The Ionothermal Synthesis of Dihydrophenazine-based Covalent Triazine Frameworks for Supercapacitors

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Abstract. The dihydrophenazine-based covalent triazine frameworks (CTFs) were prepared via a zinc chloride mediated ionothermal synthesis. The obtained dihydrophenazine-based CTFs exhibit high surface areas of up to 1213 m²/g with a high nitrogen content of 8.35 wt%. Electrochemical test of dihydrophenazine-based CTFs shows a high specific capacity of 256 F/g in an aqueous electrolyte at a current density of 0.8 A/g with excellent rate capability and cycling stability.

1. Introduction
Supercapacitor is a class of important energy storage device, which has attracted great attention for its fast charge/discharge rate and many other merits[1-2]. Due to the nature of energy storage mechanism, the enhancement of the energy density in supercapacitor is still a challenge[3]. According to the formula \( E=1/2 \times CV^2 \), the energy density can be improved by increasing the specific capacitance[4]. Heteroatom-doped carbon materials, especially the nitrogen-doped carbon materials exhibit high electrical conductivity, high specific surface area, tunable redox active sites and low cost, which make this class of electrode materials extremely promising.

Dihydrophenazine-containing molecules are redox active, which are important metabolites in many living organisms[5]. Recently, their successively one-electron electron transfer property has been utilized in organic atom transfer radical polymerization and cathode materials for different ion batteries[6]. However, dihydrophenazine-based electrode materials have seldom been incorporated in the supercapacitors. On the other hand, covalent triazine frameworks (CTFs) are an important class of porous organic polymers linked by triazine rings through covalent bonds, which can be synthesized via facile trimerization of aromatic nitrile monomers under ionothermal conditions[7]. Owing to their abundant nitrogen atoms and stable chemical structure, CTFs have found great application prospects in the fields of gas adsorption and separation, energy storage and many others[8-9]. By combining the high specific surface area, well-defined pore size and good conductivity with the redox active dihydrophenazines, dihydrophenazine-based CTF would be a promising candidate for supercapacitors, which has seldom been explored up to now.
2. Materials and Methods

2.1. Synthesis of dihydrophenazine-based covalent triazine frameworks

4,4’-(phenazine-5,10-diyl) dibenzonitrile (PDBN) (0.30 g, 0.78 mmol) and ZnCl₂ (1.06 g, 7.80 mmol) were ground together and transferred into a glass ampoule. The ampoule was subsequently evacuated and sealed, heated to 300 °C at a rate of 3 °/min and held for 5 h, and then heated to the desired temperature (400 and 600 °C) at a rate of 5 °/min and maintained for 35 h. Note, as for 800 °C, a quartz boat was used instead of the glass ampoule to avoid the fracture of the glass ampoule at high temperatures. The mixture was dispersed in 1 M HCl solution and refluxed for 12 h, washed with 1 M HCl solution and water until the pH was neutral, then washed with THF and acetone. The product was obtained by drying under vacuum at 120 °C for 12 h.

2.2. Preparation of CTF-based working electrodes

The CTF containing slurry was obtained by sonicating a mixture of CTF active material (80 wt%), super P (10 wt%) and poly (vinylidene fluoride) (10 wt%) in acetone. Drop-casting the slurry onto a piece of carbon cloth (1 cm × 2 cm).

2.3. Electrochemical measurements

In a three-electrode system, the test was carried out in 1 M H₂SO₄ aqueous solution. The specific capacitance (Cₛ, F g⁻¹) was calculated from galvanostatic charge-discharge (GCD) curves by the following equation:

\[ Cₛ = I\Delta t/m\Delta V \]  

Where I is the discharge current (A), \(\Delta t\) is the discharge time (s), m is the mass loading of CTF-based active material on the tested working electrode (g), \(\Delta V\) is the discharge potential/voltage window excluding the Ohmic drop (V).

3. Results & Discussion

CTFs based on phenazine motif were synthesized under a typical ionothermal condition with PDBN and anhydrous ZnCl₂ at 400, 600 and 800 °C, and the resultant CTFs were denoted as CTF-400, CTF-600, and CTF-800, respectively (Figure 1a). A typical hexagonal ring of dihydrophenazine-based CTFs was optimized with density functional theory (DFT) calculations, which shows that the dihydrophenazine ring is almost perpendicular to the triazine ring (Figure 1b and 1c). This distorted arrangement of building blocks impedes the effective packing of layers.

The resultant CTFs exhibit bands at 1558 and 1146 cm⁻¹ in FT-IR spectra, which correspond to the stretching/deformation vibration signals of benzene/triazine rings. Besides, the C≡N stretching vibration at 2230 cm⁻¹ from the PDBN precursor is disappeared, indicating the success of cyclotrimerization (Figure 2a). Two characteristic peaks at around 1351 and 1591 cm⁻¹ can be
observed in Raman spectra, which were assigned to the D and G bands of all the synthetic CTFs (Figure 2b). The intensity ratios of the D band and the G band (I_D/I_G) for CTF-400, CTF-600, and CTF-800 were calculated to be 0.79, 0.85 and 0.89, which show that the defect structure of CTFs increased with the elevated reaction temperature.

The porosity of the dihydrophenazine-based CTFs was examined by the nitrogen sorption analysis at 77 K. As shown in Figure 2c, the N_2 sorption isotherm of CTF-400 displays a typical type-I reversible isotherm with a Brunauer-Emmett-Teller (BET) specific surface area of 670 m^2 g^{-1} and a pore volume of 0.34 cm^3 g^{-1}. Nevertheless, CTF-600 shows a type-IV isotherms with a higher BET surface area of 1213 m^2 g^{-1} and a pore volume of 0.98 cm^3 g^{-1}. When the reaction temperature increased to 800 °C, the resultant CTF-800 changes back to a type-I reversible isotherm with a decreased BET surface area of 953 m^2 g^{-1} and a pore volume of 0.49 m^3 g^{-1}. All three CTFs exhibit micropores at around 0.8 and 1.3 nm, which would stem from the heavily interpenetrated frameworks. Besides, a large fraction of mesopores around 5.3 nm is discovered in CTF-600 (Figure 2d).

The nitrogen contents for CTF-400, CTF-600, and CTF-800 based on elemental analysis are 8.35%, 8.15% and 6.11%. The N 1s spectra of dihydrophenazine-based CTFs can be deconvoluted into five peaks, namely N_triazine (~397.3 eV), N_phenazine (~398.5 eV), N_cyano (~399.4 eV), N_graphitic (~400.3 eV) and N_oxide (~402.7 eV) (Figure 3a). The ratios of different N species among the total N content in different CTFs are shown in Figure 4b from XPS N 1s deconvolution. The ratio of N_triazine continuously decreases from 33.9% of CTF-400 to 27.0% of CTF-600, and finally to 22.2% of CTF-800. The ratios of N_cyano and N_graphitic are subtle changed in CTFs with an average ratio of 20.6% and 17.1%, respectively. However, the ratio of N_phenazine is firstly dropped from 26.5% to 14.4%, then increases to
31.1% (Figure 3b). In general, among different kinds of N species, \( N_{\text{triazine}} \) and \( N_{\text{phenazine}} \) can not only increase the wettability of the material, but also provide pseudocapacitance as the redox active sites, which are important to improve the capacitance of supercapacitors[10].

In view of the large surface area and high nitrogen content of dihydrophenazine-based CTFs, we further studied their performance as electrode materials in supercapacitors. The electrochemical performance of dihydrophenazine-based CTFs was first investigated by cyclic voltammetry (CV) and GCD curves. The shape of the CV curves for CTF-400 to CTF-800 is maintained even the scan rate is increased from 5 to 100 mV/s, indicating that dihydrophenazine-based CTFs electrode materials have good rate performance (Figure 4a, 4b and 4c).

In addition, the CV curves of CTF-400 exhibit clear redox peaks in the range of 0.2 to 0.6 V. Similarly, broad bumps in the same range are also appeared in the CV curves of CTF-600 and CTF-800. These redox peaks are mainly originated from the successive electron transfer from dihydrophenazine units as compared to the CV curve of PDBN, which provides the electrode materials a partial pseudocapacitive behavior (Figure 5a). The GCD curves of dihydrophenazine-based CTFs were recorded at different current densities and the specific capacitance was determined from the discharge curve (Figure 4d, 4e and 4f). Compared with CTF-400 and CTF-600, CTF-800 has the largest integral area in the CV curve and the longest discharge time in the GCD curve. As shown in Figure 5b, CTF-800 has a high specific capacitance of 256 F g\(^{-1}\) at a current density of 0.8 A g\(^{-1}\), which is higher than that of CTF-600 (167 F g\(^{-1}\)) and CTF-400 (48.4 F g\(^{-1}\)). This specific capacitance of CTF-800 is better than most hetero atom-doped porous carbon materials reported in recent years[4]. The reason for the high capacitance performance of CTF-800 is likely due to its large specific surface area and high content of redox active phenazine N. It is worth mentioning that the specific capacitance of CTF-800 remains 93.0.0% and the coulomb efficiency is 92.3% after 10000 cycles through the GCD cycle test at a current density of 3 A g\(^{-1}\), which shows that CTF-800 has a better cycle stability (Figure 5c).
Figure 5. (a) The CV curves of PDBN, (b) specific capacitance of CTFs at different current densities, (c) The cyclic stability and coulombic efficiency of CTF-800 at current density of 3 A g$^{-1}$ for 10000 cycles in three-electrode system.

4. Conclusions
In summary, we have designed and synthesized a series of CTFs containing dihydrophenazine with redox activity. The resultant dihydrophenazine-based CTFs exhibit tunable specific surface areas, pore distribution, nitrogen content and its composition, which is important to understand the role of dihydrophenazine-type nitrogen in electrochemical energy storage. Dihydrophenazine-based CTFs demonstrate high specific capacity of 256 F/g in aqueous H$_2$SO$_4$ electrolyte at a current density of 0.8 A/g. The redox active dihydrophenazine could be a useful electrophore to enhance the performance of other electrochemical energy storage systems.

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