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# In situ preparation of nitrogen-rich and functional ultramicroporous carbonaceous COFs by "segregated" microwave irradiation

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## ABSTRACT

The present research developed a strategy for in situ synthesizing functionalized ultra-microporous carbons by "segregated" microwave irradiation using covalent organic frameworks as simultaneous C and N source. The products have high N-doping concentration (>30 wt%), narrow pore size distribution, and the surface area of 507 and 243 $m^2/g$ at the pore size of 0.4 and 0.6 nm, which are much larger than the specific area (2 and 117 $m^2/g$) of samples prepared by conventional heating. They exhibit outstanding chemical, irradiation and thermal stabilities. Meanwhile, the carbonaceous COFs could retain the bulk morphology of the precursors and possess a unique functional group (cyano) which is helpful in material characters or in further modification. The findings support the potential use of "segregated" microwave irradiation in preparation of functional microporous carbons without any other additional process, and this method can also overcome the drawbacks of conventional heating and expand the range of microwave irradiation. The thus-prepared carbons were used as adsorbents for uranium recovery from a simulated nuclear effluent containing 12 co-existent cations with different pH value (4.5, 2.5 and 1.0). Results from batch experiments showed the amount of uranium adsorbed accounts for unreported 80% of the total adsorption amount at pH 1.0 with uranium sorption capacity of 50 mg/g. In addition, the carbonaceous COFs could be applicable to various fields, such as heavy metal removal, gas storage, and could be beneficial for exploration of the behaviors of ions in sub-nanometer pore (<1 nm) in the fields of carbon super-capacitors.

## 1. Introduction

Microporous carbons (MPC) and functional MPC have been applied to gas storage, molecular sieves and electrodes for electrochemical double-layer capacitors [1–6], which are benefited from their unique physiochemical properties. Typically synthesis methods for microporous carbons are activation method [7,8] and template carbonization method [1], and there is usually need an additional process to functionalize the as-prepared MPC for certain requirements of society demand [9–11]. The complex manufacturing process, high cost and difficulties in establishing a continuous mode production limit their large-scale application [12].

Microwave heating has been accepted as a useful method for synthesis of organic and inorganic compounds, for its distinct advantages such as uniform, rapid and volumetric heating, energy efficient, green, reducing synthesis time often by orders of magnitude and easy operation compared to conventional heating [13–16]. However, few researches utilize the intense heat generated by microwave susceptor when exposed to microwave irradiation to fabricate carbon materials [17], and the microwave approaches reported so far could be classified into two categories: (I) a special substrate act as both a rapid heating source and carbon precursor such as conducting polymers [18]; (II) a mixture of carbon precursor and microwave susceptor: the former is a poor absorber of microwave radiation; the later efficiently absorbs the radiation and transfers the energy to the former, such as SiC, metal particles [19,20]. However, the rigorous requirement requiring efficient absorption of microwave on substrate limits the sources of raw materials for the approach (I), and for the approach (II), the removal of the susceptor using harsh chemicals such as aqua regia not only makes the preparation process complicated, but leaves the product with a small amount of impurities, like metal nanoparticles survive after the harsh chemical treatment [12].

As an attempt to address the challenges above, we use a new approach named "segregated" microwave irradiation to directly convert precursors into designed carbon materials. "Segregated"

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microwave irradiation comprise the steps of (a) placing a quantity of precursors (*e.g.* covalent organic frameworks, COFs) in a container A, and (b) placing container A into another container B that contains microwave susceptor as heat source (*e.g.* graphite) and then subjecting to microwave irradiation in a microwave oven under flowing inert gas. The strategy of this approach is to create a segregation of carbon precursor and microwave susceptor. Consequently, the new approach has its advantageous features, *i.e.*, the starting reactants having not to microwave susceptor, the products being without impurities. And when compared to conventional heating, it could simultaneously prepare and functionalize microporous carbon materials without any other additional process. In this study, it is found that the carbon materials prepared by this approach have uniform ultramicropores, higher surface area and N-containing functional groups in contrast to precursors, which may due to the high heating and cooling rate of "segregated" microwave irradiation.

Recently, COFs have attracted considered attacks, which represent an emerging class of porous crystalline materials composed of light elements, typically C, N, O and/or B [21]. They not only have regular porous structure and ordered spatial arrangements, but also can adjust their structures, types and contents of elements through rational chemical design and synthesis, thus COFs could be promising precursors for the synthesis of microporous carbons containing high concentration of hetero-elements and regular pore structure. Up to now, there are two major precursors for microporous carbons synthesis by activation: either biomass (nutshell) [22–25] or polymer [26,27], they typically do not have regular pore structure and order spatial arrangements. Meanwhile, they contain a few numbers of hetero-elements, *e.g.* N, which is not conducive to modification of the as-prepared materials and increase preparation cost.

Herein, a new strategy that utilizing "segregated" microwave irradiation to directly prepare functional ultramicroporous carbonaceous covalent organic frameworks (CCOFs) using pre-synthesized N-containing COFs as simultaneous source of C and N is first reported. The resulting samples have high N-doped concentrations (33.4 and 12.9 wt%), narrow pore size discussion (0.4 and 0.6 nm), and outstanding chemical, irradiation and thermal stabilities. The as-prepared carbons were firstly used for the separation of uranium (VI) in simulated nuclear effluents and exhibited high selectivities for uranium (VI) at pH 1.0.

## 2. Experimental

### 2.1. Materials

Melamine, 1,4-phthalaldehyde, *N,N*-dimethylformamide (DMF), acetone, dichloromethane, dimethyl sulfoxide (DMSO), used in this research were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China). Trimesoyl chloride, *p*-phenylenediamine and triethylamine ($Et_3N$), all metal oxides and nitrates were purchased from Aladdin Chemistry Co., Ltd. (China). All reagents were of AR grade or of the highest purity available and were used without further purification.

### 2.2. Preparation of CCOFs

#### 2.2.1. Preparation of COF-SCU1

A solution of *p*-phenylenediamine (0.981 g, 9.0 mmol) in $CH_2Cl_2$ (100 mL) was stirred at 0 °C for 10 min. Then a solution of trimesoyl chloride (1.567 g, 6.0 mmol) in $CH_2Cl_2$ (20 mL) was added dropwise to the solution with stirring. $Et_3N$ (1.821 g, 18 mmol) was added and the mixture was kept at 0 °C for 6 h, then were allowed to warm to room temperature over 12 h. The solid was isolated by filtration over a Büchner funnel and washed with acetone, ethanol, DMSO and deionized water. The residue was dried at 50 °C under vacuum for 24 h to give a yellow powder.

#### 2.2.2. Synthesis of COF-SCU2

Melamine (0.313 g, 2.48 mmol), terephthalaldehyde (0.500 g, 3.72 mmol) were reacted in DMSO (15.5 ml) at 180 °C for 72 h. After cooling to room temperature, the formed solid was isolated by filtration over a Büchner funnel and washed with acetone, THF and $CH_2Cl_2$. The residue was dried at 50 °C under vacuum for 24 h to give an off-white powders.

#### 2.2.3. Preparation of CCOF-SCU1 by "segregated" microwave irradiation

Accurately weighted amount (20 mg) of the COF-SCU1 was placed in a porcelain crucible, and the porcelain crucible was placed in another porcelain crucible that contains graphite. Then they all were put into the modified domestic oven and the gas of Ar was passed for 5 min ($3\ L\ min^{-1}$). After the microwave oven working continuously at 800 W for 3 min under flowing Ar gas, the sample was cooled down to room temperature and the black powder was collected.

#### 2.2.4. Preparation of CCOF-SCU2 by "segregated" microwave irradiation

Accurately weighted amount (10 mg) of the COF-SCU2 was placed in a porcelain crucible, and the porcelain crucible was placed in another porcelain crucible that contains graphite. Then they were put into the modified domestic oven and the gas of Ar was passed for 5 min ($3\ L\ min^{-1}$). After the microwave oven working continuously at 800 W for 3 min under flowing Ar gas, the sample cool down to room temperature and the black powder was collected.

#### 2.2.5. Calcination of precursors in muffle furnace

A weighted amount of COF-SCU1 was calcined under flowing Ar at 950 °C for 3 h in a muffle furnace, then the sample was cooled down to room temperature and the black powder was collected.

A weighted amount of COF-SCU2 was calcined in Ar at 450 °C for 3 h in a muffle furnace, then the sample was cooled down to room temperature and the black powder was collected. If COF-SCU2 was calcined in a muffle furnace over 550 °C, there is very little product.

### 2.3. Batch experiment of uranium (VI) adsorption

Batch experiments were performed to study the adsorption behavior of CCOFs toward U(VI). The as-prepared carbons 10 mg was added to a conical flask with 25 mL of multi-ion solution containing 12 ions (Table S1) as well as uranium(VI) at given pH (4.5, 2.5 and 1.0) at room temperature and shaken for 3 h. The supernatant were separated from the solid by centrifugation. The initial and equilibrium concentrations are determined by ICP-AES.

Adsorption amount ($q_e$, $mg\ g^{-1}$) of U(VI) or other metal ions were calculated by the following equations [28]:

$$q_e = \frac{(C_0 - C_e) \times v}{w}$$

where $C_0$ and $C_e$ are the initial and the equilibrium concentration of metal ion ($mg\ L^{-1}$), respectively; $v$ is the volume of the testing solution use for adsorption (L); and $w$ is the amount of sorbent (g).

All glassware used was previously soaked overnight in 10.0 wt% $HNO_3$ to remove impurities that might be present and to prevent further adsorption of metal ions on the walls of glassware. All tests were carried out at least in duplicates.