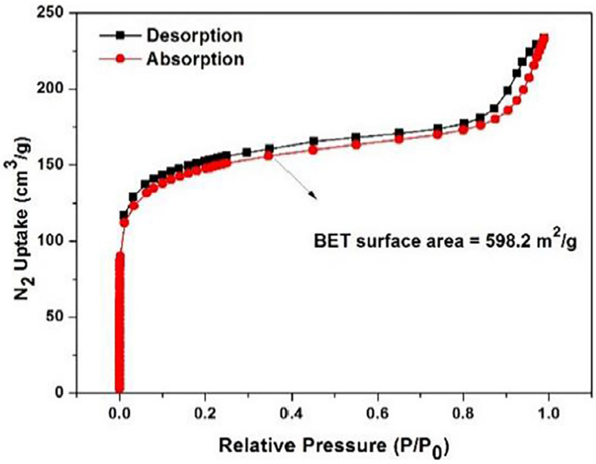

Fig. 3. Nitrogen uptake data of **Zn@CTF.**

3. Results and discussion

Zn@CTF was synthesized via $ZnCl_2$ promoted one-pot procedure under ionothermal conditions including trimerization of bicyano monomer *N*,*N*′-Bis(5-cyano-salicylidene)-1,2-benzendiamine and the direct complexation of the salen ligand with $ZnCl_2$. In order to find the relationship between the reaction conditions and the porosity properties, the molar ratio of monomer to $ZnCl_2$ was set as 1:2, 1:6 and 1:10, and the results were shown in Table S1. **Zn@CTF** is insoluble in water or common organic solvents such as hexane, ethylol, acetone, 1,4-dioxane, and dimethyl sulfoxide (DMSO). The thermal stability of the obtained polymer was confirmed by TGA. As shown in Fig. 2, **Zn@CTF** was stable up to 421 °C with weight loss 10%. PXRD analysis indicated the formation of the amorphous polymer material as shown in Fig. S1. The structure of **Zn@CTF** was characterized by FT-IR spectroscopy (Fig. S2). A low intensity peak near 2200 cm^{-1} related to the vibrations of C≡N group was disappear in the resulting polymer, while the characteristic vibrations at 1613 and 1370 cm^{-1} were observed for the presence of the triazine rings. Furthermore, the chemical structure of **Zn@CTF** was confirmed at the molecular level by solid state ^{13}C CP-MAS NMR (Fig. S3). The chemical shift at 159.8 ppm is assigned to the carbon signal from triazine rings, and the chemical shift at 127.6 ppm could be assigned to the carbons in phenyl groups. Especially, the characteristic signal around 143.5 ppm is unambiguously assigned to the imine carbons in salen groups. Elemental analysis results indicated a relatively lower nitrogen content in comparison to the theoretical values for the obtained **CTF**, as shown in Table S2, which was in accordance with the previous studies on **CTF** materials [10]. The Zn-salen functional **CTF** was characterized by energy dispersive X-ray spectroscopy (EDS)

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